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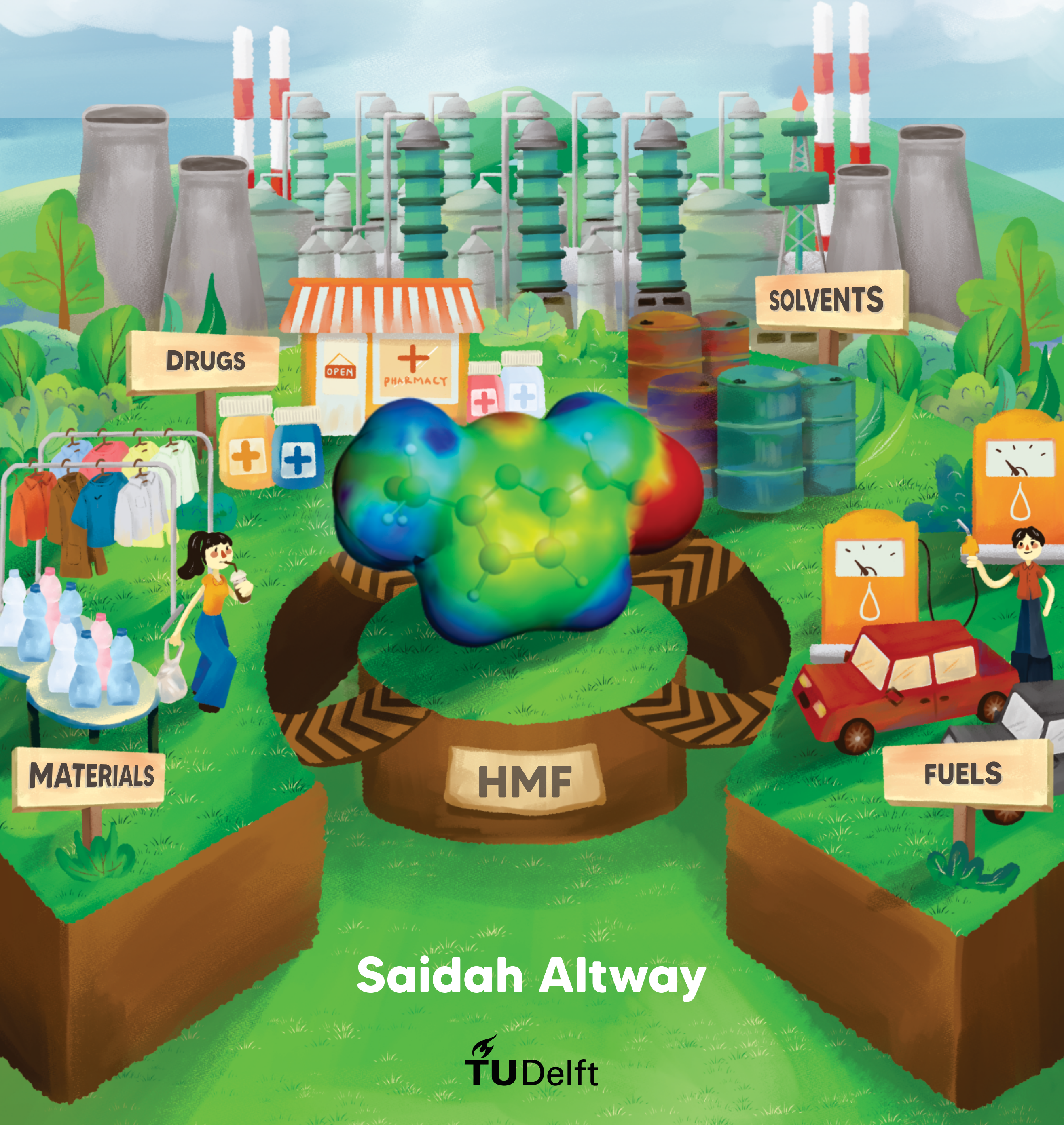
# Effect of Biphasic System Constituents on Liquid-liquid Extraction of 5-Hydroxymethylfurfural



**Saidah Altway**

TU Delft

# Effect of biphasic system constituents on liquid-liquid extraction of 5-hydroxymethylfurfural

Dissertation

For the purpose of obtaining the degree of doctor
at Delft University of Technology,
by the authority of the Rector Magnificus Prof. dr. ir. T.H.J.J. van der Hagen,
Chair of the Board for Doctorates,
to be defended publicly on
Friday 14 April 2023 at 10:00 hours

by
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Master of Science in Chemical Engineering,
ITS-NTUST, Indonesia-Taiwan,
born in Pasuruan, Indonesia

This dissertation has been approved by the promotor:
Prof. dr. ir. A.B. de Haan

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# Effect of biphasic system constituents on liquid-liquid extraction of 5-hydroxymethylfurfural

Proefschrift

Ter verkrijging van de grad van doctor
aan de Technische Universiteit Delft,
op gezag van de Rector Magnificus Prof. dr. ir. T.H.J.J. van der Hagen,
Voorzitter van het College voor Promoties,
in het openbaar te verdedigen op
Vrijdag 14 April 2023 om 10:00 uur

door
Saidah ALTWAY

Master of Science in Chemical Engineering,
ITS-NTUST, Indonesia-Taiwan,
geboren te Pasuruan, Indonesia

Dit proefschrift is goedgekeurd door de promotor:
Prof. dr. ir. A.B. de Haan

Samenstelling promotiecommissie bestaat uit:

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| Rector Magnificus | voorzitter |
| Prof. dr. ir. A.B. de Haan | TU Delft, promotor |

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# Summary

HMF (5-hydroxymethylfurfural) is one of the bio renewable materials that can be used as an important platform chemical to produce biofuel and various chemical products. The main application of HMF in the chemical industry is a platform chemical for the production of plant-based polyethylene terephthalate (PET). HMF is produced through hexose dehydration which fructose or glucose is arranged as a feedstock. Liquid-liquid extraction can be applied in HMF production to enhance the selectivity and yield of HMF. HMF can be extracted from aqueous solution into the organic phase which prevents the degradation of HMF. Furthermore, it has been recognized that ionic liquid (IL) and deep eutectic solvent (DES) can be used as stabilizing agent in HMF production by suppressing the formation of side-products, hence increase the HMF yield as well. However, research on the systematic thermodynamics of HMF extraction is quite limited and needed to be developed. The thermodynamic data, such as phase equilibrium data and partitioning of HMF into organic phase are needed as basis for a rational design and optimal separation of HMF from the aqueous solution.

The objective of this research is systematically study the effect of biphasic system constituents on the liquid-liquid extraction of HMF at 313.15 K and atmospheric pressure (0.1 MPa). The extraction performance was evaluated based on the values of separation factor and HMF distribution coefficient which were determined from liquid-liquid equilibrium (LLE) data. The experimental LLE data of the investigated systems were also correlated well using thermodynamics models. The NRTL and UNIQUAC models were used to correlate the ternary

experimental LLE data, whilst the experimental LLE data containing salt, IL, DES, and sugar were correlated using the NRTL model. We used aqueous-organic biphasic systems, and also added IL [EMIM][$BF_4$] (1-ethyl-3-methylimidazolium tetrafluoroborate) or DES ChCl-urea (choline chloride-urea) in the aqueous phase. The effect of the addition of sugar (fructose) and salt in the variety of cation ($Na^+$, $K^+$) and anion ($Cl^-$, $SO_4^{2-}$) were also studied. Three different extraction solvents, methyl isobutyl ketone (MIBK), 2-pentanol, and tributyl phosphate (TBP), were used for the comparison.

According to the results in this study, it indicated that for 2-pentanol the HMF distribution coefficient is up to 1.4 times higher than MIBK. Besides, MIBK has a 2-3 times higher separation factor than 2-pentanol. While TBP is more selective as extraction solvent than the other two solvents, TBP is also superior in terms of HMF distribution coefficient. The salting-out strength of salts for organic solvent (MIBK or 2-pentanol)-HMF-water-salt systems are in the order NaCl > $Na_2SO_4$ > KCl > $K_2SO_4$. NaCl was found superior in both separation factor and distribution coefficient of HMF compared to the other salts studied. Furthermore, the separation factor and HMF distribution coefficient decreased with the increase of IL [EMIM][$BF_4$] and DES (ChCl-urea) concentrations. However, DES (ChCl-urea) decreased the extraction performance less than IL [EMIM][$BF_4$]. The addition of salt (NaCl) enhanced the separation factor and the distribution coefficient of HMF, enabling compensation of the IL and DES effects. The presence of salt can enhance both the extraction performance parameters up to 2-4 times for all the investigated systems studied using three different organic solvents and also in the presence of IL or DES. While, the presence of fructose in the solution had limited effect on the extraction performance. In general, it can be inferred that by taking the advantage of IL/DES as stabilizing agent, aqueous IL/DES with NaCl is a good combination applied in HMF extraction process to achieve good extraction performance.

# Samenvatting

HMF (5-hydroxymethylfurfural) is een van de duurzame materialen verkregen uit biomassa die gebruikt kan worden als uitgangspunt voor de productie van biobrandstoffen en andere chemische producten. De grootste toepassing van HMF in de chemische industrie is als platformchemicalie voor de productie van polyethyleen terephthalaat (PET) uit biomassa. HMF wordt geproduceerd door middel van dehydratatie van hexoses, met fructose of glucose als grondstof. Vloeistof-vloeistof extractie kan in het productieproces van HMF worden toegepast om de selectiviteit en opbrengst van HMF te verhogen. HMF kan worden geëxtraheerd uit een waterfase naar een organische fase. Dit voorkomt de degradatie van HMF. Daarnaast is het bekend dat ionische vloeistoffen (IL) en diep-eutectische oplosmiddelen (DES) gebruikt kunnen worden om het proces te stabiliseren, door het onderdrukken van de formatie van bijproducten, hetgeen de opbrengst van HMF verhoogt. Het ontbreekt echter aan uitgebreid onderzoek over de systematische thermodynamica van HMF extractie. Dit zal zodoende ontwikkeld moeten worden. De thermodynamische data, zoals fase evenwicht gegevens en verdeling van HMF naar de organische fase zijn nodig als basis voor rationeel procesontwerp en optimale scheiding van HMF uit de waterige oplossing.

Het doel van dit onderzoek is het systematisch onderzoeken van het effect van de verschillende componenten van het twee-fasensysteem op de vloeistof-vloeistof extractie van HMF bij 313.15 K en atmosferische druk (0.1MPa). De extractieve prestatie is geëvalueerd op basis van de waardes van de scheidingsfactor en distributiecoëfficiënt van HMF, die

berekend kunnen worden uit de vloeistof-vloeistof evenwicht (VVE) data. De experimentele VVE data van de onderzochte systemen zijn in overeenstemming met de thermodynamische modellen. De NRTL en UNIQUAC modellen zijn gebruikt bij de ternaire experimentele VVE data, terwijl de experimentele data inclusief zout, IL, DES en suiker zijn gecorreleerd met het NTRL model. Water-organische twee-fasensystemen zijn onderzocht, waarbij ook IL [EMIM][$BF_4$] (1-ethyl-3-methylimidazolium tetrafluoroboraat) of DES ChCl-urea (choline chloride-urea) aan de waterfase werd toegevoegd. Het effect van de toevoeging van suiker (fructose) en zout, verscheidene kationen ($Na^+$, $K^+$) en anionen ($Cl^-$, $SO_4^{2-}$), zijn tevens onderzocht. Drie verschillende organische oplosmiddelen, methyl isobutylketon (MIBK), 2-pentanol en tributylfosfaat (TBP), zijn gebruikt en vergeleken.

De resultaten wijzen erop dat de HMF distributiecoëfficiënt van 2-pentanol tot 1,4 keer hoger ligt dan voor MIBK. Daartegen staat, dat MIBK een scheidingsfactor heeft die 2 tot 3 keer zo hoog is als voor 2-pentanol. TBP is als oplosmiddel zowel selectiever, als superieur vanuit het oogpunt van de distributiecoëfficiënt, in vergelijking met de andere twee oplosmiddelen. De uitzoutsterktes van de zouten voor systemen, organisch oplosmiddel (MIBK of 2-pentanol)-HMF-water-zout, zijn, in volgorde, $NaCl > Na_2SO_4 > KCl > K_2SO_4$. De bevindingen laten zien dat NaCl wat betreft scheidingsfactor en distributiecoëfficiënt een gunstiger effect had dan de overige zouten. Daarnaast is gebleken dat de scheidingsfactor en distributiecoëfficiënt van HMF afnemen met een toename in IL [EMIM][$BF_4$] and DES (choline chloride-urea) concentraties. Hierbij geldt dat DES (choline chloride-urea) de extractieve prestaties minder verlaagt dan IL

[EMIM][$BF_4$]. De toevoeging van zout (NaCl) verbetert de scheidingsfactor en distributiecoëfficiënt van HMF, wat het mogelijk maakt om te compenseren voor de effecten van IL en DES. De aanwezigheid van zout kan beide indicatoren voor extractieve prestatie tussen de 2 en 4 keer verhogen voor alle onderzochte oplosmiddelen, zelfs in de aanwezigheid van IL of DES. De aanwezigheid van fructose in de oplossing heeft een gering effect op de extractie. In het algemeen, kan het gezegd worden dat door de voordelen van de stabiliserende eigenschappen van IL/DES, een waterige oplossing van IL/DES met NaCl een goede combinatie is voor de toepassing in een HMF extractie proces om goede extractieve prestaties te behalen.

# Chapter 1

# Introduction

## 1.1 Research Background

The use of bio renewable feedstocks seems to be particularly promising to overcome the dependence on fossil-fuel resources for energy and chemical building blocks. The increase of the worldwide population growth causes an increase in the world energy consumption and petroleum demand. Hence, biomass can be used as a potential material which is sustainable and biodegradable [1]. HMF (5-hydroxymethylfurfural) is one of the bio renewable materials that can be used as an important platform chemical to produce biofuel and various chemical products, as seen in Figure 1.1 [2]. Carbohydrates such as fructose, glucose, sucrose, and cellulose are the renewable feedstocks to produce HMF which are abundantly available in nature. The main application of HMF in the chemical industry is for the production of renewable FDCA (2,5-Furandicarboxylic acid). The FDCA can be used to replace PTA (Terephthalic acid), a monomer used for the synthesis of polyethylene terephthalate (PET), which is applied for the large-scale manufacture of synthetic fibers and plastic bottles [3]. Commonly, PTA is generated from the oxidation of petroleum-derived p-xylene. In recent years, there is an alternative way to produce renewable PTA by Diels-Alder reactions between ethylene and oxidized derivatives of HMF [3].

Research on the production of HMF has increased greatly and focussed on examination of various solvents, catalytic system design and reaction engineering studies, and techno-economic analysis [4-19]. Recently, researchers have investigated various processes to achieve high yield of HMF in monophasic systems, biphasic systems, and also ionic liquid solutions using homogeneous and heterogeneous catalysts [4-19]. Amongst all researches that have been examined indicated that either glucose or fructose can be converted to HMF with high yields in biphasic system (aqueous-organic phase) [12, 13, 15-17]. Beside that, the use of various metal chlorides (MClx)/ ionic liquids in glucose or fructose dehydration can improve HMF yields significantly [20].

Liquid-liquid extraction is one of the separation technologies that can be applied in HMF production to enhance the yield and selectivity of HMF. HMF can be extracted from aqueous solution into the organic phase which prevents the degradation of HMF. Few researches have investigated the systematic thermodynamics of HMF extraction [21-26]. There is still a great need for the thermodynamic data, such as partitioning of HMF into organic phase as function of process conditions and the liquid-liquid equilibria of HMF with various extraction solvents. Generally, there are four solvent systems which have been recommended for the production and extraction process of HMF, i.e. the reaction medium water, biphasic systems, aprotic organic solvents, and ionic liquids [22, 27-28]. Ionic liquids (IL) are green chemical solvents that have been applied in chemical industries. These compounds are salts which are liquid at room temperature. Because of the unique structure of physico-chemical properties, ionic liquid can be used in many applications in which conventional organic solvents are not effective and efficient [29]. Like ionic liquids, Abbott *et al.* [30-32] have indicated that solid organic salt and complexing agent mixtures can also form a liquid at temperatures below 100°C, which is called deep eutectic solvents (DES). The DES is a green solvent, it can be prepared easily from low-cost and non-toxic chemicals. Since its introduction in 2003, DES have also been adopted in the conversion of carbohydrates to HMF. Higher yields of HMF can be realized in IL or DES media [14-16,25,33-35] however the drawback is that the following separation of HMF from pure IL or DES is difficult, result in lower partition coefficient of HMF [25, 36]. Therefore, the presence of water in the solution is essential to enhance the efficiency of HMF extraction process [37].

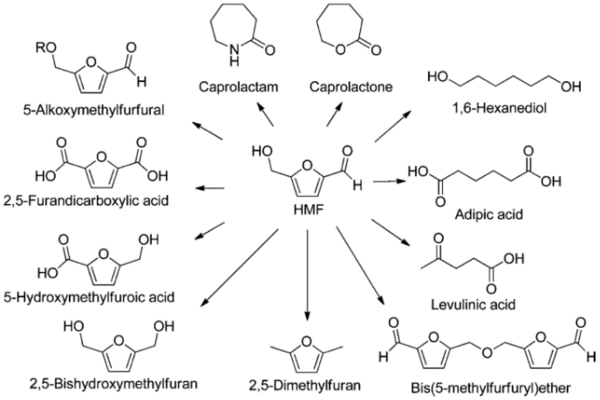


**Figure 1.1** HMF as a platform chemical [2]

## 1.2 State of Art

### 1.2.1 HMF Production Process

HMF is synthesized from a triple dehydration product of hexose which glucose or fructose is arranged as a feedstock with a low melting point (30–34°C), as shown in Figure 1.2 [20]. Both homogeneous and heterogeneous catalysts in aqueous, biphasic (aqueous-organic), and ionic liquid media have been utilized in the dehydration reaction.

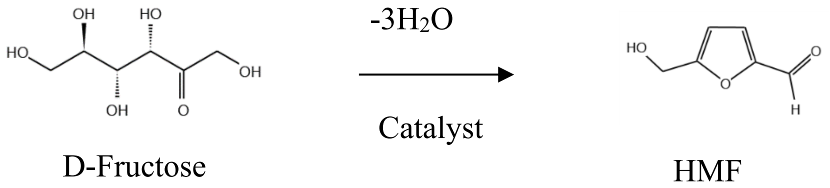


**Figure 1.2** Triple dehydration in HMF production [20]

The high of HMF yields depend on the type of catalysts which can dehydrate fructose rapidly and the use of substance which can promote the partitioning of HMF to the organic phase [20]. In the biphasic system, selection of the organic solvent plays a crucial role in improving partitioning of HMF to the organic phase as well as increasing the yield of HMF. The physical and chemical properties, such as molecular structure, density, polarity, and also boiling point must be considered when an organic solvent is chosen [38]. Volatile polar compounds like alcohol and ketone have been widely used as promising solvents in HMF production [11,20,23,26,39]. The polarity of alcohol and ketone make them interact with HMF via hydrogen bonds. Furthermore, the use of high boiling solvent, such as DMSO (Dimethylsulfoxide) or TBP (Tributyl Phosphate), can give higher yield of HMF. However, it also requires higher energy and cost for the separation of HMF by distillation [20]. For high boiling solvent, back extraction method may be conducted for further product and solvent recovery processes. Besides, salt can also be added to the aqueous phase to extract HMF into the organic phase efficiently [21-22,24]. Dumesic group [40] confirmed that the use of salt in the aqueous phase can favor the partitioning of HMF into the organic phase that increases the selectivity and yield of HMF.

### 1.2.2 Concept of extraction process in HMF production

The organic solvent can be used as extracting agent to extract HMF from its aqueous solution through the concept of extraction process as seen in Figure 1.3. The feed stream contains fructose, water, and catalyst as aqueous phase. In addition, the organic solvent is included in the reactor. The reaction takes place and HMF is extracted to the organic phase in the reactor which prevents the formation of side product. The aqueous phase from the bottom of the reactor which is still containing HMF enters to the extraction unit. Furthermore, the raffinate is recycled to the reaction unit and partially purged in order to inhibit the accumulation of side products in the process. The extract from extraction column is mixed with the organic phase leaving reactor and evaporated, hence the high purity of HMF can be achieved. The concentrated organic solvent from evaporation unit is condensed, then it is separated and recycled to the biphasic reaction and the extraction unit. Impurities in which the boiling point are higher than the organic solvent are leaving from evaporation unit together with HMF.

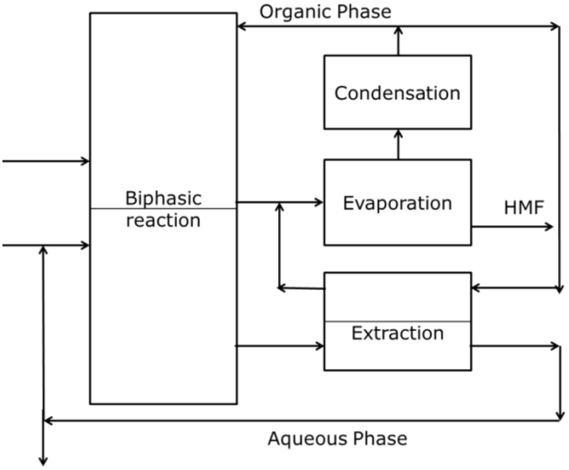


**Figure 1.3** Block diagram for biphasic HMF production process

### 1.2.3 Ionic Liquid and Deep Eutectic Solvent in HMF Production

In HMF production, the cationic part in ionic liquids (ILs) can interact with the fructose molecules and direct them in the optimization of the configuration for the dehydration process more readily. Thus, the hydrophilic/ hydrophobic properties and spatial position which is given by alkyl groups attached to the cation core can play an important role in controlling the efficacy of ionic liquids for fructose dehydration reaction. Instead, the anion in ionic liquids is not relevant for the fructose dehydration activity.

Furthermore, recent years, the use of deep eutectic solvents (DES) have developed for many applications, such as biodiesel synthesis [41], electrodeposition, nanomaterials, biochemistry, separation of by-products from biodiesel, purification of biodiesel, analysis [42], and also in HMF production process [25]. The choline chloride (ChCl) is one of DES which is popularly used as the salt component, because it is biodegradable, low cost, and low toxicity, thus it is appropriate to be applied in a wide range of applications. Urea, ethylene glycol, and glycerol are also popular hydrogen bond donors because of their low cost and easy fusion [42]. The formation mechanism of the DES is the complexing agent (typically a hydrogen bond donor) interacts with the anion and increases its effective size, and then it can reduce the interaction of anion with cation, so that it decreases the freezing point (Tf) of the mixture.

Currently, many efforts have been devoted to the dehydration process of carbohydrates into HMF in the presence of IL and DES. The dehydration of fructose in methyl imadizolium chloride reached a HMF yield of 92% [43]. The conversion of glucose to HMF using $CrCl_2$ as catalyst in 1-ethyl-3-methylimadazolium chloride also gave a 70% HMF yield [44]. Kobayashi *et al.* [25] reported that the use of choline chloride-citric acid with ethyl acetate as solvent (biphasic reaction system) was effective in improving the yield of HMF, mainly at high fructose concentration. Besides, the addition of choline chloride to water+MIBK system also increased the HMF yield to 70% in a mixture of ChCl/$H_2O$ ratio of 1 using $AlCl_3 \cdot 6H_2O$ as catalyst [45]. The presence of choline chloride in aqueous solution can enhance the selectivity and yield of HMF by stabilizing effect and allows the conversion of highly concentrated feed [46].

### 1.2.4 Liquid-Liquid Extraction

Liquid-liquid extraction is a separation method to separate one or more components in a homogeneous mixture with the addition of liquid solvent which make them separate into two phases. The separation depends on physical and chemical properties of the components [47,48]. In liquid-liquid extraction, the separation factor is used to determine the capability of an extraction solvent to extract solute (material extracted) from the solution. The higher the separation value, the greater the separation ability. The definition of the separation factor is defined as the ratio of distribution coefficient of solute ($D_2$) to water ($D_3$), as shown in Eq. 1.1 :

$$S = \frac{D_2}{D_3} = \frac{w_2^I / w_2^{II}}{w_3^I / w_3^{II}} \tag{1.1}$$

The superscript I and II in Eq. 1.1 represent the extract phase and the raffinate phase, respectively. Then, $w_2$ and $w_3$ are weight fraction of solute (HMF) and water, respectively.

### 1.2.5 Thermodynamic models

The NRTL (nonrandom two-liquid) [49] and UNIQUAC (UNIversal QUAsi Chemical) [50] activity coefficient models were used to correlate the experimental LLE tie-line data, which are able to calculate the multicomponent LLE phase compositions by only using the constituent binary parameters, as listed in Eq. (1.2) and (1.3), respectively.

$$\ln \gamma_i = \frac{\sum_j^N \tau_{ji} G_{ji} x_j}{\sum_k^N G_{ki} x_k} + \sum_j^N \frac{x_j G_{ij}}{\sum_k^N G_{kj} x_k} \left( \tau_{ij} - \frac{\sum_k^N x_k \tau_{kj} G_{kj}}{\sum_k^N G_{kj} x_k} \right) \tag{1.2}$$

$$\ln \gamma_i = \ln \frac{\phi_i}{x_i} + \frac{z}{2} q_i \ln \frac{\theta_i}{\phi_i} + l_i - \frac{\theta_i}{x_i} \sum_j^N x_j l_i + q_i \left( 1 - \ln \sum_j^N \theta_j \tau_{ij} - \sum_j^N \frac{\theta_j \tau_{ij}}{\sum_k^N \theta_k \tau_{kj}} \right) \tag{1.3}$$

with

$$\phi_i = \frac{r_i x_i}{\sum_k^N r_k x_k}; \quad \theta_i = \frac{q_i x_i}{\sum_k^N q_k x_k}; \quad l_i = \frac{z}{2}(r_i - q_i) + 1 - r_i$$

in which $\gamma_i$ is the activity coefficient of component $i$, $N$ is the number of components, the dimensionless interaction parameters $\tau_{ij} = b_{ij}/T$ (for NRTL), $\tau_{ij} = \exp(b_{ij}/T)$ (for UNIQUAC), $G_{ij} = \exp(-\alpha_{ij}\tau_{ij})$, $G_{ji} = \exp(-\alpha_{ji}\tau_{ji})$, $\tau_{ii} = \tau_{jj} = 0$, $G_{ii} = G_{jj} = 1$, and $\alpha_{ij} = \alpha_{ji}$. $b_{ij}$ is the binary interaction parameter between molecule $i$ and $j$, and $\alpha_{ij}$ is the non-randomness parameter, representing the local composition of the system. Furthermore, the UNIQUAC parameters $r_i$ and $q_i$ are the van der Waals volume and surface area, respectively. z is the coordination number which is set equal to 10.

Reliable thermodynamic models and their parameter values are needed to enhance the operational efficiency of the separation process and to reduce the production costs, thus the process can be run economically. Therefore, the NRTL and UNIQUAC activity coefficient models were used in this study to correlate the experimental LLE tie-line data. The reliability of the thermodynamics models are determined using root mean square deviation (RMSD) which is the deviation of the composition between the experimental data and the calculation using the thermodynamic model :

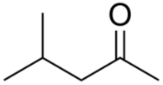
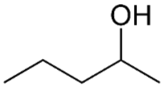
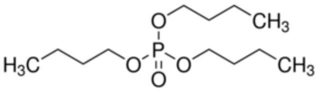
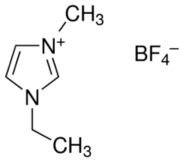
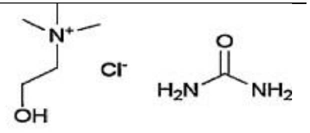
$$\mathrm{RMSD} = \sqrt{\frac{\sum_{k=1}^{M}\sum_{i=1}^{N}\sum_{j=I}^{II}\left(w_{ijk}^{expt} - w_{ijk}^{calc}\right)^2}{2NM}}\, x100\% \qquad (1.4)$$

where $w_{ijk}^{expt}$ and $w_{ijk}^{calc}$ are the experimental and calculated mass fractions of component *i* in phase *j* on tie-line *k*, respectively. Furthermore, *N* is the number of components and *M* is the number of tie-lines.

## 1.3 Overview of this research

The aim of this study is systematically study the effect of biphasic system constituents on the liquid-liquid extraction of HMF at 313.15 K and atmospheric pressure (0.1 MPa). The separation factor and distribution coefficient of HMF were determined from liquid-liquid equilibrium (LLE) data to interpret the extraction performance. The experimental LLE data of the investigated systems were also correlated using thermodynamics model. We used aqueous-organic biphasic systems, and also added IL [EMIM][$BF_4$] (1-ethyl-3-methylimidazolium tetrafluoroborate) or DES ChCl-urea (choline chloride urea) in the aqueous phase. The effect of the addition of sugar (fructose) and salt in the variety of cation and anion (NaCl, KCl, $Na_2SO_4$, and $K_2SO_4$) were also studied. Three different extraction solvents, methyl isobutyl ketone (MIBK), 2-pentanol, and tributyl phosphate (TBP), were used for the comparison. The physical properties for the [EMIM][$BF_4$], ChCl-urea, and organic solvents studied are presented in Table 1.1. To our best knowledge, there are still no thermodynamic studies using these systems in LLE containing HMF. Hence, we introduce new systems for HMF extraction in this study. The phase equilibrium data are needed for the rational design and optimal separation operation of HMF from the aqueous solution.

**Table 1.1** Physical properties of organic solvents, IL, and DES used in this study [51]

| Properties | Unit | MIBK | 2-pentanol | TBP | [EMIM][BF$_4$] | ChCl-urea |
|---|---|---|---|---|---|---|
| Molecular structure | - |  |  |  |  |  |
| Molecular weight | g/mol | 100.161 | 88.148 | 266.318 | 197.97 | 259.74 |
| Boiling point | °C | 117 | 119 | 289 | >350 | 445.6 |
| Melting point | °C | -84 | -73 | <-80 | 15 | 12 |
| Flash point | °C | 14 | 33 | 146 | 113 | - |
| Density | g/cm$^3$ | 0.8010[52] | 0.8090[53] | 0.9767[54] | 1.2844[55] | 1.2001[56] |

## 1.4 Outline

This thesis is divided into seven parts which is organized as follows :

**Chapter 1** gives the general introduction that provides the background of this research, the state of art about HMF production and extraction process, theory about liquid-liquid extraction and the thermodynamic models for phase equilibria, and overview of this research.

**Chapter 2** provides liquid-liquid equilibrium data of ternary and quaternary systems involving 5-hydroxymethylfurfural, water, organic solvents (MIBK or 2-pentanol), and salts at 313.15 K and atmospheric pressure. Then, the ternary LLE data were correlated using NRTL and UNIQUAC models. While, the quaternary LLE systems containing salt were correlated using NRTL model. We determined the salting-out strength based on the separation factor and distribution coefficient of HMF, and selected the inorganic salt with good extraction performance.

**Chapter 3** presents the study of the effect of 1-ethyl-3-methylimidazolium tetrafluoroborate on the phase equilibria for systems containing 5-hydroxymethylfurfural, water, organic solvent in the absence and presence of sodium chloride. The experimental LLE data were correlated using NRTL model. We also compared the ability of extraction solvent, MIBK and 2-pentanol, and selected the better extraction solvent for HMF extraction in the presence of ionic liquid and salt (NaCl) with the good separation factor and HMF distribution coefficient.

**Chapter 4** presents the study of choline chloride urea effect on the liquid-liquid equilibria of 5-hydroxymethylfurfural, water, organic solvent systems in the absence and presence of sodium chloride. The experimental LLE data were also correlated with NRTL model. In the end, we compared the ability of organic solvent (MIBK and 2-pentanol) to extract HMF based on the values of separation factor and HMF distribution coefficient. We selected one organic solvent to be used further on the LLE experiment with the addition of sugar (fructose).

**Chapter 5** reports the study of fructose effect on the extraction performance of 5 - hydroxymethylfurfural in water - 1- ethyl – 3 - methylimidazolium tetrafluoroborate (or choline chloride urea) - sodium chloride solution using methyl isobutyl ketone extraction solvent. The NRTL model was used to correlate the experimental data. We also compared the effect of the presence of IL and DES in the HMF extraction.

**Chapter 6** provides the liquid-liquid equilibrium data for 5-hydroxymethylfurfural separation from aqueous solution using tributyl phosphate as extraction solvent. We added DES (ChCl-urea) in the aqueous phase. Furthermore, the combined effect of aqueous ChCl-urea with salt (NaCl) in the absence and presence of sugar (fructose) were investigated. The performance of TBP solvent was also compared to that of MIBK and 2-pentanol extraction solvents. The NRTL and UNIQUAC models were applied for correlating the ternary experimental LLE data, while the experimental LLE data containing ChCl-urea, NaCl, and fructose were correlated using the NRTL model.

**Chapter 7** gives the conclusion of this research and at the end of this chapter, further recommendations are presented.

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# Chapter 2

## Liquid-liquid equilibria of ternary and quaternary systems involving 5-hydroxymethylfurfural, water, organic solvents, and salts at 313.15 K and atmospheric pressure

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# ABSTRACT

HMF (5-hydroxymethylfurfural) is one of the bio renewable materials that can be used to produce a wide range of chemical products. In the HMF production process, yield and selectivity may be increased by liquid-liquid extraction of HMF using an organic solvent to prevent its degradation. Phase equilibrium data are required for rational design and optimal separation of HMF from the aqueous solution. In this study, liquid-liquid equilibrium (LLE) data of HMF, water, and methyl isobutyl ketone (MIBK) or 2-pentanol at 313.15 K (40°C) and atmospheric pressure were measured and correlated using the NRTL and UNIQUAC models. The root mean square deviations (RMSD) of the NRTL and UNIQUAC models were 0.42% and 0.48% for the MIBK-HMF-water and 0.76% and 0.75% for the 2-pentanol-HMF-water system, respectively. The results indicated that higher distribution coefficients are achieved in the 2-pentanol-HMF-water system compared to the MIBK-HMF-water system. On the other hand, the separation ability of MIBK is better than that of 2-pentanol. In liquid-liquid extraction, not only a high distribution coefficient of HMF is important, but also a high separation factor is desirable to reduce the amount of co-extracted water. Therefore, in the present study the distribution coefficient of HMF from MIBK-HMF-water and the separation factor of the 2-pentanol-HMF-water system was improved by introducing a certain amount of salt into the aqueous solution. The salts examined in this study were based on the variety of cation ($Na^+$, $K^+$) and anion ($Cl^-$, $SO_4^{2-}$). The NRTL model was applied to correlate the LLE of organic solvent-HMF-water-salt systems, the results of which provided good agreement with the experimental data. The presence of salt can enhance the partitioning of HMF into the organic phase as well as the separation factor up to 2 times indicating the salting-out ability of the studied salts. The order of salting-out strength was $NaCl > Na_2SO_4 > KCl > K_2SO_4$ in which $Cl^-$ and $Na^+$ demonstrated stronger salting-out ability than $SO_4^{2-}$ and $K^+$.

*Keywords*: Distribution coefficient; 5-Hydroxymethylfurfural; Liquid-liquid equilibria; Salting-out; Separation factor

## 2.1 Introduction

Liquid-liquid extraction is one of the separation methods that can be applied in HMF production to enhance HMF yield and selectivity. The organic solvent is used to extract the HMF from its aqueous solution. As we know that HMF can be more easily degraded at high temperature, as studied by Girisuta *et al.* [1]. They studied the decomposition of HMF in a temperature window of 98-181°C which are in the range of reaction condition. Therefore, the extraction process is preferably carried out at a lower temperature than the reaction condition to optimally extract HMF. Furthermore, in order to consume less energy for cooling after the reaction, typically conducted at 80-250°C [2-4], the temperature in the extraction unit should be higher than room temperature. Hence 40°C (313.15 K) was selected in this study as a moderate operating temperature for the HMF extraction.

In this study, the extraction solvents applied are methyl isobutyl ketone (MIBK) and 2-pentanol, that interact well with HMF molecule and have limited solubility in water. The extraction performance evaluation is based on values of two important parameter which is the separation factor and the distribution coefficient of HMF from the aqueous phase into the organic phase. Furthermore, the use of salt in the aqueous phase can enhance the partitioning of HMF into organic phase [5,6]. Hence, different salts composed of various cations and anions were studied, i.e. NaCl (Sodium Chloride), KCl (Potassium Chloride), $Na_2SO_4$ (Sodium Sulfate), and $K_2SO_4$ (Potassium Sulfate).

To our best knowledge, only few researchers have investigated the thermodynamics of HMF extraction [5, 6-10]. Xiong *et al.* [7] have used the COSMO-SAC model [11] to predict the LLE systems containing HMF using primary alcohol as extraction solvent at 30°C. The ePC-SAFT [12,13] was used to especially correlate the experimental LLE systems involving HMF using MIBK solvent in the presence of salt at 25°C [6]. Dalmolin *et al.* [10] reported the LLE in systems containing HMF using alcohol as solvent at 25°C and used the NRTL (Non-Random Two-Liquid) [14] as correlation model. There is still a great need for experimental equilibrium LLE data containing HMF in various aqueous-organic biphasic systems and their correlation with process conditions. Therefore, in the present study we investigated and provided LLE data for multi-component systems containing HMF using MIBK or 2-pentanol as extraction solvents at 40°C (313.15 K) as a moderate operating temperature ensuring HMF stability selected in this work. Furthermore, the experimental ternary LLE data were correlated by the NRTL (Non-Random Two-Liquid) and UNIQUAC (Universal Quasi-Chemical) Thermodynamic models. Among all thermodynamic models, the NRTL [14] and UNIQUAC [15] activity coefficient models are good correlation models which are widely applied for describing phase equilibrium data in various systems [16-20]. They are direct models available in ASPEN Plus and much easier to use in process simulation. However, the thermodynamics study using these two well-known activity coefficient models, NRTL and UNIQUAC, is quite limited for correlating the LLE data of systems containing HMF and providing the binary interaction parameters [10]. Besides, the NRTL model can also be used to correlate LLE systems containing salts [21,22]. The NRTL model using de Haan and Niemann approach [21,22] provides a more simple calculation compared to the e-NRTL [23,24] and ePC-SAFT [12,13] models. Hence, in this study, we also measured LLE data for multi-component systems of HMF-water-organic solvent-salt at constant temperature (313.15 K) and correlated these data using the NRTL model. The LLE data provided in this work provide the basis for a rational design and optimal HMF extraction operation. The binary interaction parameters obtained are also needed for improving the operational efficiency of the HMF extraction process. Furthermore, this work can open a scope for the thermodynamics studies of HMF biphasic extraction systems.

## 2.2 Experimental Section

### 2.2.1 Chemicals

All chemicals used in this study are described in Table A.1. The water used for the experiments was deionized ultrapure water with resistance of 18.2 MΩ.cm.

### 2.2.2 HMF stability validation

The stability of HMF in the aqueous and organic phase was evaluated using BHA (Butylated hydroxyanisole) [25]. Sanborn *et al.* [25] indicated that the stability of HMF can be improved by adding 1000 ppm of BHA as antioxidant. Two samples with 10.07 wt% of HMF in water and two samples of 10.40 wt% of HMF in MIBK were prepared. For both mixtures 1000 ppm equivalent of BHA was added to one of the two samples. All samples were stirred and then placed in an oven set to 313.15 K. The concentration of HMF was analyzed by gas chromatography (GC) using the internal standard method at the start, after 1 day, 2 days, 5 days, 9 days, and finally after 15 days.

### 2.2.3 Tie-line measurements

The LLE tie-lines were measured with a jacketed equilibrium cell at 313.15 K and atmospheric pressure. The water bath (Tamson-instruments TC 6B, Holland) was used to circulate water and maintain the equilibrium cell at constant temperature with a standard uncertainty u(*T*) of 0.02 K. Aqueous feeds containing HMF-water and HMF-water-salts in different concentrations were prepared using a Mettler Toledo (MS 304S/01, Switzerland) analytical balance with a precision of ± 0.0001 g. In all tie-line experiments a mass ratio of 1:1 between organic solvent and aqueous feed solution was used with a varying HMF concentration and constant salt concentration in the feed. The mixture was stirred with a magnetic stirrer bar in the equilibrium cell for 1.5 hours and allowed to settle for 20 hours for low HMF concentration and at least 22 hours for high HMF concentration at 313.15 K until the two liquid phases were completely separated. This equilibrium time was checked prior to the LLE experiment and it is adequate to reach equilibrium. Then, 1.2 g of sample was taken from each phase to determine the concentrations of HMF, organic solvent, water, and salt.

### 2.2.4 Analytical measurements

The samples from the equilibrium experiments were analysed using a gas chromatography (Varian Technologies 430) system equipped with a flame ionization detector (FID). The concentrations of HMF and organic solvents were analyzed using DMF as internal standard. A DB-624 column was employed for the sample analysis. The column flow was 2.0 mL/min and 25:1 split ratio. Initially the column temperature was kept at 60°C for 4 min, then ramped to 250°C at 10°C/min, and finally held at 250°C for 4 min, resulting in an analysis time of 27 minutes. Calibration curves were prepared for these systems before using the analytical method. The ratio in the quantity of the analyte to the quantity of the internal standard was plotted versus the ratio of the analyte peak area to the peak area of the internal standard. For the analysis of samples containing salts, a filter was placed before packed column to prevent salt from entering the packed column and detector. The salt concentrations in the aqueous and organic phases were analyzed using ICP-OES (Inductively Coupled Plasma Optical Emission Spectroscopy, Spectro Arcos EOP, Holland). The samples were diluted with 3% of nitric acid ($HNO_3$) with a dilution factor of 10000 and 1000 times for aqueous and organic samples, respectively. The water content in the organic phase was measured by Karl Fischer titration using a Metrohm 756 KF and the water content of the aqueous phase was determined by subtracting the sum of the other mass fractions from a value of 1. The mass fractions of each component in each phase were averaged from three replicated samples. The standard uncertainties $u(w_i)$ of MIBK, 2-pentanol, HMF, and water were estimated to be 0.0006, 0.0007, 0.0008, and 0.0006 in mass fraction, respectively. Furthermore, the standard uncertainties $u(w_i)$ of salt were 0.0004, 0.0004, 0.0002, and 0.0001 in mass fraction for NaCl, KCl, $Na_2SO_4$, and $K_2SO_4$, respectively.

## 2.3 Results and discussion

### 2.3.1 HMF stability

The stability of HMF was tested using BHA as antioxidant as described in the experimental section before conducting LLE experiments. HMF should be stable during LLE experiments in order to obtain reliable thermodynamic data about its distribution between the aqueous solution and the organic solvent phase. As shown in Figure A.1, the changes of HMF concentration are not significant from the beginning to 15th days for the samples containing HMF-water with and without BHA, and for the sample containing HMF-MIBK with BHA with standard deviations $s(\overline{w}_i)$ less than 0.1%. Whereas, the HMF concentration decreases gradually from 2nd days until 15th days for the sample containing HMF-MIBK without BHA. However, it can be seen that the changes in HMF concentration are not clearly visible up to 2 days for all samples. HMF concentration is stable with standard deviations $s(\overline{w}_i)$ 0.02% in both water and organic solvent without adding BHA for 2 days. Therefore addition of the antioxidant is not necessary as the degradation of HMF might not occur during LLE experiment at 313.15 K which is conducted for less than 2 days.

### 2.3.2 LLE of organic solvent-HMF-water systems

#### 2.3.2.1 Tie-lines organic solvent-HMF-water systems

Experimental LLE tie-line data for the MIBK-HMF-water and 2-pentanol-HMF-water systems at 313.15 K and atmospheric pressure were measured for initial HMF concentrations in aqueous solution ranging from 5-50 wt% and listed in Table A.2-A.3. Figures 2.1 and 2.2 illustrate that the area of the two phase region for MIBK-HMF-water is larger than that for the 2-pentanol-HMF-water system. The smaller area of the 2-pentanol-HMF-water system is due to the higher concentration of water in the organic-rich phase (right hand side) compared to that in the MIBK-HMF-water system which shows the drawback of 2-pentanol as extraction solvent. However, the tie-line slope is more positive in the 2-pentanol-HMF-water system than in the MIBK-HMF-water system. This higher positive slope indicates that 2-pentanol has a better ability to extract HMF compared to MIBK.

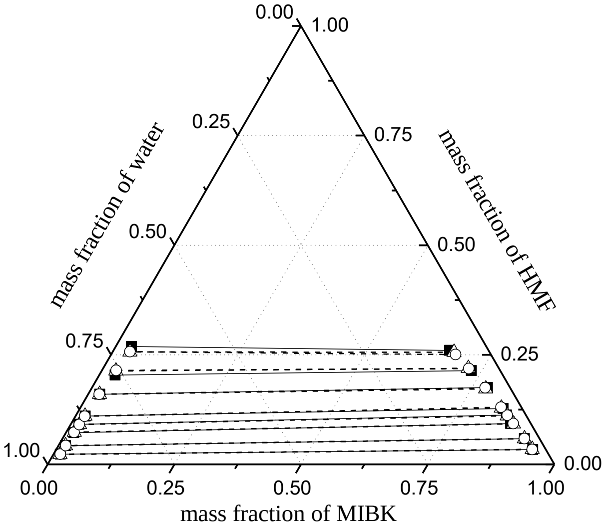


**Figure 2.1** Phase diagram of the experimental and calculated LLE tie-line data for the ternary system MIBK-HMF-water at *T*= 313.15 K and atmospheric pressure using NRTL and UNIQUAC models; (—■—) experimental data; (- -△- - -) NRTL model; (- -○- - -) UNIQUAC model.

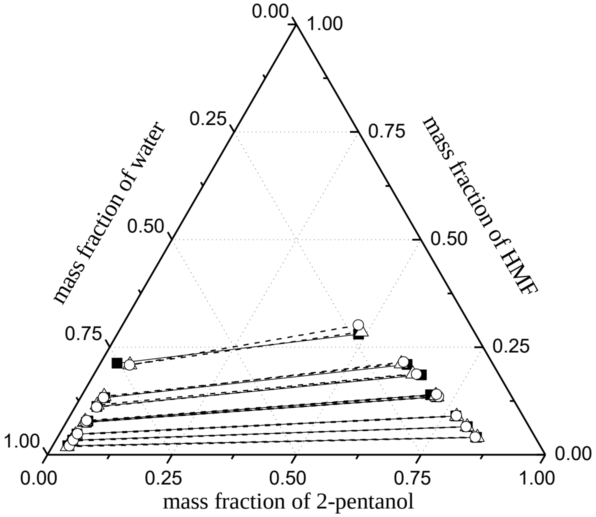


**Figure 2.2** Phase diagram of the experimental and calculated LLE tie-line data for the ternary system 2-pentanol-HMF-water at *T*= 313.15 K and atmospheric pressure using NRTL and UNIQUAC models; (—■—) experimental data; (- -△- -) NRTL model; (- -○- -) UNIQUAC model.

#### 2.3.2.2 Correlation of ternary LLE data for organic solvent-HMF-water systems

The NRTL [14] and UNIQUAC [15] activity coefficient models were used to correlate the experimental LLE tie-line data, which are able to calculate the multicomponent LLE phase compositions by only using the constituent binary parameters. The correlations were performed in mole fractions using Aspen Plus V8.8. The binary interaction parameters $b_{ij}$ *and* $b_{ji}$ were obtained by regressing the experimental LLE tie-line data by minimizing the maximum likelihood objective function using the Britt and Luecke algorithm [26]. The non-randomness parameter ($\alpha_{ij}$) was fixed at 0.2 for each pair (*i-j*) as default for systems that exhibit liquid-liquid immiscibility. The determined binary interaction parameters for the NRTL and UNIQUAC models among the organic solvents (MIBK and 2-pentanol), HMF, and water are listed in Table A.4. In this case, the $b_{ij}$ and $b_{ji}$ among MIBK, HMF, water were regressed, then the $b_{ij}$ and $b_{ji}$ between HMF and water obtained from the regression results of the MIBK-HMF-water were fixed in the correlation of the 2-pentanol-HMF-water system. While, the $b_{ij}$ and $b_{ji}$ were regressed in the LLE of 2-pentanol-HMF-water for the interactions of 2-pentanol with HMF and water. The van der Waals volume ($r_i$) and surface area ($q_i$) parameters for the UNIQUAC model were estimated by Bondi method [27], as seen in Table A.5. The topological analysis of the Gibbs energy of mixing function ($G^M$) for liquid-liquid equilibrium correlations in these investigated systems are also provided in Figures A.2-A.13 to confirm the consistency of the determined binary interaction parameters.

The calculated LLE tie-line data from the NRTL and UNIQUAC models and the experimental LLE tie-line data are compared in Figures 2.1 and 2.2. The closed and open symbols represent the LLE tie-lines from experimental data and thermodynamics models, respectively. As can be seen in these ternary phase diagrams, the NRTL and UNIQUAC models correlate the experimental LLE tie-line data well. The RMSD (root mean square deviation) of NRTL and UNIQUAC models are 0.42% and 0.48% for MIBK-HMF-water and 0.76% and 0.75% for 2-pentanol-HMF-water, as listed in Table A.4. From Figure 2.2, it can be seen that the larger deviations occur especially at higher concentrations of HMF. This indicates that the distribution coefficient of HMF in 2-pentanol-HMF-water system at higher HMF concentration is less good correlated with NRTL and UNIQUAC models compared to that of

MIBK-HMF-water system. This also represents that the interaction between HMF, water, and organic solvent are better regressed in the MIBK-HMF-water system.

### 2.3.2.3 Distribution coefficient and separation factor

Extraction processes depend on the physical and chemical properties of the solute and its interaction with the solvent [28,29]. The two main parameters for liquid-liquid extraction are the distribution coefficient ($D_2$) and the separation factor ($S$). The separation factor and distribution coefficient of HMF and water with MIBK and 2-pentanol as extraction solvent are shown in Figure 2.3 and Table A.6. It is seen that the separation factors are much higher than 1 and also the distribution coefficients of HMF are mostly higher than 1 for the two investigated systems. The results indicate that the extraction of HMF from aqueous solution by the organic solvents used in this study is favourable. Furthermore, the comparison of separation factor and distribution coefficient of HMF for the systems in this study at 313.15 K and 298.15 K [19, 23] are also demonstrated in Figure 2.3. It represents that the distribution coefficient of HMF and the separation factor slightly increase with increasing temperature from room temperature to 313.15 K. Figure 2.3 and Table A.6 show that the separation factors of MIBK-HMF-water are higher than that of 2-pentanol-HMF-water over the whole HMF mass fraction range. The separation factors can reach up to 54.4 and 15.6 for MIBK-HMF-water and 2-pentanol-HMF-water systems, respectively. On the other hand, the use of 2-pentanol as extraction solvent gives higher distribution coefficients compared to MIBK because of its stronger hydrogen bond interactions with HMF than MIBK. This is also clearly visible from the more pronounced positive slope of the tie-lines in Figures 2.1 and 2.2 for the 2-pentanol-HMF-water system relative to that of the MIBK-HMF-water system.

MIBK exhibits a higher separation factor due to the lower solubility of water in MIBK which is represented by the lower value of the distribution coefficient of water. The intermolecular bond between C=O from MIBK with –OH from water is less strong compared to that between –OH from 2-pentanol with –OH from water. Typically, after extraction, the solute (HMF) and solvent are recovered from the extract by distillation. As water has the highest heat of evaporation [29] and the lowest boiling point, co-extracted water will increase the energy demand from the solvent/solute recovery process steps. At the same time MIBK has a lower distribution coefficient compared to 2-pentanol, requiring more solvent to achieve the same extraction factor and thus increased energy costs for solvent recovery. Hence, the aim of the present study is to evaluate whether the addition of inorganic salts can improve the distribution coefficient of HMF in the MIBK-HMF-water system and/or to increase the separation factor in the 2-pentanol-HMF-water system to further enhance the efficiency of HMF extraction.

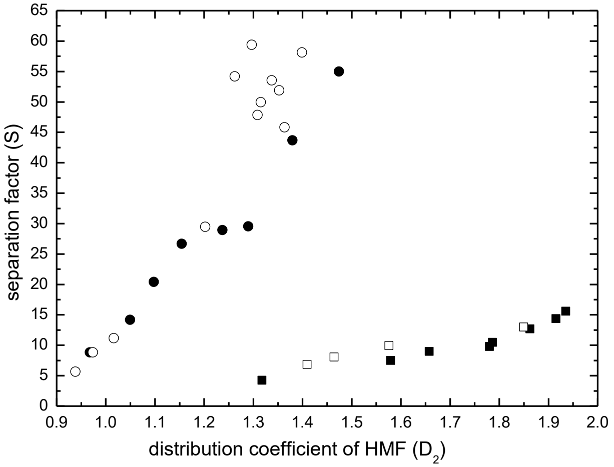


**Figure 2.3** Relationship between separation factor (S) and distribution coefficient of HMF ($D_2$) for the organic solvent-HMF-water systems at *T*= 313.15 K and 298.15 K, and atmospheric pressure; ( ● ) MIBK-HMF-water at 313.15 K (this study) ; ( ○) MIBK-HMF-water at 298.15 K [19]; (■) 2-pentanol-HMF-water at 313.15 K (this study); (□) 2-pentanol-HMF-water at 298.15 K [23].

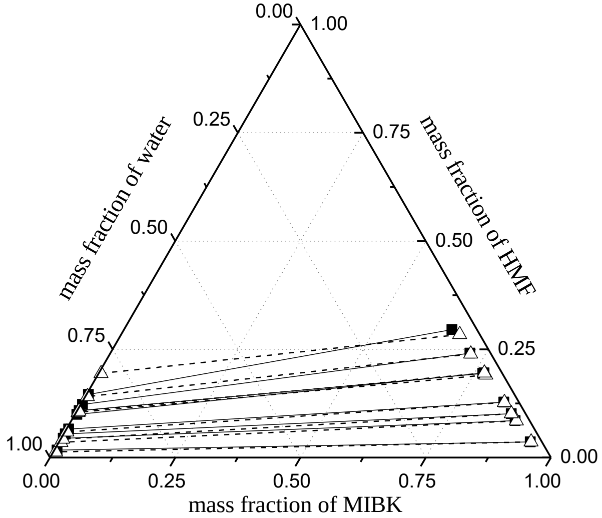
### 2.3.3 LLE of organic solvent-HMF-water-salt systems

#### 2.3.3.1 Tie lines organic solvent-HMF-water-salt systems

The obtained experimental LLE tie-line data for the MIBK-HMF-water-salt and 2-pentanol-HMF-water-salt systems at 313.15 K and atmospheric pressure are listed in Tables A.7 and A.8. The LLE data were determined for initial HMF concentrations in the aqueous solution ranging from 5 wt% to 40 wt% while keeping the salt concentration constant. The organic solvent was added with a mass ratio of 1:1 between organic solvent and HMF aqueous solution in the presence of salt. The LLE of organic solvent-HMF-water-salt systems were measured at salt concentrations near the maximum salt solubility in a 40 wt% HMF aqueous solution for all salts studied. The concentration of NaCl and KCl added into the HMF aqueous solution were fixed at 10 wt%. While, for $Na_2SO_4$ and $K_2SO_4$, the LLE data were investigated at 3 wt% and 2.5 wt%, respectively. Figures 2.4 and 2.5 show the LLE data of organic solvent-HMF-water-salt systems at 313.15 K and atmospheric pressure in free-salt base. It can be observed from comparing Figure 2.1 with Figure 2.4 and Figure 2.2 with Figure 2.5 that the two liquid phases regions become broader by introducing salts into the LLE systems. Besides that, the addition of salt increases the tie-line slope compared to the systems without salt. The increased slopes of the tie-lines represent the increase in distribution coefficient by the salting-out effect of the salts. This is caused by the reduced interaction between HMF and water when the ions are dissolved. As the water molecules prefer to surround the ions from the salt, they become unavailable for interaction with the HMF molecules, being a nonelectrolyte compound. As a result the HMF molecules are salted out from the aqueous solution and more easily extracted into the organic solvent. By comparing Figures 2.4 and 2.5 (a and c) with Figures 2.4 and 2.5 (b and d), it can be observed from the steeper tie-line slope that for both anions, the salting-out effect of the $Na^+$ cation is stronger than that of the $K^+$ cation. Because $Na^+$ has a smaller relative atomic mass than $K^+$, the outer electrons are closer to the nucleus, yielding a stronger ionic potential and interaction with water, resulting in a higher salting-out strength.

Furthermore, from comparing Figures 2.1 and 2.2 with Figures 2.4 and 2.5, these phase equilibria diagrams illustrate that the addition of salt reduces the organic solvent content in the aqueous (raffinate) phase. For all salt containing systems the aqueous phase concentrations, which are on the left hand side of the ternary diagram, have shifted more towards left axis. Typically the concentrations of MIBK and 2-pentanol in the aqueous phase decrease from 1-5 wt% in the absence of salt (Table A.2 and A.3) to values significantly below 1 wt% with the addition of salt (Table A.7 and A.8). In this case, the salting out effect can decrease the interaction between organic solvent with water, thus the organic solvent concentration in the aqueous (raffinate) phase can be reduced as well. It is clear that this lower organic solvent content in the raffinate phase is beneficial for industrial scale HMF extraction as the energy consumption for solvent recovery and potential solvent losses will be reduced.

An additional effect of the presence of salt is the reduction of the water content in the organic (extract) phase. As illustrated by the ternary diagrams, the organic phase concentrations, which are on the right hand side, shift further to the right by the addition of salt into the systems. This effect is most pronounced for the 2-pentanol-HMF-water system with NaCl or KCl, where the water concentrations in the organic phase reduce from 12-23 wt% (Table A.3) to 9-11 wt% (Table A.8) after introducing the salt. This reduced water content due to the hydration effect of water as explained earlier will eventually improve the energy efficiency of the solvent recovery from the extracted HMF by decreasing the need of water evaporation.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mass fraction of water
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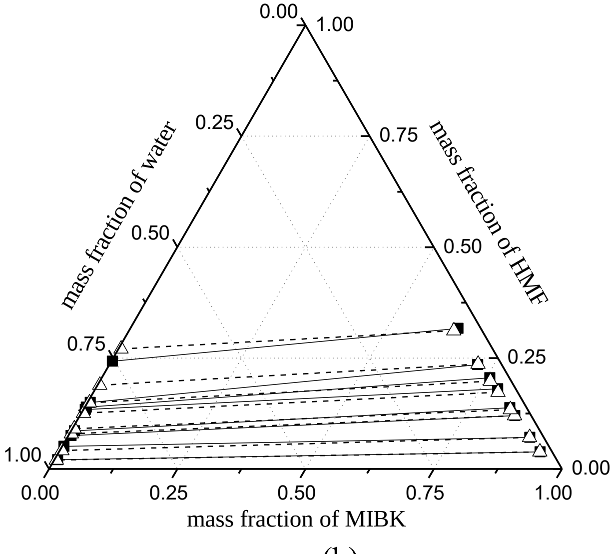
(a)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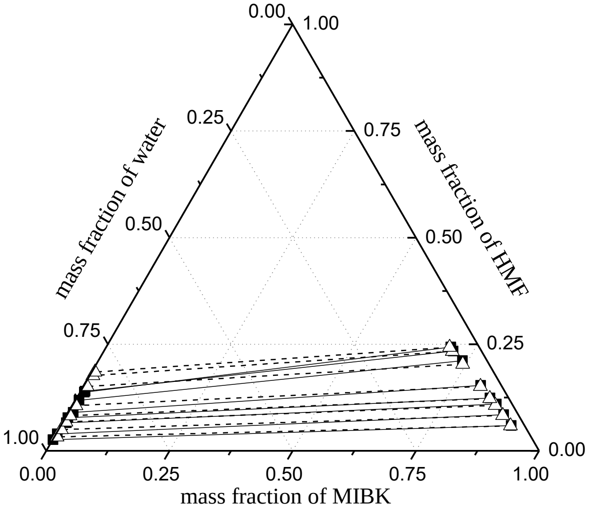
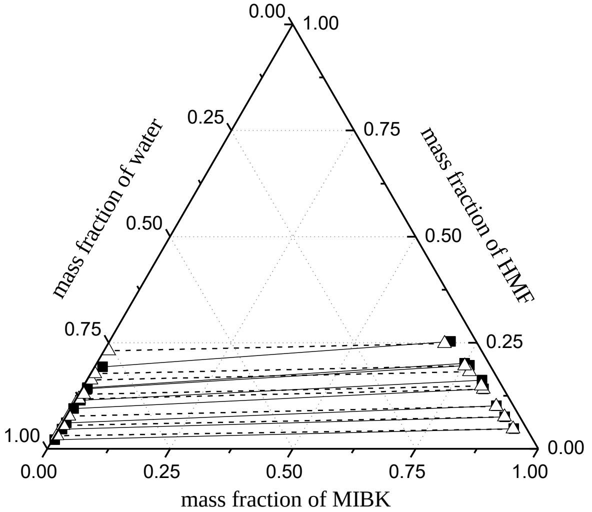
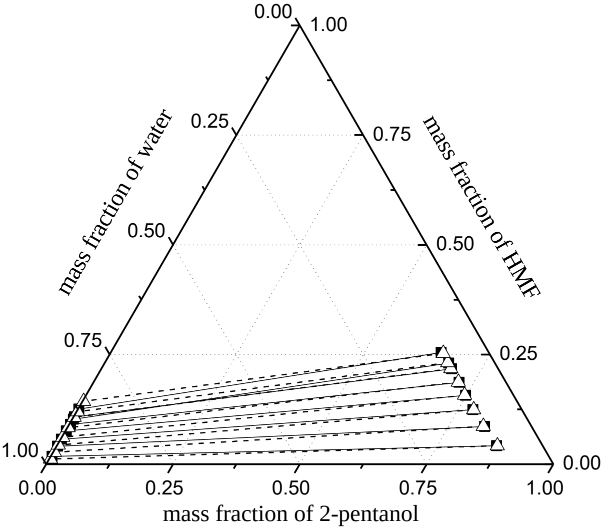


(c)



(d)

**Figure 2.4** Phase diagram of the experimental and calculated LLE tie-line data of the quaternary systems MIBK-HMF-water-salt in free-salt base at *T*= 313.15 K and atmospheric pressure using NRTL model; (a) 10 wt% NaCl; (b) 10 wt% KCl; (c) 3 wt% $Na_2SO_4$; (d) 2.5 wt% $K_2SO_4$; ( —■—) experimental data; (- - △- - - ) NRTL model.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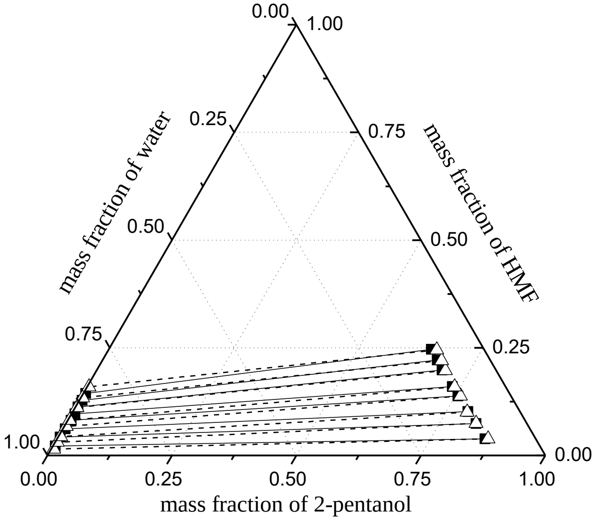
mass fraction of water
mass fraction of HMF
mass fraction of 2-pentanol

(a)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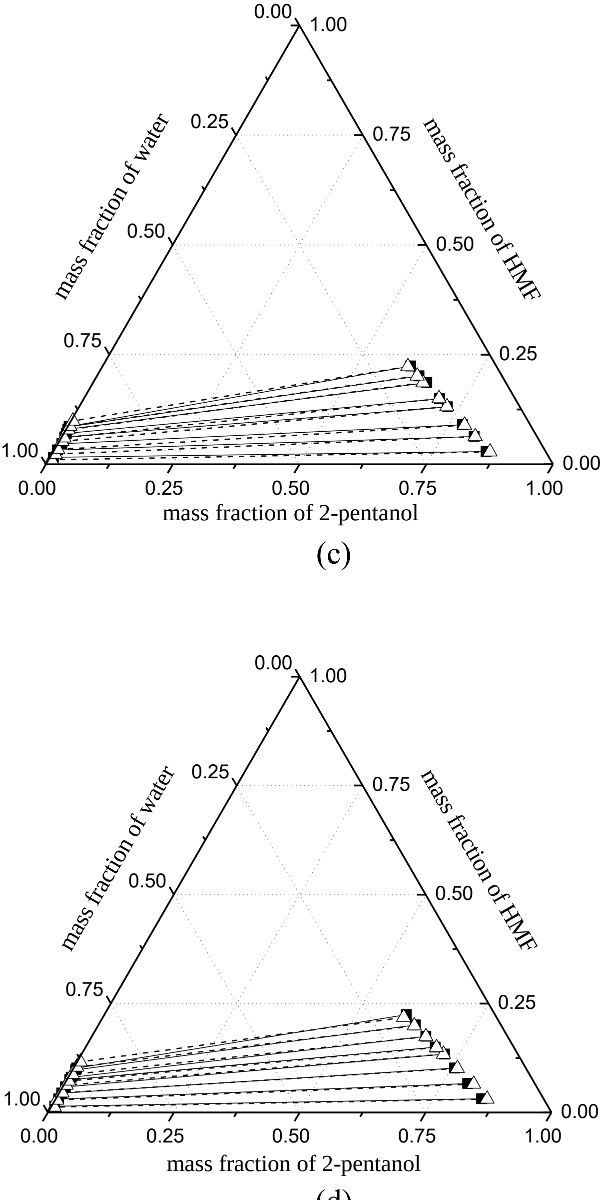
mass fraction of water
mass fraction of HMF
mass fraction of 2-pentanol

(b)



(c)

(d)

**Figure 2.5** Phase diagram of the experimental and calculated LLE tie-line data of the quaternary systems 2-pentanol-HMF-water-salt in free-salt base at *T*= 313.15 K and atmospheric pressure using NRTL model; (a) 10 wt% NaCl; (b) 10 wt% KCl; (c) 3 wt% Na$_2$SO$_4$; (d) 2.5 wt% K$_2$SO$_4$;(—■—) experimental data; (- - -△- - -) NRTL model.

#### 2.3.3.2 Correlation of quaternary LLE data for organic solvent-HMF-water-salt systems

The experimental LLE tie-line data for organic solvent-HMF-water-salt systems were correlated using NRTL model as illustrated in Figures 2.4 and 2.5. In this correlation, salt was considered as one molecular species and in addition to the binary interaction parameters ($b_{ij}$ and $b_{ji}$) also the nonrandomness parameters ($\alpha_{ij}$) were regressed instead of setting it to the default value for the interactions of the salt with water, HMF and solvent [21,22]. The NRTL parameters ($b_{ij}$, $b_{ji}$, and $\alpha_{ij}$) among organic solvents (MIBK and 2-pentanol), HMF, and water binary pairs were taken from the correlation results obtained in the ternary LLE data, as listed in Table A.4. The resulting parameters for the interactions with the salts are presented in Table A.9.

The results show that the experimental LLE tie-line data containing salts were accurately correlated with the NRTL model with the RMSD values of the MIBK-HMF-water-salt systems being 1.09%, 0.83%, 1.44%, and 1.54% for NaCl, KCl, $Na_2SO_4$, and $K_2SO_4$, respectively. Moreover, the RMSD values of the 2-pentanol-HMF-water-salt systems are 0.98%, 0.63%, 0.64%, and 0.50% for NaCl, KCl, $Na_2SO_4$, and $K_2SO_4$, respectively, as seen in Table A.9. Therefore, the NRTL model using de Haan and Niemann approach [21,22] can be used further to develop process designs for the extraction of HMF from aqueous solution in the presence of salt which gives a more simple and easier calculation compared to the e-NRTL [23,24] and ePC-SAFT [12,13] models. Even though the negative values were obtained for $\alpha_{ij}$ which are physically unrealistic and the NRTL model is reduced to a fit procedure, it is allowed to be used in the correlation.

Moreover, from the results in this study, it can be inferred that the $\alpha_{ij}$ value also plays an important role in obtaining a good correlation of the experimental LLE system containing salt, which was also reported in the previous studies [21,22].

#### 2.3.3.3 Impact of salt addition

The results of separation factors (*S*) and distribution coefficients of HMF ($D_2$) in presence of all the salts used in this study are shown in Figure 2.6. The highest separation factor represents the LLE of organic solvent-HMF-water-salt systems at the lowest initial HMF concentration in aqueous solution, and vice versa. A good salt which can be used to enhance the HMF separation from the aqueous phase is a salt with *S* and $D_2$ located from the top middle to the top right over the whole range of initial HMF concentrations in the aqueous solution. Figure 2.6 shows that $K_2SO_4$ has lower *S* and $D_2$ values at higher HMF concentrations, whereas, NaCl yields good *S* and $D_2$ for the whole range of initial HMF concentrations with MIBK as extraction solvent. In addition, $Na_2SO_4$ represents higher *S* and $D_2$ over the whole range of initial HMF concentrations than KCl and $K_2SO_4$ for both extraction solvents. The increase in separation factor and distribution coefficient represent a good salting-out ability as well. As mentioned earlier, the salting-out strength of the $Na^+$ cation is greater than that of the $K^+$ cation. Generally in the HMF system, the separation ability of the salts are in the order of NaCl > $Na_2SO_4$ > KCl > $K_2SO_4$. The sequence of these anions corresponds to the reversal of the Hofmeister series [30]. The Hofmeister series is the ranking of ions of salts with respect to their ability either to salt out or salt in solutes [31]. Lyklema [32] stated that the sequence can be direct or reverse, which is depending on the system. Several researchers studied that one of the factors that can induce the Hofmeister series reversal is the modification of the functional surface groups from hydrophobic to hydrophilic [30,32]. In the investigated systems, HMF is a hydrophilic molecule which needs to be transferred from the aqueous solution into the organic solvent phase in the presence of salt. In this case, the binding affinity of $Cl^-$ anion on HMF surface is weaker than that of $SO_4^{2-}$, resulting in a reduced stabilization. Therefore, with the same cation, $Cl^-$ anion gives greater salting-out ability than $SO_4^{2-}$.

Figure 2.6, also shows that the HMF distribution coefficients in the 2-pentanol-HMF-water-salt systems are higher than those in the MIBK-HMF-water-salt systems. However, in all cases the separation factors in the LLE systems using MIBK as extraction solvent are higher compared to that of in the 2-pentanol-HMF-water-salt systems. Thus, MIBK is more selective as extraction solvent, whereas 2-pentanol is superior in terms of distribution coefficient. As described previously, the distribution coefficient and the separation factor are the two key factors to evaluate the extraction performance. From Tables A.10 and A.11 it can be seen that introducing the salts into the HMF aqueous solution, increases the distribution coefficient of HMF and separation factor for both systems up to 2 times. Furthermore, the separation factor for 2-pentanol-HMF-water-salt systems can reach values up to 26.0 especially with the addition of NaCl, and over the whole range of initial HMF concentrations, the separation factors are higher than 10. Compared to the system in the absence of salt, the separation factors range from 4.2-15.6, as listed in Tables A.6 and A.11. Furthermore, in general $SO_4^{2-}$ which is divalent anion yields a stronger ionic strength effect relative to $Cl^-$ as monovalent anion. However, the maximum solubilities of salts containing the $Cl^-$ anion in a 40 wt% HMF aqueous solution are much higher than those of salts containing the $SO_4^{2-}$ anion. Besides, as described earlier in the HMF system, the $Cl^-$ anion has stronger salting-out ability than $SO_4^{2-}$ with the same cation. Therefore, at fixed salt concentrations near the maximum salt solubility in a 40 wt% HMF aqueous solution, NaCl was superior to the other salts studied, whereas $K_2SO_4$ showed the lowest salting-out strength.

From the discussion above, it can be inferred that in this study we can improve the distribution coefficient of HMF especially for LLE in the MIBK-HMF-water system and the separation factor for LLE in the 2-pentanol-HMF-water system by introducing the appropriate salt. The salting-out effect makes the extraction more efficient and selective. Although the use of salt in industry has some drawbacks such as corrosion, precipitation, etc. However, these issues can be solved by providing salt recovery [33,34] in the process after HMF extraction. While, according to the results in this study, the HMF extraction in the absence of salt generated lower separation factor and distribution coefficient of HMF which required higher energy and cost for the following product purification and solvent recovery. Therefore, the use of salt is promising and competitive proposal for HMF extraction.

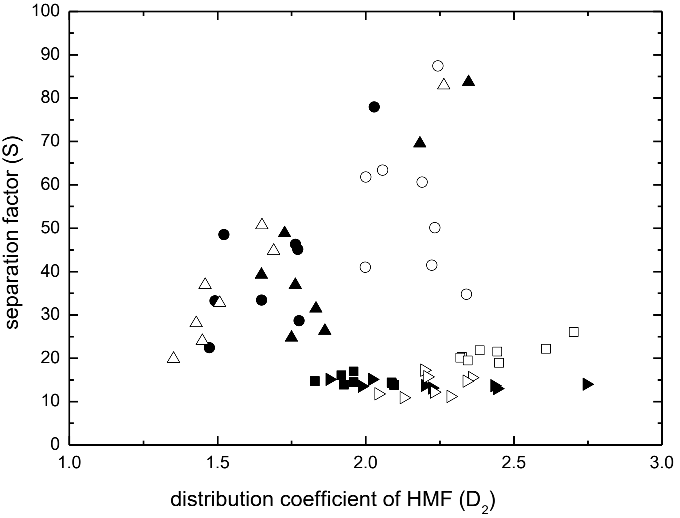


**Figure 2.6** Relationship between separation factor (S) and distribution coefficient of HMF ($D_2$) for the organic solvent-HMF-water-salt systems at *T*= 313.15 K and atmospheric pressure; (○ ) MIBK-HMF-water-NaCl; (●) MIBK-HMF-water-KCl; (▲) MIBK-HMF-water-$Na_2SO_4$; ( △ ) MIBK-HMF-water-$K_2SO_4$; ( □ ) 2-pentanol-HMF-water-NaCl; ( ■ ) 2-pentanol-HMF-water-KCl; (▷) 2-pentanol-HMF-water-$Na_2SO_4$; (▶) 2-pentanol-HMF-water-$K_2SO_4$.

## 2.4 Conclusions

The LLE of organic solvent (MIBK and 2-pentanol)-HMF-water and organic solvent-HMF-water-salt were investigated in this study at 313.15 K and atmospheric pressure. The salts studied were NaCl, KCl, $Na_2SO_4$, and $K_2SO_4$ which based on the variety of cation and anion. The NRTL and UNIQUAC models can give good agreement with the experimental LLE tie-line data of MIBK-HMF-water and 2-pentanol-HMF-water systems with RMSD below 1% for both systems. The experimental LLE tie-line data of organic solvent-HMF-water-salt systems were also satisfactorily correlated using NRTL model. According to the results, LLE in the MIBK-HMF-water system generated higher separation factors at the expense of a lower HMF distribution coefficient compared to the 2-pentanol-HMF-water system. Hence, in this study we improved the distribution coefficient of HMF particularly for LLE in the MIBK-HMF-water system and the separation factor for LLE in the 2-pentanol-HMF-water system by adding an appropriate salt. The addition of salt into the aqueous HMF solution induces stronger two liquid phase splitting represented by the more positive tie-line slopes compared to the LLE systems in absence of salt. The salting-out strength of salts for organic solvent-HMF-water-salt systems are in the order $NaCl > Na_2SO_4 > KCl > K_2SO_4$, in which the salt containing the $Cl^-$ anion yields stronger salting-out ability than $SO_4^{2-}$. Furthermore, the $Na^+$ cation has stronger salting-out strength than $K^+$. The addition of salt can enhance the distribution coefficient of HMF and the separation factor up to 2 times compared to the LLE system without salt.

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# Chapter 3

## Effect of 1-ethyl-3-methylimidazolium tetrafluoroborate on the phase equilibria for systems containing 5-hydroxymethylfurfural, water, organic solvent in the absence and presence of sodium chloride

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## ABSTRACT

HMF (5-hydroxymethylfurfural) is a well-known promising product from hexose dehydration used for production of biofuels and chemicals. Liquid-liquid extraction is an essential process in HMF production to recover HMF from reaction medium. One of the important parameters needed in the extraction process design is liquid-liquid equilibrium (LLE) data. Organic solvent (methyl isobutyl ketone or 2-pentanol) was applied as extraction solvent to induce phase separation and extract HMF from the aqueous solution in the presence of the ionic liquid [EMIM][$BF_4$] (1-ethyl-3-methylimidazolium tetrafluoroborate) and NaCl (sodium chloride). The aim of this study is to investigate the effect of [EMIM][$BF_4$] on the phase equilibria of methyl isobutyl ketone (MIBK) or 2-pentanol, HMF, water systems in the absence and presence of NaCl at 313.15 K and atmospheric pressure (0.1 MPa). The separation factor and the distribution coefficient of HMF were obtained for interpreting liquid-liquid extraction performance. The results indicated that the presence of [EMIM][$BF_4$] caused negative effect on the LLE of organic solvent-HMF-water systems. The slope of tie-lines became more negative with increasing [EMIM][$BF_4$] concentration, indicating lower HMF distribution coefficients and separation factors. However, the presence of NaCl in the HMF aqueous ionic liquid solution can enhance both the separation factor and the distribution coefficient making the HMF extraction more favorable with the HMF distribution coefficient values higher than 1 over the whole range of initial HMF concentrations. According to the results in the present study, MIBK was found superior as an extraction solvent for HMF in the presence of [EMIM][$BF_4$] and NaCl exhibited from the better extraction performance with the separation factors 2.0 times higher than those of 2-pentanol. Furthermore, the NRTL activity coefficient model satisfactorily correlated all the experimental phase equilibrium data provided in this study. The RMSD (root mean square deviations) of the NRTL model were 1.03% and 0.86% for the investigated LLE systems with MIBK and 2-pentanol as solvent in the absence of NaCl, respectively. Whereas, the RMSD of the LLE systems containing NaCl were 0.82% for MIBK-HMF-water-[EMIM][$BF_4$]-NaCl and 1.69% for 2-pentanol-HMF-water-[EMIM][$BF_4$]-NaCl.

*Keywords*: Extraction performance; [EMIM][$BF_4$]; 5-Hydroxymethylfurfural; NaCl; Phase equilibria

## 3.1 Introduction

Ionic liquid (IL) has been used for the dehydration process of carbohydrates into HMF to achieve yields up to 96% over a wide range of ionic liquid concentration 3-100 wt% [1-10]. The advantage of ionic liquid is that it can stabilize HMF by suppressing the formation of side product, resulting in a higher yield of HMF. Ionic liquid is a salt which is liquid at room temperature. Ionic liquid has been used in chemical industries for many applications, since it is a green chemical solvent and has a unique physico-chemical properties [11]. The imidazole group based ionic liquid as cation with chloride and tetrafluoroborate as anion are the most common ionic liquids used in HMF synthesis [1-9]. However, the separation of HMF from pure ionic liquid is challenging [12] and its high viscosity can be a drawback especially in the extraction process due to resulting mass transfer limitations. Therefore, the presence of water in the solution is beneficial to facilitate the extraction and reduce the viscosity. Hence, the efficiency of extraction can be enhanced [9]. In this case, a hydrophilic ionic liquid is preferred which has a high solubility in water. In the present study, the combination of aqueous ionic liquid with inorganic salt (NaCl) was applied, thus the extraction of HMF by organic solvent (MIBK or 2-pentanol) may be improved.

Research on the production of HMF using ionic liquid has increased greatly. However, systematic research on the thermodynamics of HMF production and separation in the presence of ionic liquid is quite limited and needed to be developed [12-15]. In addition, based on our best knowledge there is still no liquid-liquid equilibrium (LLE) data available for the systems containing HMF aqueous solution in the presence of ionic liquid. In the extraction process, LLE data are required for designing the extraction column and optimal operation of HMF extraction. Hence, in the present study we investigated the LLE of MIBK or 2-pentanol, HMF, water, ionic liquid systems at 313.15 K and atmospheric pressure (0.1 MPa). [EMIM][$BF_4$] (1-ethyl-3-methylimidazolium tetrafluoroborate) as one of hydrophilic ionic liquid was applied in this work. The effect of ionic liquid on the LLE phase diagram was also studied. The separation factor and the distribution coefficient of HMF were obtained from the LLE data to determine the extraction performance. Then, we introduced a certain amount of inorganic salt (NaCl) into the aqueous solution and also studied the effect of adding NaCl on the investigated LLE systems. The experimental LLE data were correlated with the NRTL activity coefficient model. The NRTL binary interaction parameters obtained can be applied to perform liquid-liquid equilibrium calculation in extraction column design over a wide range of HMF concentrations. Furthermore, this work introduces new systems for liquid-liquid extraction of HMF and expands the scope for the thermodynamic studies of HMF extraction in aqueous biphasic systems.

## 3.2 Experimental Section

### 3.2.1 Chemicals

The description of chemicals used in this study are presented in Table B.1. The experimental and literature values of densities (ρ) of all chemicals are also described in Table B.2. The water used for the LLE experiments and analysis was deionized ultrapure water with resistance of 18.2 MΩ.cm. The water content of ionic liquid [EMIM][$BF_4$] was

910.7 ppm determined by Karl Fischer titration. All the chemicals were used without further purification.

### 3.2.2 Tie-line measurements

The LLE tie-lines of organic solvent-HMF-water-[EMIM][$BF_4$] in the absence and presence of NaCl were measured with a jacketed equilibrium cell at constant temperature (313.15 K) and atmospheric pressure (0.1 MPa) using the same procedure reported in our previous study [16]. Initial HMF concentration in aqueous solution ranged from 5 wt% to 40 wt% with constant [EMIM][$BF_4$] and NaCl concentrations. Subsequently, the mixture in the equilibrium cell was stirred for 2 hours and left to settle for 20 hours for low HMF concentrations and at least 22 hours for high HMF concentrations at 313.15 K until it reached equilibrium and the two liquid phases were completely separated. For analytical measurements, 5 mL of the organic and aqueous samples were taken from upper and lower phases, respectively. All samples were placed in an oven at 40°C before further sample preparation for analytical measurements to avoid phase separation. The experimental method has been validated using the experimental LLE data of MIBK-HMF-water at 298.15 K from Mohammad *et al.* [17] as comparison. The results are presented in Figures B.1 and B.2 with the same trend and the deviation was 2.87%. This can be explained as the initial concentrations of the compounds were not exactly the same.

### 3.2.3 Analytical measurements

High-performance liquid chromatography (HPLC) equipped with a reversed phase column C18 Zorbax ODS was used to determine the concentrations of HMF and organic solvents (MIBK and 2-pentanol) in the organic and aqueous phases at 42°C. HMF and MIBK were determined using UV/VIS (ultraviolet–visible) detector at a UV-wavelength of 278 nm. RI (refractive index) detector was used to determine 2-pentanol. A mixture of water and methanol with volume ratio of 25:75 and 50:50 was prepared as eluent at flowrate of 1 and 0.6 mL/min to detect the peak area of MIBK and 2-pentanol with peak maxima at 3.6 and 8.2 mins, respectively. The volume ratio was changed to 95:5 to detect the peak area of HMF with peak maxima at 6.7 min. Calibration curves for these components were made prior to the analysis as presented in Figure B.3. The concentration of analyte in weight% was plotted versus the peak area of analyte. The concentrations of inorganic salt in the organic and aqueous phases were analysed by ICP-OES (Inductively Coupled Plasma Optical Emission Spectroscopy, Spectro Arcos EOP) using 3% of nitric acid ($HNO_3$) as diluent. Furthermore, the concentrations of ionic liquid in the both phases were also analysed using ICP-OES by Boron balance. The water concentration in the organic phase was measured by Karl Fischer titration using a Metrohm 756 KF, while the water concentration in the aqueous phase was determined by subtracting the sum of the other mass fractions from a value of 1. The mass fractions of organic solvent, HMF, water, ionic liquid, and inorganic salt in the both phases were averaged from three replicated samples. The standard uncertainties u($w_i$) of MIBK, 2-pentanol, HMF, water, [EMIM][$BF_4$], and NaCl were estimated to be 0.0012, 0.0008, 0.0015, 0.0015, 0.0008, and 0.0004 in mass fraction, respectively.

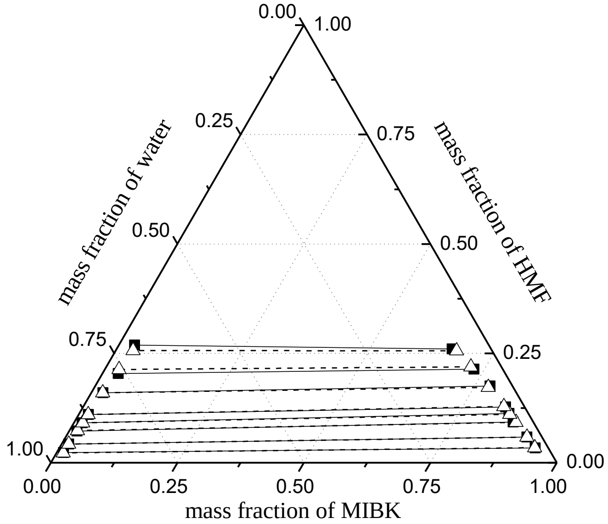
## 3.3 Results and discussion

### 3.3.1 LLE of organic solvent-HMF-water-IL systems

LLE tie-line data were determined at 313.15 K and atmospheric pressure (0.1 MPa) for organic solvent (MIBK or 2-pentanol)-HMF-water-[EMIM][$BF_4$] systems, as listed in Tables B.3 and B.4. HMF concentrations in the feed were varied from 5 wt% to 40 wt% with constant [EMIM][$BF_4$] concentration. The effect of ionic liquid [EMIM][$BF_4$] on the LLE phase diagram was investigated for different concentrations of [EMIM][$BF_4$] in the aqueous solution, i.e 5 wt%, 10 wt%, and 30 wt% for the MIBK-HMF-water-[EMIM][$BF_4$] system and also 10 wt% and 30 wt% for the 2-pentanol-HMF-water-[EMIM][$BF_4$] system, which were then compared with the LLE data in the absence of IL (0 wt% of [EMIM][$BF_4$]) [16]. Figures 3.1 and 3.2 represent the phase diagrams of the investigated systems on IL-free basis. These phase equilibrium diagrams indicate that the organic solvent concentrations in the aqueous-rich phase shift more toward the right side by increasing the [EMIM][$BF_4$] concentration from 0 wt% to 30 wt% for both MIBK and 2-pentanol as extraction solvents. With the higher concentration of organic solvent in the aqueous-rich phase, it can increase the solvent losses and energy costs for solvent recovery which is not good for extraction. Furthermore, as seen in Figures 3.1 and 3.2, the tie-line slopes are positive for the LLE systems in the absence of [EMIM][$BF_4$], then with increasing [EMIM][$BF_4$] concentration the slope of tie-lines become more pronounced negative, especially at 30 wt% of [EMIM][$BF_4$] for both solvents. The negative slopes in LLE phase diagram indicate that less HMF molecules are extracted to the organic-rich phase.

Furthermore, from comparing Figures 3.1 (c and d) with Figures 3.2 (b and c), and also Table B.3 with Table B.4, it becomes evident that at the same [EMIM][$BF_4$] concentration, the solubility of MIBK is much lower than that of 2-pentanol in the aqueous-rich phase located more toward left side. Additionally, the water content of MIBK-HMF-water-[EMIM][$BF_4$] system in the organic-rich phase is also much lower than that of 2-pentanol-HMF-water-[EMIM][$BF_4$] located more towards the right side. This results in a larger two-phase area using MIBK as extraction solvent compared to that of LLE system using 2-pentanol. Considering about the energy efficiency, the lower water content in MIBK rich phase is beneficial for extraction process, as it would decrease the energy demand in the following product purification and solvent recycling processes.

It can also be observed from comparing Figure 3.1 (c) with 3.2 (b) and Figure 3.1 (d) with Figure 3.2 (c) that the tie-line slopes in the MIBK-HMF-water-[EMIM][$BF_4$] system are more negative than that in the 2-pentanol-HMF-water-[EMIM][$BF_4$] system, especially at higher HMF concentrations for 10 wt% of [EMIM][$BF_4$]. These tie line slopes confirm the better ability of 2-pentanol to extract HMF from aqueous solution. However, in the LLE of 2-pentanol-HMF-water-[EMIM][$BF_4$], the [EMIM][$BF_4$] content in the organic-rich phase is higher than in the MIBK-HMF-water-[EMIM][$BF_4$] system at the same ionic liquid concentrations indicating the lower solubility of [EMIM][$BF_4$] in MIBK solvent, as listed in Tables B.3 and B.4. For an optimal separation, the ionic liquid concentration in the organic-rich phase should be low to attain a more efficient and economical product purification.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mass fraction of water
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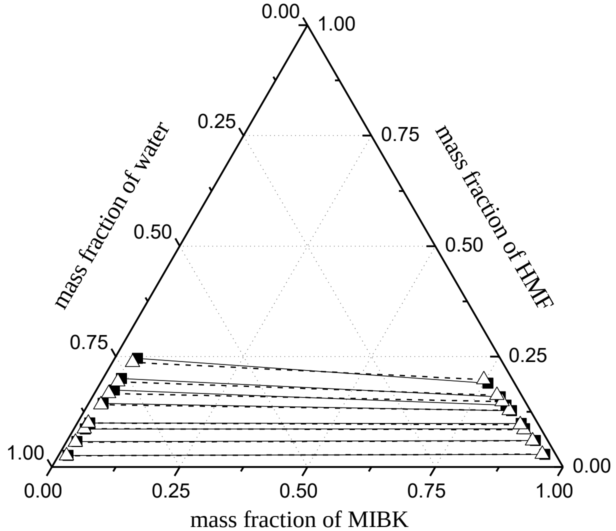
(a)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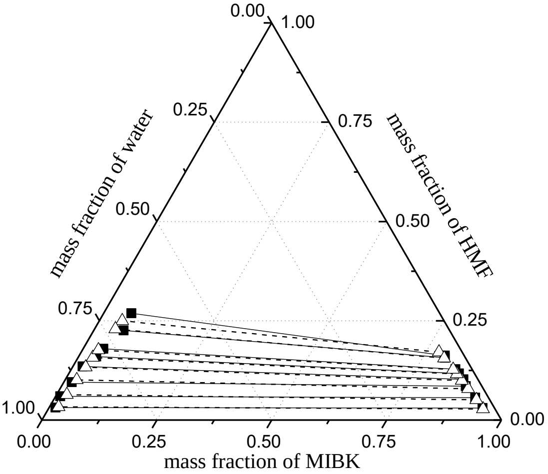
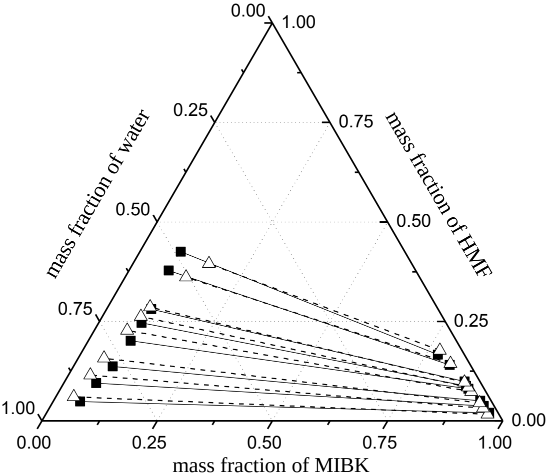
(b)

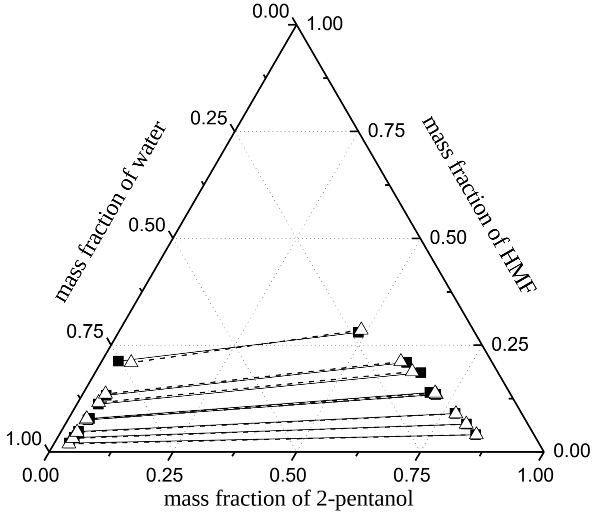


(c)



(d)

**Figure 3.1** Phase diagram of the experimental and calculated LLE tie-line data for MIBK – HMF – water and MIBK – HMF – water – [EMIM][$BF_4$] systems on IL-free basis at *T*= 313.15 K and atmospheric pressure (0.1 MPa) using NRTL model; (a) 0 wt% [EMIM][$BF_4$] [16]; (b) 5 wt% [EMIM][$BF_4$]; (c) 10 wt% [EMIM][$BF_4$]; (d) 30 wt% [EMIM][$BF_4$]; —■— : experimental data; - - △- - - : NRTL model.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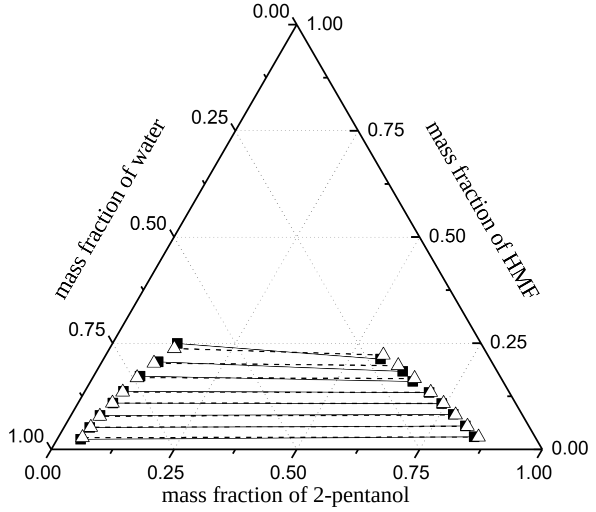
mass fraction of water
mass fraction of HMF
mass fraction of 2-pentanol

(a)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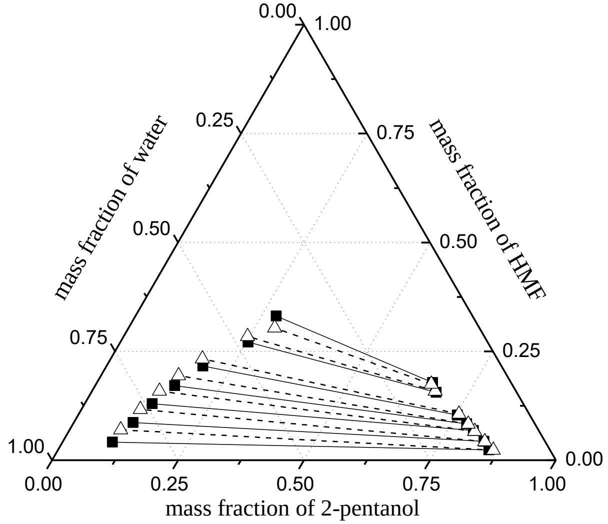
0.75
1.00
mass fraction of water
mass fraction of HMF
mass fraction of 2-pentanol

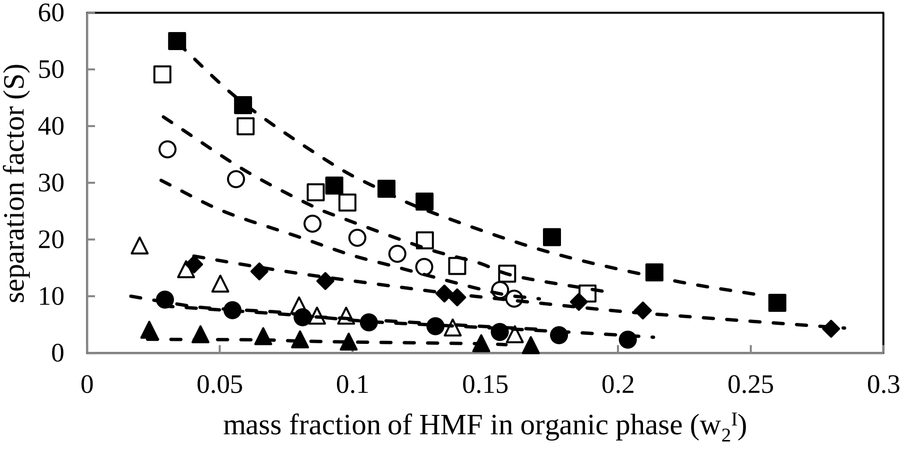
(b)



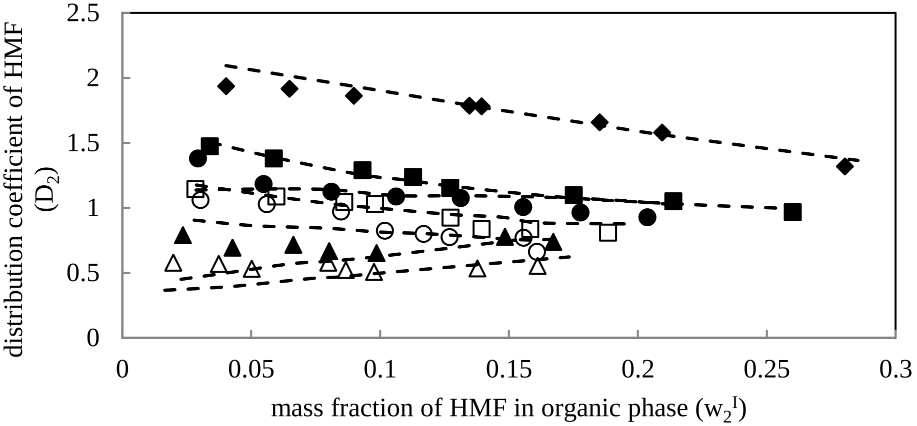
(c)

**Figure 3.2** Phase diagram of the experimental and calculated LLE tie-line data for 2-pentanol – HMF - water and 2-pentanol – HMF – water - [EMIM][BF4] systems on IL-free basis at *T*= 313.15 K and atmospheric pressure (0.1 MPa) using NRTL model; (a) 0 wt% [EMIM][BF4] [16]; (b) 10 wt% [EMIM][BF4]; (c) 30 wt% [EMIM][BF4]; —■— : experimental data; - - -△- - - : NRTL model.

The values of the separation factors and the distribution coefficients for MIBK – HMF – water - [EMIM][BF4] and 2-pentanol – HMF – water - [EMIM][BF4] systems are listed in Table B.5 and shown in Figure 3.3. It can be seen that the separation factors are much higher than 1 over the whole range of initial HMF concentrations. While, the distribution coefficients of HMF ($D_2$) are higher than 1 at lower HMF and [EMIM][BF4] concentrations, demonstrating a favorable HMF extraction. Additionally, the biphasic systems using aqueous IL show much better HMF distribution coefficients compared to the systems using pure IL reported by Wang *et al.* [12] with the distribution coefficients of HMF ranging from 0.028-0.287. The highest HMF distribution coefficient, 0.287, was achieved using [$BF_4^-$] as anion of IL. They confirmed that [$BF_4^-$] has the weakest hydrogen bond acceptor ability. Therefore, [$BF_4^-$] is a better anion of IL applied in the HMF extraction process. The interactions between IL and HMF are mainly controlled by the strong hydrogen bonding interactions of anion of IL with −OH group of HMF [12]. In this case, extraction solvent and anion of IL compete each other to make hydrogen bonding interaction with HMF. This phenomenon makes the HMF extraction more difficult. Hence, the presence of water in the mixture is essential for HMF extraction process. Water as a hydrogen bond donor molecule can also interact with anion of IL. As a result the interaction between anion of IL and HMF is decreased and HMF can be more easily extracted.



(a)



(b)

**Figure 3.3** (a) Separation factor (S) and (b) distribution coefficient of HMF ($D_2$) for organic solvent-HMF-water and organic solvent-HMF-water-[EMIM][$BF_4$] systems at *T*= 313.15 K and atmospheric pressure (0.1 MPa); ■ : MIBK-HMF-water (0 wt% [EMIM][$BF_4$]) [16]; □ : MIBK-HMF-water-[EMIM][$BF_4$] (5 wt% [EMIM][$BF_4$]); ○ : MIBK-HMF-water-[EMIM][$BF_4$] (10 wt% [EMIM][$BF_4$]); △ : MIBK-HMF-water-[EMIM][$BF_4$] (30 wt% [EMIM][$BF_4$]); ◆ : 2-pentanol-HMF-water (0 wt% [EMIM][$BF_4$]) [10]; ● : 2-pentanol-HMF-water-[EMIM][$BF_4$] (10 wt% [EMIM][$BF_4$]); ▲ : 2-pentanol-HMF-water-[EMIM][$BF_4$] (30 wt% [EMIM][$BF_4$]); – – – : NRTL model.

From Figure 3.3, it can also be seen that the separation factors (S) and the distribution coefficients of HMF ($D_2$) decrease with increasing [EMIM][$BF_4$] concentration for all initial HMF concentrations. The S and $D_2$ values also decrease with the increase of HMF concentration. The figure shows that the distribution coefficients of HMF for the LLE systems using 2-pentanol are higher than those for the LLE systems using MIBK at the same [EMIM][$BF_4$] concentration which are also visible from the more negative tie-lines slope of MIBK-HMF-water-[EMIM][$BF_4$] systems in Figure 3.1 (c and d). The

LLE in the 2-pentanol-HMF-water-[EMIM][$BF_4$] system at 10% of [EMIM][$BF_4$] generates an around 1.2 times higher distribution coefficient of HMF compared to the LLE in the MIBK-HMF-water-[EMIM][$BF_4$] systems at 5% and 10% of [EMIM][$BF_4$] concentrations, as seen in Table A.5 and Figure 3.3. These confirm that HMF has a higher affinity with 2-pentanol than with MIBK. On the other hand, the 2-pentanol-HMF-water-[EMIM][$BF_4$] system gives lower separation factors compared to the MIBK-HMF-water-[EMIM][$BF_4$] system over the whole range of HMF and [EMIM][$BF_4$] concentrations, indicating the higher amount of co-extracted water in the organic-rich phase for these systems. As a result the distribution coefficients of water are higher, making the separation factors lower, as seen in Table B.5. The lower separation factors in the 2-pentanol-HMF-water-[EMIM][$BF_4$] system imply higher energy costs for solvent recovery.

Furthermore, it is shown in Figure 3.3 that the LLE systems of organic solvent (MIBK or 2-pentanol)-HMF-water-[EMIM][$BF_4$] at 30 wt% ionic liquid has the lowest S and $D_2$ with $D_2$ lower than 1 over the whole range of initial HMF concentrations. In this case, the $D_2$ values for the LLE system using MIBK are about 1.3 times lower than those for LLE system using 2-pentanol. However, the S values of the MIBK-HMF-water-[EMIM][$BF_4$] at 30 wt% are about 3.9 times higher than those of the 2-pentanol-HMF-water-[EMIM][$BF_4$] system, as seen in Table B.5. In general, the presence of [EMIM][$BF_4$] from 0 wt% to 30 wt% in the solution decreases the separation factors and the distribution coefficients of HMF around 2.3 and 3.3 times for MIBK and 2.6 and 4.5 times for 2-pentanol as extraction solvent, respectively.

The effect of [EMIM][$BF_4$] concentration on the separation factor and the distribution coefficient of HMF at fixed initial HMF concentration (10 wt% and 30 wt%) and variation of [EMIM][$BF_4$] concentration up to 60 wt% was also evaluated using MIBK extraction solvent, as shown in Figures B.4 and B.5. It is clear that the presence of [EMIM][$BF_4$] in the HMF aqueous solution has negative effect on the separation factor and the distribution coefficient. The systems with higher ionic liquid concentrations achieve much lower separation factors and distribution coefficients of HMF compared to the one without. The separation factors decrease up to 12.5 and 5.2 times with the increase of [EMIM][$BF_4$] concentration from 0 to 60 wt% for 10 wt% of HMF and from 0 to 40 wt% for 30 wt% of HMF, respectively. The distribution coefficients of HMF also decrease gradually from 1.38 to 0.39 and from 1.10 to 0.48 with the increase of [EMIM][$BF_4$] up to 60 wt% for 10 wt% of HMF and up to 40 wt% for 30 wt% of HMF, respectively. These results demonstrate that the extraction of HMF is much more difficult with increasing [EMIM][$BF_4$] concentration.

### 3.3.2 Correlation of LLE data for organic solvent-HMF-water-IL systems

The NRTL (Non-Random Two-Liquid) is one of the activity coefficient models [18] which is able to calculate the multicomponent LLE compositions only using the constituent binary parameters. The NRTL model can also be applied for the correlation of LLE systems containing ionic liquid [19-21]. Therefore, this activity coefficient model was used in the present study to correlate the experimental LLE tie-line data for the investigated systems. The nonrandomness parameter ($\alpha_{ij}$)

was fixed at 0.2 for each pair (*i*-*j*). The binary interaction parameters ($b_{ij}$ and $b_{ji}$) among HMF, organic solvents (MIBK and 2-pentanol), and water were taken from the ternary LLE correlation results of organic solvent-HMF-water systems [Chapter 2]. The $b_{ij}$ and $b_{ji}$ were regressed only for the interactions of [EMIM][$BF_4$] with HMF, organic solvents, and water using Aspen Plus V8.8, as listed in Table B.6. The calculated LLE tie-lines from the NRTL model and experimental LLE tie-lines are compared in Figures 3.1 and 3.2. The closed and open symbols represent the experimental and calculated LLE data, respectively. It shows that the NRTL model provides good agreement with the LLE experimental tie-line data. The RMSD (root mean square deviation) are 1.03% for MIBK – HMF – water - [EMIM][$BF_4$] and 0.86% for 2-pentanol – HMF – water - [EMIM][$BF_4$] systems. Besides, it can be seen in Figure 3.3 that the NRTL model also gives good description of S and $D_2$, except for higher concentration of IL, the $D_2$ shows larger deviation. However, overall the NRTL model correlates well the experimental data.

### 3.3.3 LLE of organic solvent-HMF-water-IL-salt systems

The experimental LLE tie-line data of organic solvent (MIBK or 2-pentanol)-HMF-water-[EMIM][$BF_4$]-NaCl systems were investigated at 313.15 K and atmospheric pressure (0.1 MPa), as given in Table B.7 and Figures 3.4-3.5 (on IL and salt free basis). The initial HMF concentrations ranged from 5 wt% to 40 wt% and kept the [EMIM][$BF_4$] and NaCl at constant concentrations. For a good comparison, we use the same [EMIM][$BF_4$] concentration in the MIBK – HMF – water - [EMIM][$BF_4$]- NaCl and 2-pentanol – HMF – water - [EMIM][$BF_4$] - NaCl systems. The concentration of [EMIM][$BF_4$] was fixed at 10 wt%

for the LLE systems containing NaCl. The concentration of NaCl was also fixed at 10 wt% which is close to the maximum solubility of NaCl in a 40 wt% HMF aqueous solution [16].

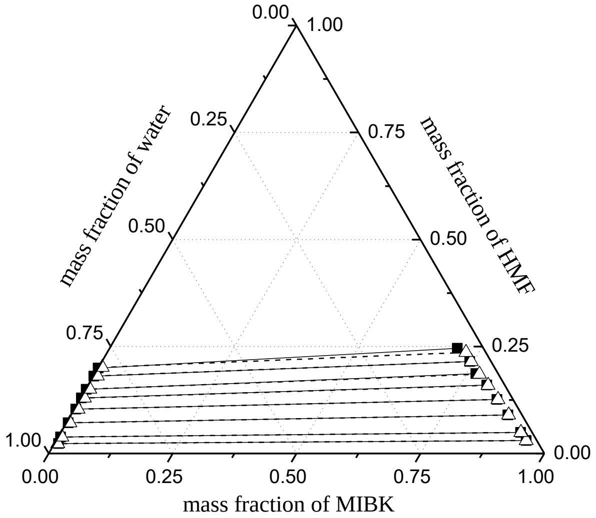


**Figure 3.4** Phase diagram of the experimental and calculated LLE tie-line data for MIBK-HMF-water-[EMIM][$BF_4$]-NaCl system on IL and salt free basis at $T$= 313.15 K and atmospheric pressure (0.1 MPa) for 10 wt% [EMIM][$BF_4$] and 10 wt% NaCl using NRTL model ; ---△--- : experimental data; —■— : NRTL model.

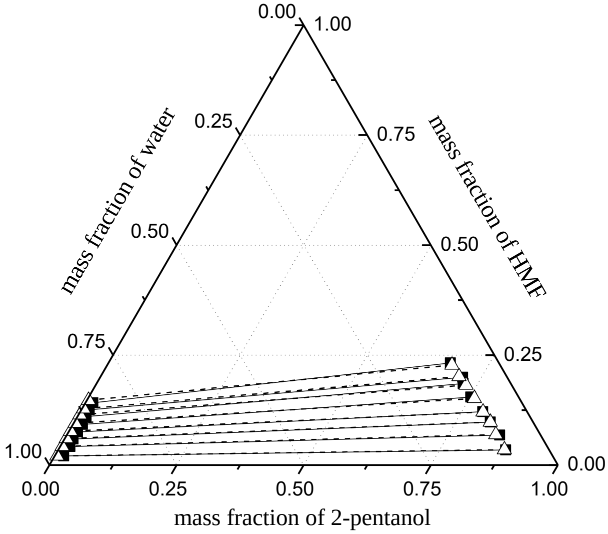
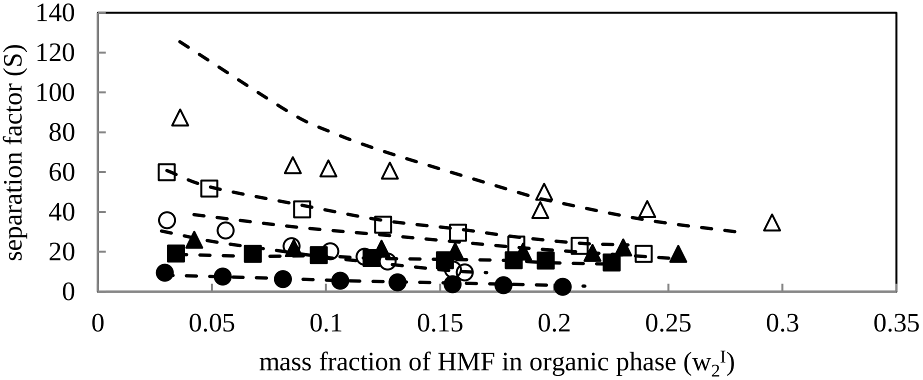


**Figure 3.5** Phase diagram of the experimental and calculated LLE tie-line data for 2-pentanol-HMF-water-[EMIM][BF$_4$]-NaCl system on IL and salt free basis at $T$= 313.15 K and atmospheric pressure (0.1 MPa) for 10 wt% [EMIM][BF$_4$] and 10 wt% NaCl using NRTL model; —■— : experimental data; - - -△- - - : NRTL model.

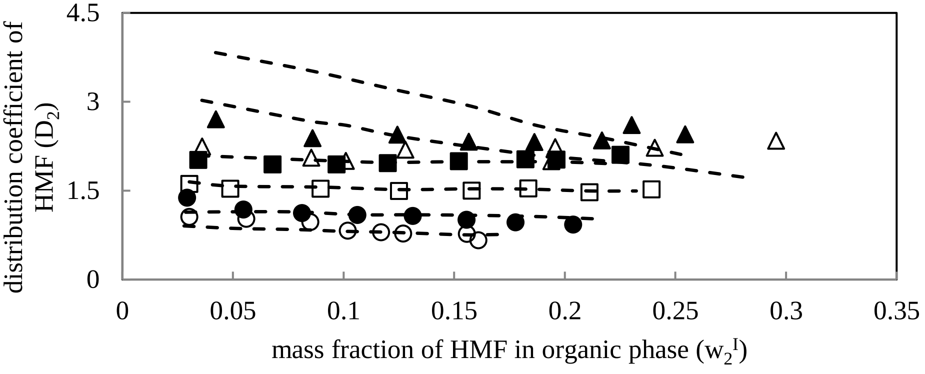
Figures 3.4 and 3.5 illustrate that the addition of NaCl can enhance the liquid phase splitting strongly. The positive effect on the phase equilibria is illustrated from the increased tie-line slope compared to the LLE of organic solvent-HMF-water-[EMIM][BF$_4$] system in the absence of NaCl, as shown in Figures 3.1 c and 3.2 b. The tie-lines slopes for the LLE system with salt become positive for all initial HMF concentrations and for both solvents, as shown in Figures 3.4 and 3.5, respectively. The increased slopes of the tie-lines represent the salting-out effect of NaCl resulting from the interaction between the salt ions and water molecules. This interaction decreases the solubility of HMF in the aqueous-rich phase, which brings out a salting-out effect that transfers more HMF molecules into the organic solvent phase [17]. This salting out effect improves the separation factor and the distribution coefficient of HMF, as seen in Table B.8 and Figure 3.6. From Figure 3.6, it can be seen that the S and $D_2$ values of the LLE systems with salt for both MIBK and 2-pentanol solvents are higher than those of the LLE systems without salt over the whole range of initial HMF concentrations. By introducing NaCl into the aqueous solution, the $D_2$ values can be enhanced to above 1 for organic solvent (MIBK or 2-pentanol) – HMF – water - [EMIM][$BF_4$] - NaCl systems over the whole range of initial HMF concentrations. Particularly for 2-pentanol, it can reach values above 2. The S and $D_2$ values increase about 1.8 times higher compared to the LLE systems without salt for MIBK, whereas, the S and $D_2$ values increase about 3.7 and 1.9 times compared to the values without salt for 2-pentanol, as listed in Tables B.5 and B.8. Furthermore, the S and $D_2$ values of the systems in the presence of [EMIM][$BF_4$] and NaCl were also compared with the values of organic solvent-HMF-water-NaCl systems [17], as shown in Figures 3.6 for both solvents. It represents that the organic solvent-HMF-water-NaCl systems generate around 1.6 and 1.3 times higher separation factors for MIBK and 2-pentanol solvents, respectively. Besides, the HMF distribution coefficients are around 1.4 and 1.2 times higher for MIBK-HMF-water-NaCl and 2-pentanol-HMF-water-NaCl systems, respectively. The organic solvent-HMF-water-[EMIM][$BF_4$]-NaCl systems exhibit lower extraction performance than the LLE systems in the presence of NaCl without ionic liquid. However the results in this study showed that the HMF extraction is favorable for the systems with the presence of ionic liquid and NaCl over the whole range of initial HMF concentrations, as seen in Table B.8. Therefore, by taking the advantage of ionic liquid as stabilizing agent in the HMF production, an aqueous [EMIM][$BF_4$] with NaCl is a good combination applied in the HMF extraction process to achieve good extraction performance.

Table B.8 and Figure 3.6 also show that the $D_2$ values in the presence of [EMIM][$BF_4$] and NaCl for 2-pentanol are around 1.3 times higher than those for MIBK as extraction solvent, which can also be seen from the steeper tie-lines for the LLE of 2-pentanol-HMF-water-[EMIM][$BF_4$]-NaCl system (Figure 3.5) compared to those for the LLE system with salt using MIBK (Figure 3.4). On the other hand, the LLE area of MIBK-HMF-water-[EMIM][$BF_4$]-NaCl is larger than that of 2-pentanol-HMF-water-[EMIM][$BF_4$]-NaCl system, result in higher separation factors which are about 2.0 times higher than those for 2-pentanol solvent. Furthermore, the concentrations of organic solvent in the aqueous-rich phase are considerably reduced from 1-6 wt% (Table B.3) to below 1 wt% (Table B.7) with the addition of NaCl for MIBK and from 4-12 wt% (Table B.4) to around 1 wt% (Table B.7) for 2-pentanol over the whole range of initial HMF concentrations. It can be seen in Tables B.4 and B.7 that the water content in the organic-rich phase also decreases, mainly in the 2-pentanol-HMF-water-[EMIM][$BF_4$] system ranging from 12-21 wt% to significantly below 10 wt% in the presence of NaCl for the whole range of initial HMF concentrations in the aqueous solution. In addition, Figures 3.4-3.5 and Table B.7 demonstrate that the organic solvent concentrations in the aqueous-rich phase and the water concentrations in the organic-rich phase of MIBK – HMF – water - [EMIM][$BF_4$] - NaCl are much lower than those in the 2-pentanol – HMF – water - [EMIM][$BF_4$] - NaCl system, generating a better extraction and purification process.

According to the discussion above, it can be inferred that MIBK is a better extraction solvent relative to 2-pentanol. This was observed from the separation factors for the LLE system with salt using MIBK solvent which are superior to 2-pentanol. Besides, the LLE of MIBK-HMF-water-[EMIM][BF4]-NaCl also exhibit sufficiently high, above 1.4 over the whole range of initial HMF concentrations, distribution coefficients of HMF. Even though, in the extraction process the presence of ionic liquid generates negative effect on both, HMF separation factor and distribution coefficient, this study confirmed that the combination of an aqueous ionic liquid ([EMIM][BF4]) with inorganic salt (NaCl) can improve the extraction performance, making the extraction of HMF more favorable over the whole range of initial HMF concentrations.



(a)



(b)

**Figure 3.6** (a) Separation factor (S) and (b) distribution coefficient of HMF ($D_2$) for organic solvent-HMF-water-[EMIM][$BF_4$] in the absence and presence of NaCl and organic solvent-HMF-water-NaCl systems at $T$= 313.15 K and atmospheric pressure (0.1 MPa); ○ : MIBK-HMF-water-[EMIM][$BF_4$] (10 wt% [EMIM][$BF_4$]); ● : 2-pentanol-HMF-water-[EMIM][$BF_4$] (10 wt% [EMIM][$BF_4$]); □ : MIBK-HMF-water-[EMIM][$BF_4$]-NaCl; ■ :2-pentanol-HMF-water-[EMIM][$BF_4$]-NaCl; △ : MIBK-HMF-water-NaCl [23]; ▲ : 2-pentanol-HMF-water-NaCl [16]; – – – : NRTL model.

### 3.3.4 Correlation of LLE data for organic solvent-HMF-water-IL-salt systems

The NRTL activity coefficient model was also applied to correlate the experimental LLE tie-line data for organic solvent-HMF-water-[EMIM][$BF_4$]-NaCl systems, as shown in Figures 3.4 and 3.5. NaCl was assumed as one molecular species, additionally the nonrandomness parameter ($\alpha_{ij}$) and the binary interaction parameters ($b_{ij}$ and $b_{ji}$) were regressed for the interaction of NaCl with [EMIM][$BF_4$], as seen in Table B.9. Whereas, the $\alpha_{ij}$, $b_{ij}$ and $b_{ji}$ parameters for the interactions of NaCl with organic solvents (MIBK and 2-pentanol), HMF, and water were taken from the correlation results generated in the quaternary LLE systems of organic solvent-HMF-water-NaCl [Chapter 2]. The $b_{ij}$ and $b_{ji}$ parameters among organic solvents, HMF, water, and [EMIM][$BF_4$] were fixed from the determined optimal values in the ternary LLE of organic solvent-HMF-water [Chapter 2] and quaternary LLE of organic solvent-HMF-water-[EMIM][$BF_4$] systems, as given in Table B.6. The results in Figures 3.4 and 3.5 show that the NRTL model gives good agreement with the experimental LLE tie-line data. The RMSD of MIBK- HMF- water- [EMIM][$BF_4$]- NaCl and 2-pentanol – HMF –water -[EMIM][$BF_4$]-NaCl systems are 0.82% and 1.69%, respectively, as listed in Table B.9. Besides, it represents in Figure 3.6 that the NRTL model also gives good description of S and $D_2$. From this figure, it can also be inferred that the separation factor and distribution coefficient of HMF of MIBK-HMF-water-[EMIM][$BF_4$]-NaCl system are better correlated with NRTL model compared to those of 2-pentanol-HMF-water- [EMIM][$BF_4$]- NaCl system. In addition, basically the negative values of $\alpha_{ij}$ obtained are physically unrealistic and the NRTL model is reduced to a fit procedure. However, the NRTL model offers more flexibility to the correlation allowing negative values for $\alpha_{ij}$. In this case, the determined $\alpha_{ij}$ values also give a crucial effect in generating a good correlation with the experimental LLE data involving salt [22,23]. This NRTL model provides a simple and much easier calculation than the electrolyte NRTL [24] and electrolyte Perturbed Chain-SAFT [25] models. Hence, this NRTL model can be applied further for development of the HMF extraction process design in the presence of salt and ionic liquid.

### 3.4 Conclusions

In the present study, the effect [EMIM][BF$_4$] on the phase equilibria of organic solvent (MIBK or 2-pentanol), HMF, water systems were investigated in the absence and presence of inorganic salt (NaCl) at 313.15 K and atmospheric pressure (0.1 MPa). The distribution coefficient of HMF and the separation factor were also determined based on the LLE data measured to interpret the extraction performance. According to the results, the presence of [EMIM][BF$_4$] had negative effect on the phase diagram, the separation factor and the distribution coefficient of HMF. Increasing [EMIM][BF$_4$] concentration caused tie-lines slope more negative for LLE systems using MIBK and 2-pentanol as solvent, indicating lower distribution coefficients of HMF and separation factors. However, the introduction of NaCl into the aqueous ionic liquid solution strongly enhances the HMF separation indicated from the rise and positive tie-line slopes of the investigated LLE systems. Therefore, by taking the advantage of ionic liquid as stabilizing agent, the combined effect of aqueous ionic liquid ([EMIM][BF$_4$]) with inorganic salt (NaCl) can enhance both extraction performance parameters, making the HMF extraction more favorable with values of the HMF distribution coefficient higher than 1 over the whole range of initial HMF concentrations. Furthermore, by comparing MIBK and 2-pentanol as extraction solvents it can be concluded that the LLE system of MIBK-HMF-water-[EMIM][BF$_4$]-NaCl generates a better extraction performance.

The experimental LLE tie-line data for all investigated systems were also correlated with the NRTL activity coefficient model. The correlation results proved that the NRTL model was in good agreement with the experimental data. The RMSD (root mean square deviations) of the NRTL model were 1.03% for the MIBK-HMF-water-[EMIM][$BF_4$] and 0.86% for the 2-pentanol-HMF-water-[EMIM][$BF_4$] system. While, the RMSD of the organic solvent-HMF-water-[EMIM][$BF_4$]-NaCl systems were 0.82% and 1.69% for MIBK and 2-pentanol as extraction solvents, respectively.

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# Chapter 4

## Choline chloride urea effect on liquid–liquid equilibria of 5-hydroxymethylfurfural–water–organic solvent systems in the absence and presence of sodium chloride

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## ABSTRACT

Deep eutectic solvent (DES) has demonstrated its ability to improve the yield and selectivity in 5-hydroxymethylfurfural (HMF) production process. Liquid-liquid extraction is a beneficial process in HMF production to recover HMF from the reaction medium. In the present study, the effect of DES (choline chloride urea) on the liquid-liquid equilibria (LLE) of HMF, water, organic solvent (methyl isobutyl ketone (MIBK) or 2-pentanol) systems in the absence and presence of sodium chloride (NaCl) were investigated at 313.15 K and atmospheric pressure (0.1 MPa). The tie-line of the multicomponent systems were measured using several analytical methods. According to the experimental results, the extraction performance decreased with the increase of DES concentration. However, the addition of 10 wt% NaCl into HMF aqueous DES solution can induce stronger liquid-liquid phase splitting, enhancing separation factors and distribution coefficients of HMF around 2.7 and 1.6 times, respectively. Additionally, MIBK showed better extraction performance in the presence of DES and NaCl with the separation factors 2.6 times higher than those of 2-pentanol and the HMF distribution coefficients above 1.8. The LLE of the multicomponent systems were correlated well with the nonrandom two-liquid (NRTL) model.

*Keywords*: Choline chloride urea; Extraction performance; 5-Hydroxymethylfurfural; Liquid-liquid equilibria; NaCl

## 4.1 Introduction

The dependence on fossil-fuel resources for energy and chemical building blocks can be replaced with the use of renewable feedstocks, such as 5-hydroxymethylfurfural (HMF), because of its rich chemistry and potential availability [1]. HMF is also known as a platform chemical for the synthesis of plant-based polyethylene terephthalate (PET) [2]. Various investigations on the production of HMF have been performed in order to obtain more effective and efficient methods for the transformation of carbohydrates into HMF [1,3-13]. In addition, the application of liquid-liquid extraction in HMF production process is also essential to improve the selectivity and yield for HMF. HMF can be extracted from the reaction medium into an organic phase which prevents the degradation of HMF. The use of high boiling organic solvents can give high yields of HMF, but require considerably more energy and cost for separating HMF by distillation [14,15]. In this study, methyl isobutyl ketone (MIBK) and 2-pentanol were used as extraction solvent for HMF. Alcohols and ketones, which are more volatile polar compounds, can also interact well with the HMF molecule and have been more widely studied for HMF extraction [14,16-18]. Besides, the addition of sodium chloride (NaCl) into the aqueous phase can favour the partitioning of HMF into the organic phase [16,19-22]. This also increases the yield and selectivity in the HMF production process [20].

Furthermore, several studies indicated that ionic liquid (IL) and deep eutectic solvent (DES) can be used as stabilizing agent in HMF production [11,12,23-27]. The use of IL and DES can enhance the HMF yield by suppressing the formation of side-products. Additionally, several more complex carbohydrates such as starch, cellulose, and inulin are also able to be used as raw materials for the formation of HMF in IL or DES containing reaction medium [11,12,24,25]. Abbott and co-workers [28-30] introduced the concept of DES, which has been proposed as an alternative to IL, since its physical and chemical properties resemble those of IL. DES is a solid organic salt and complexing agent mixture, which forms a liquid at temperatures below 100°C. The main advantage of DES is that it can be produced from cheap, non-toxic, and biodegradable materials [31]. The DES can be prepared easily which requires only heating and stirring. Therefore, the production of DES is much cheaper than that of IL.

It has been recognized that DES can bring advantages in the production of HMF. However, the separation of HMF from pure DES is difficult resulting in a low distribution coefficient of HMF [23]. The presence of water in the mixture can enhance the extraction efficiency and reduce the viscosity of the solution [32,33]. Therefore, in the present study, we try to obtain a better extraction of HMF using aqueous DES (ChCl-urea) and introducing NaCl into aqueous solution. Jérôme *et al.* [34] indicated that the yield and selectivity of HMF can also be enhanced in aqueous ChCl solution using MIBK as extraction solvent. Furthermore, to our best knowledge, there is still no liquid-liquid equilibrium (LLE) data available for the combination of the systems containing HMF, aqueous DES (ChCl-urea) solution, and organic solvent in the absence and presence of NaCl. It is important to provide information about the thermodynamic data which are required as basis in the HMF extraction process design. Therefore, in this study we provide LLE data of organic solvent (MIBK or 2-pentanol), HMF, water, DES (ChCl-urea) systems at 313.15 K and atmospheric pressure (0.1 MPa) in the absence and presence of NaCl. The separation factor and the distribution coefficient of HMF were obtained from LLE data to interpret the extraction performance. The effect of DES and NaCl on the LLE phase diagram, the separation factor, and the distribution coefficient of HMF were also investigated. Furthermore, the NRTL activity coefficient model was applied to correlate the experimental LLE data for the investigated systems. The binary interaction parameters of NRTL model generated in this study are also essential for development of the HMF extraction process. Besides, this study introduces new systems for HMF extraction process and open a scope for the thermodynamic studies of HMF production and extraction in biphasic aqueous-organic systems.

## 4.2 Experimental Section

### 4.2.1 Chemicals

All chemicals used in this study are described in Table C.1. The experimental and literature values of densities (ρ) for all chemicals are also listed in Table C.2 determined by Density meter (Anton Paar, DMA 5000) with a standard uncertainty u(ρ) of 0.0008 g/cm$^3$. Methanol and water were used for eluent in HPLC (High-performance liquid chromatography) analysis. Aqueous methanesulfonic acid and aqueous nitric acid ($HNO_3$) solutions were used for eluent in IC (Ion exchange chromatography) and for diluent in salt analysis, respectively. Water used for the LLE experiments and analysis was deionized ultrapure water with resistance of 18.2 MΩ.cm. The water content of DES was 0.0017 in mass fraction determined by Karl Fischer titration. All the chemicals were used without further purification.

### 4.2.2 Tie-line measurements

DES (ChCl-urea) was prepared prior to the LLE tie-line measurements according to the procedure reported by Abbott *et al*. [28] Choline chloride and urea were mixed with a molar ratio of 1:2 and heated at 80°C for 1 hour until a homogeneous liquid was formed. Then, the LLE tie-lines of organic solvent, HMF, water, DES and organic solvent, HMF, water, DES, NaCl systems were measured using a jacketed equilibrium cell at 313.15 K and atmospheric pressure (0.1 MPa). The method validation has been conducted in our previous study [33]. The equilibrium cell was controlled by a thermostated water from a heating circulator bath (Tamson-instruments TC 6B, Holland) with a standard uncertainty u($T$) of 0.02 K. Known quantities of HMF, water, DES in the absence and presence of NaCl were prepared and weighed on an analytical balance Mettler Toledo (MS 304S/01, Switzerland) with a precision of ± 0.0001 g. The HMF concentration in aqueous solution was varied in the range of 5 wt% to 40 wt% while keeping the DES and NaCl at constant concentrations. Subsequently, MIBK or 2-pentanol was added into aqueous feeds with a mass ratio of 1:1 between organic solvent and aqueous feeds. Afterwards, the mixture of organic solvent-HMF-water-DES-(or NaCl) was stirred for 2 hours and left without stirring for 20 hours for low HMF concentrations and at least 22 hours for high HMF concentrations at 313.15 K to reach equilibrium and the two liquid phases were completely separated. The organic and aqueous samples required for analytical measurements were approximately 5 mL from each phase. The samples were placed in an oven at 40°C before further sample preparation for analytical measurements.

### 4.2.3 Analytical measurements

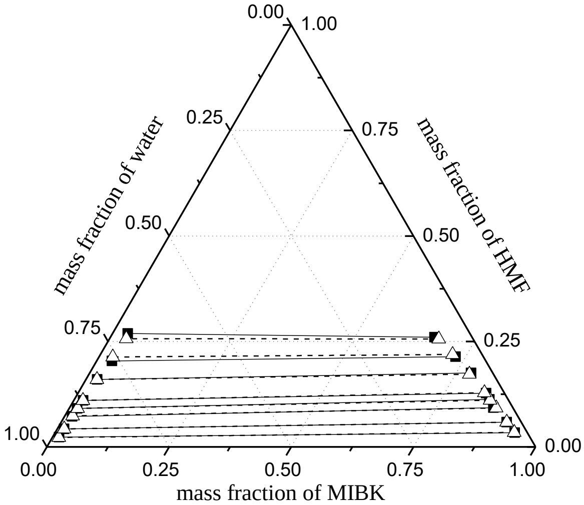
HPLC equipped with a reversed phase column C18 Zorbax ODS was applied to determine MIBK, 2-pentanol, and HMF concentrations in both phases at 42°C. The UV/VIS (ultraviolet–visible) detector was used to determine HMF and MIBK at a UV-wavelength of 278 nm. Whereas, for 2-pentanol analysis, the HPLC was equipped with RI (refractive index) detector. The method of HPLC analysis was based on our previous study using water and methanol as eluent [33]. For the LLE of MIBK, HMF, water, DES, NaCl system, a mixture of water and methanol with a volume ratio of 60:40 was prepared with a flowrate of 0.6 mL/min to detect the peak area of MIBK with peak maxima at 15.5 min (calibration curve in Figure C.1). The amount of water in the organic phase was measured by Karl Fischer titration using a Metrohm 756 KF. Whereas, the water content in the aqueous phase was determined by subtracting the sum of the other mass fractions from a value of 1. The DES concentrations in the organic and aqueous phases were analysed using IC performed with Dionex DX-120 Ion Chromatograph. A mixture of methanesulfonic acid and water with a volume ratio of 2.6 mL : 2 L was prepared as eluent with a flowrate of 1.35 mL/min and peak maxima at 5.2 min. In addition, ICP-OES (Inductively Coupled Plasma Optical Emission Spectroscopy, Spectro Arcos EOP) was used to analyse the concentrations of NaCl in both phases using 3% of $HNO_3$ as diluent. The mass fractions of each component in each phase were averaged from three replicated samples.

The standard uncertainties u($w_i$) of MIBK, 2-pentanol, HMF, water, DES, and NaCl were estimated to be 0.0010, 0.0006, 0.0009, 0.0012, 0.0007, and 0.0004 in mass fraction, respectively.

## 4.3 Results and discussion

### 4.3.1 LLE of organic solvent-HMF-water-DES systems

LLE tie-lines for the systems of organic solvent (MIBK or 2-pentanol)-HMF-water-DES (ChCl-urea) at 313.15 K and atmospheric pressure (0.1 MPa) are reported in Tables C.3 and C.4. The LLE phase diagrams for MIBK and 2-pentanol as extraction solvents with three different initial concentrations of DES, i.e. 10 wt%, 20 wt%, and 30 wt%, are plotted in Figures 4.1 and 4.2 (on DES-free basis). The initial HMF concentrations varied from 5 wt% to 40 wt% with constant amount of DES added in the aqueous solution. The phase diagrams for the systems in the presence of DES were also compared with the LLE phase diagram without DES (0 wt% of DES) [22], as shown in Figures 4.1 and 4.2 for both solvents. The DES effect on the LLE can be seen from the tie-lines slope that indicates the extraction performance. It can be shown in Figures 4.1 (a-d) and Figures 4.2 (a-d) that the tie-lines slope decrease gradually with the increase of DES concentration from 0 wt% to 30 wt%, which means less HMF molecules extracted, thus the extraction performance decreases as well. In addition, from comparing Figures 4.1 (a-c) with Figures 4.2 (a-c), it demonstrates that with the same DES concentration the slope of tie-lines for LLE of MIBK-HMF-water-DES are more negative than those for LLE of 2-pentanol-HMF-water-DES systems, mainly at higher initial HMF concentrations. These results exhibit that 2-pentanol has a better capability to extract HMF from aqueous DES solution. However, 2-pentanol has a higher mutual solubility with water compared to MIBK, resulting in higher water content in organic phase and higher organic solvent content in aqueous phase, as seen in Tables C.3-C.4 and Figures 4.1-4.2. The aqueous phase concentrations, which are on the left-hand side of the ternary diagram, locate more towards right axis for 2-pentanol-HMF-water-DES systems, representing the higher organic solvent content in aqueous phase. Similarly, the organic phase concentrations, which are on the right-hand side, locate more towards left axis which demonstrate the higher water content in organic phase. These would cost more energy in the following product purification and solvent recycling processes which are less efficient.



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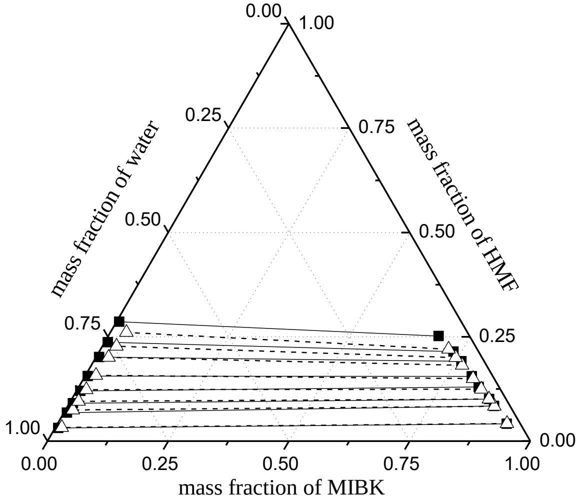
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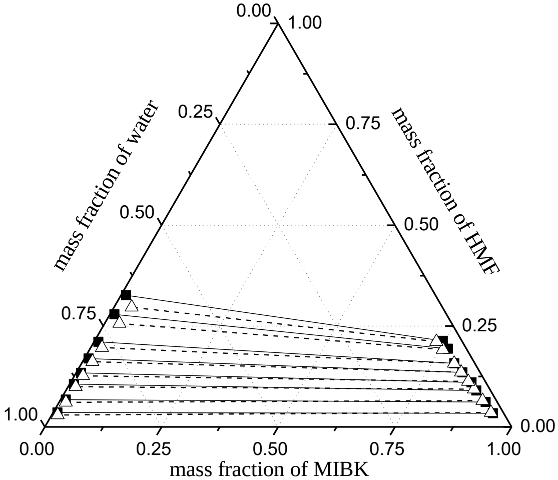
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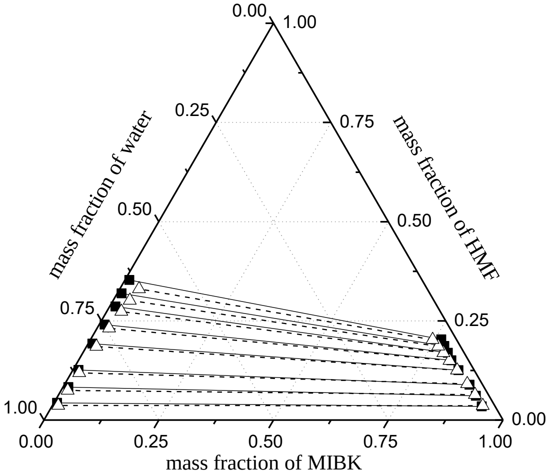
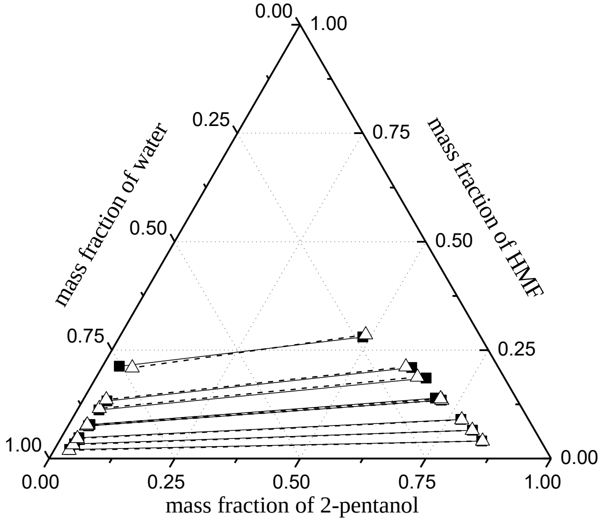


(d)

**Figure 4.1** Phase diagram of the experimental and calculated LLE tie-line data for MIBK-HMF-water and MIBK-HMF-water-DES (ChCl-urea) systems on DES-free basis at *T*= 313.15 K and atmospheric pressure (0.1 MPa) using NRTL model; (a) 0 wt% DES [22]; (b) 10 wt% DES; (c) 20 wt% DES; (d) 30 wt% DES; —■— : experimental data; - - -△- - - : NRTL model.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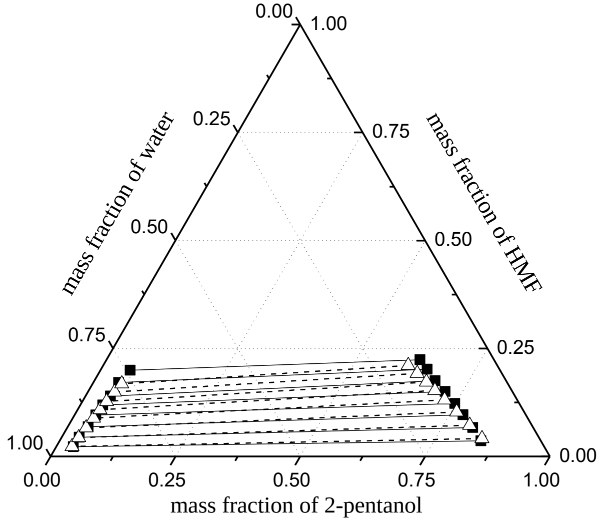
(a)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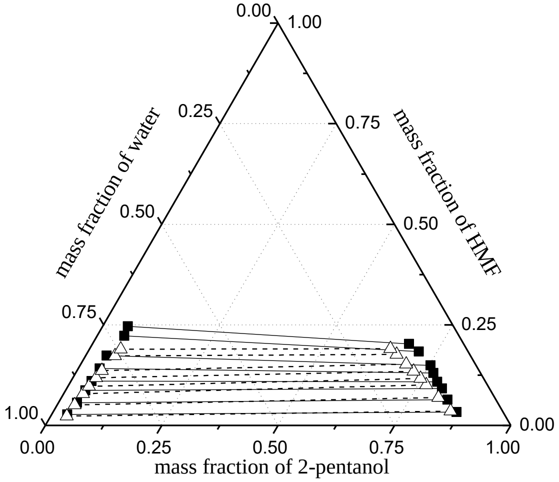

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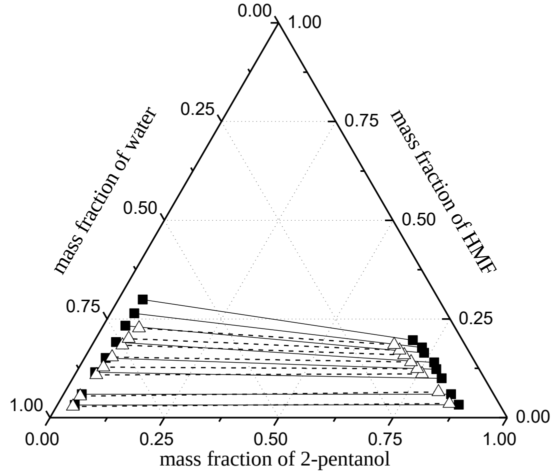


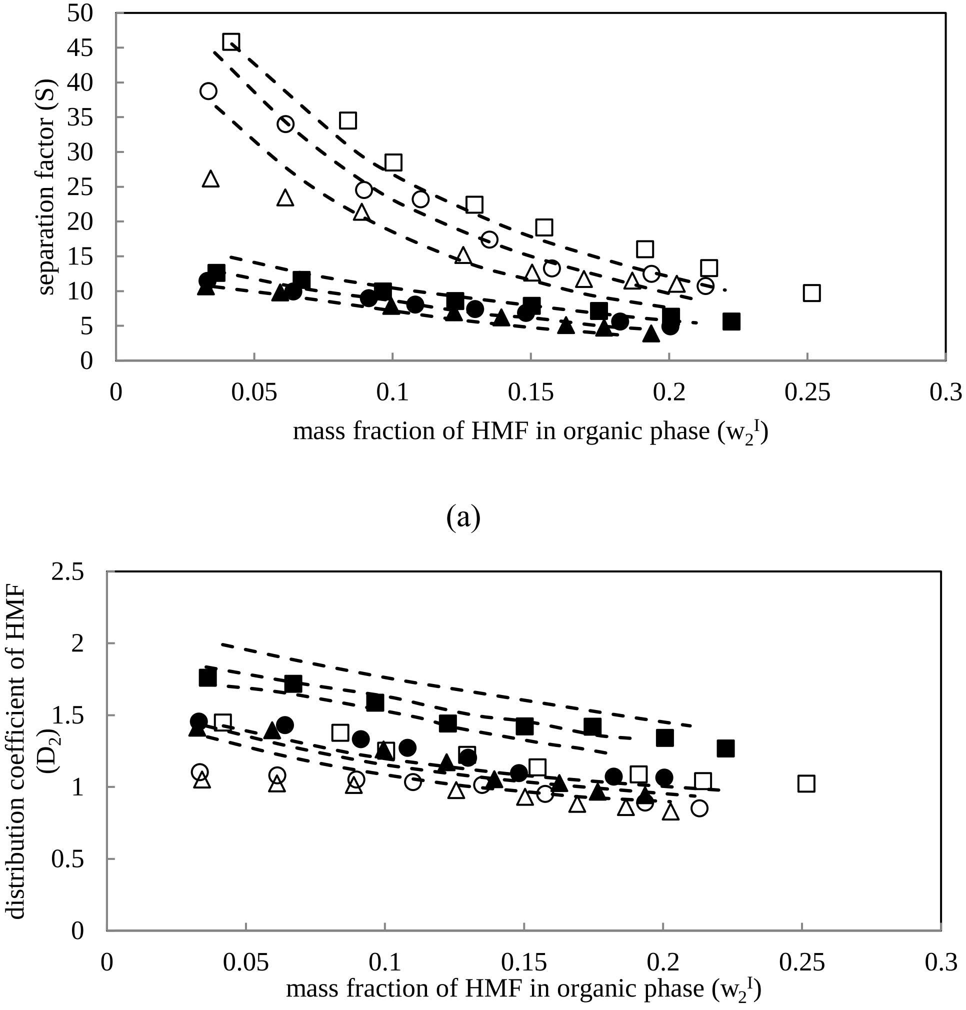
(d)

**Figure 4.2** Phase diagram of the experimental and calculated LLE tie-line data for 2-pentanol-HMF-water and 2-pentanol-HMF-water-DES (ChCl-urea) systems on DES-free basis at *T*= 313.15 K and atmospheric pressure (0.1 MPa) using NRTL model; (a) 0 wt% DES [22]; (b) 10 wt% DES; (c) 20 wt% DES; (d) 30 wt% DES; —■— : experimental data; - - -△- - - : NRTL model.

The separation factors and the distribution coefficients for the LLE systems containing organic solvent-HMF-water-DES are seen in Table C.5 and Figure 4.3. It represents that the separations factors are much higher than 1 for all initial HMF concentrations in both solvents, MIBK and 2-pentanol. The distribution coefficients of HMF are all higher than 1 for LLE of MIBK-HMF-water-DES at 10 wt% of DES and LLE of 2-pentanol-HMF-water-DES at 10 and 20 wt%. Whereas, for LLE of MIBK-HMF-water-DES systems at 20 and 30 wt% and 2-pentanol-HMF-water-DES at 30 wt%, the distribution coefficients of HMF are higher than 1 only for lower initial HMF concentrations. From these results, it can be confirmed that the HMF extraction from aqueous solution in the presence of DES using MIBK and 2-pentanol as extraction solvents is favorable at these ranges of HMF and DES feed concentrations in the aqueous solution.

Furthermore, from Figure 4.3, the DES concentration effect on the separation factor and the distribution coefficient of HMF can be observed. The values of the separation factor and the distribution coefficient of HMF have an apparent downward trend as HMF concentrations in organic phase increase. The separation factors and the distribution coefficients of HMF also decrease with increasing concentrations of DES for both organic solvents, demonstrating that the low DES concentration (10 wt% of DES) has a better extraction performance. The higher feed of ChCl-urea in the aqueous phase provides more groups of –OH and $Cl^-$ anion from ChCl and $–NH_2$ from urea which interact with the hydroxyl group (–OH) of HMF, making the extraction of HMF to organic phase more difficult. However, the biphasic systems with aqueous DES in this study show better extraction performance than using pure DES, which generated a much lower distribution coefficient of HMF with a value of 0.45 using MIBK solvent [23]. In this case, the presence of water can decrease the interactions between ChCl-urea and HMF through the interactions of –OH group from water with $Cl^-$ anion, –OH, and $–NH_2$ from ChCl-urea. Another advantage is that the viscosity of ChCl-urea considerably decreases in the presence of water which is also beneficial for extraction process.

The comparison of the solvent effect on the performance of extraction can also be observed from Figure 4.3 and Table C.5. It represents that the distribution coefficients of HMF for the 2-pentanol-HMF-water-DES systems are higher 1.2 times than those for the MIBK-HMF-water-DES systems, demonstrating that 2-pentanol can extract HMF more easily from aqueous DES solution. 2-Pentanol has a hydroxyl group (–OH) which possesses stronger polarity, therefore the interaction between HMF and 2-pentanol is stronger than that between HMF and MIBK. However, the separation factors for 2-pentanol as extraction solvent are about 2.5 times lower than that for MIBK solvent, which can also be explained by the stronger interaction between the hydroxyl group of 2-pentanol and water via hydrogen bonds than that between MIBK and water. Hence, the separation factors decrease as the distribution coefficients of water increase for the 2-pentanol-HMF-water-DES systems. Furthermore, due to the weaker interaction between MIBK and water, the concentrations of organic solvent in the aqueous phase and water content in the organic phase are much lower for MIBK compared to those for 2-pentanol, making the separation and recovery processes easier.

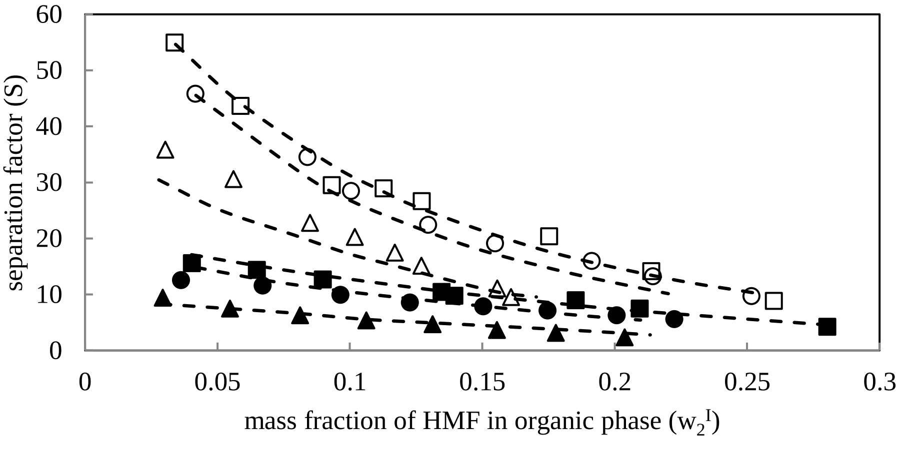


(a)

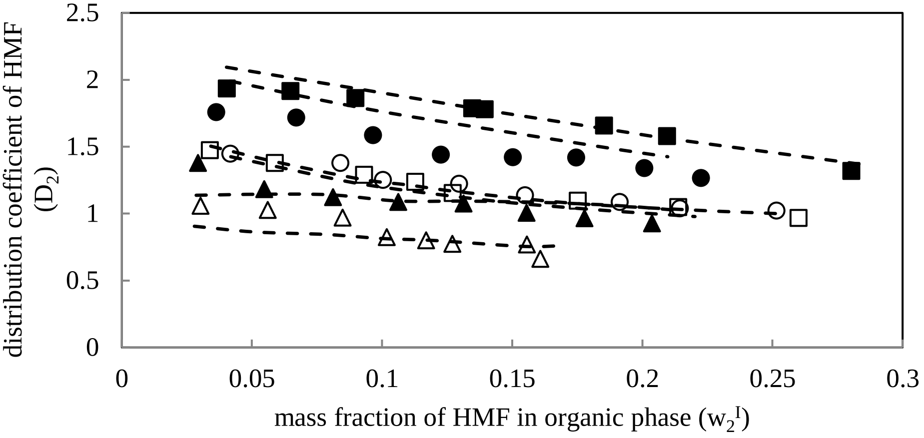
(b)

**Figure 4.3** (a) Separation factor (S) and (b) distribution coefficient of HMF ($D_2$) for organic solvent-HMF-water- DES (ChCl-urea) systems at *T*= 313.15 K and atmospheric pressure (0.1 MPa); □ : MIBK-HMF-water-DES (10 wt% DES); ○ : MIBK-HMF-water-DES (20 wt% DES); △ : MIBK-HMF-water-DES (30 wt% DES); ■ : 2-pentanol-HMF-water-DES (10 wt% DES); ● : 2-pentanol-HMF-water-DES (20 wt% DES); ▲ : 2-pentanol-HMF-water-DES (30 wt% DES); –·–·– : NRTL model.

The extraction performance is also compared in the LLE systems containing DES (ChCl-urea), IL ([EMIM][BF4]) [33], and in the absence of DES/IL [22], as seen in Figure 4.4. It represents that the separation factors and the distribution coefficients of HMF for the LLE systems containing 10 wt% of DES (ChCl-urea) and IL ([EMIM][BF4]) are lower than those for the LLE systems in the absence of DES/IL for both extraction solvents. However, DES (ChCl-urea) decreases the separation factors and the distribution coefficients of HMF much less than IL ([EMIM][BF4]). The separation factors decrease around 1.3 times for both MIBK and 2-pentanol in the LLE systems containing 10 wt% of DES. Moreover, the distribution coefficients of HMF decrease 1.2 times for 2-pentanol and show comparable for MIBK solvent. While, the presence of 10 wt% of IL decreases both the separation factors and the distribution coefficients of HMF around 1.4 times for MIBK and also 2.2 and 1.6 times for 2-pentanol, respectively. These results confirm that the extraction of HMF from aqueous DES performs better compared to that from aqueous IL.



(a)



(b)

**Figure 4.4** (a) Separation factor (S) and (b) distribution coefficient of HMF (D2) for organic solvent-HMF-water and organic solvent-HMF-water-DES (ChCl-urea) or IL ([EMIM][BF4]) systems at *T*= 313.15 K and atmospheric pressure (0.1 MPa) ; □ : MIBK-HMF-water [22]; ○ : MIBK-HMF-water-DES (10 wt% DES); △ : MIBK-HMF-water-IL (10 wt% IL) [33]; ■ : 2-pentanol-HMF-water [22]; ● : 2-pentanol-HMF-water-DES (10 wt% DES); ▲ : 2-pentanol-HMF-water-IL (10 wt% IL) [33]; –·–·– : NRTL model.

### 4.3.2 LLE of organic solvent-HMF-water-DES-NaCl systems

The experimental LLE data of organic solvent (MIBK or 2-pentanol)-HMF-water-DES in the presence of NaCl were investigated in this study at 313.15 K and atmospheric pressure (0.1 MPa), as listed in Table C.6. The LLE phase diagrams are also plotted for HMF feed concentrations in aqueous solution ranging from 5 wt% to 40 wt% while keeping the DES and NaCl concentrations constant, as shown in Figures 4.5 and 4.6 (on DES and salt free basis). The NaCl feed concentration was fixed at 10 wt%, this concentration is near the maximum solubility of NaCl in a 40 wt% HMF aqueous solution [22]. Furthermore, as discussed earlier in the LLE of organic solvent-HMF-water-DES systems, the presence of 10 wt% DES in HMF aqueous solution showed better extraction performance compared to the higher DES concentrations for both organic solvents. Thus, for the study of the combination of aqueous DES with NaCl on the LLE, the DES concentration was fixed at 10 wt%. The several experimental LLE data of the studied systems taken from Tables C.3 and C.6 were also validated via comparisons with the results from different analytical instruments as shown in Table C.7. The validation results represent satisfactorily agree with the experimental LLE data. Under the same experimental procedure and different analytical instruments, the experimental LLE data of the studied systems were reproducible with the validation results.

The results for the effect of NaCl in the LLE of the studied systems indicate that the addition of NaCl into aqueous DES solution significantly alters the LLE phase diagram of the MIBK-HMF-water-DES and 2-pentanol-HMF-water-DES systems. The tie-lines slope become more positive with the introduction of NaCl for the whole range of initial HMF concentrations, which means a better extraction performance, as shown in Figures 4.5 and 4.6. Tables C.5 and C.8 and also Figure 4.7 represent that the separation factors and the distribution coefficients of HMF in the presence of NaCl using MIBK as extraction solvent increase about 2.8 and 1.6 times, respectively, in comparison with the non-salt systems. Whereas, for 2-pentanol solvent the separation factors and the distribution coefficients of HMF increase about 2.7 and 1.6 times, respectively. The significant improvement in the extraction performance is attributed to the salting-out effect in which the presence of ions from the salt in solution reduce the interaction between HMF and water. The water molecules prefer to surround the salt ions, resulting in decreased solubility of HMF in aqueous phase. Thus, HMF molecules are salted out from aqueous phase and more easily transferred to the organic phase.

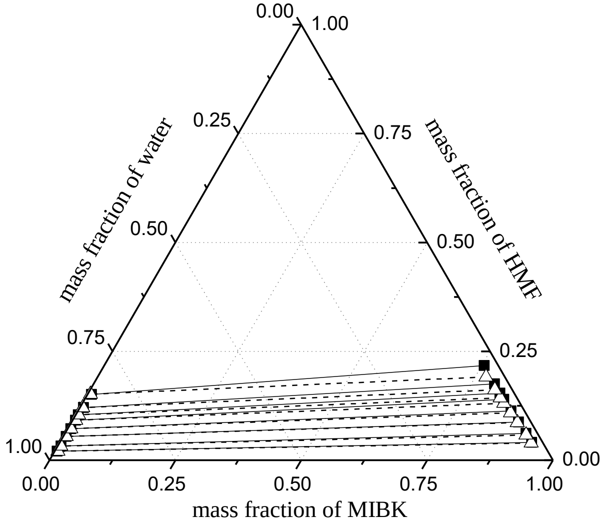


**Figure 4.5** Phase diagram of the experimental and calculated LLE tie-line data for MIBK-HMF-water-DES (ChCl-urea)-NaCl system on DES and salt free basis at *T*= 313.15 K and atmospheric pressure (0.1 MPa) for 10 wt% DES and 10 wt% NaCl using NRTL model; —■— : experimental data; - - △- - -: NRTL model.

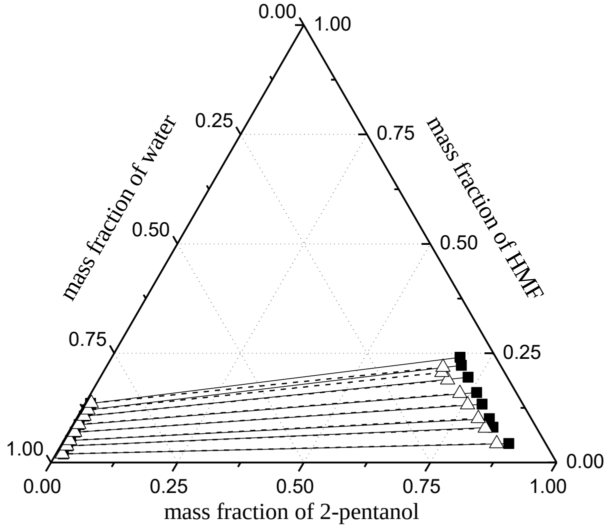


**Figure 4.6** Phase diagram of the experimental and calculated LLE tie-line data for 2-pentanol-HMF-water-DES (ChCl-urea)-NaCl system on DES and salt free basis at *T*= 313.15 K and atmospheric pressure (0.1 MPa) for 10 wt% DES and 10 wt% NaCl using NRTL model; —■— : experimental data; - - △- - - : NRTL model.

The extraction performance for the organic solvent-HMF-water-DES-NaCl were compared with those for organic solvent-HMF-water-NaCl systems [22], as represented in Figures 4.7. It indicates that the separation factors and the distribution coefficients of HMF are comparable for both solvents, only for MIBK-HMF-water-NaCl system the HMF distribution coefficients are around 1.1 times higher than those for MIBK-HMF-water-DES-NaCl. The LLE systems in the presence of DES and NaCl also showed better extraction performance compared to the LLE systems using a combination of aqueous ionic liquid ([EMIM][$BF_4$]) with NaCl which were reported in our previous study [33]. Hence, by taking the benefit of

DES as stabilizing agent for HMF, an aqueous DES as an alternative to ionic liquid with NaCl is a better combination to apply in the HMF extraction process because it generates better extraction performance. Figure 4.7 and Table C.8 also demonstrate that for the 2-pentanol solvent, the distribution coefficients of HMF in the presence of NaCl are about 1.2 times higher than those for MIBK. These are also indicated from the more positive tie-lines slope for 2-pentanol-HMF-water-DES-NaCl (Figure 4.6) compared to those for MIBK-HMF-water-DES-NaCl system (Figure 4.5). However, the LLE system in the presence of NaCl with MIBK solvent generates much higher separation factors, which are around 2.6 times higher than those with 2-pentanol solvent.

Furthermore, the organic solvent concentrations in the aqueous phase and the water concentrations in the organic phase for both MIBK-HMF-water-DES-NaCl (Figure 4.5 and Table C.6) and 2-pentanol-HMF-water-DES-NaCl (Figure 4.6 and Table C.6) systems decrease compared to those for MIBK-HMF-water-DES (Figure 4.1 a and Table C.3) and 2-pentanol-HMF-water-DES (Figure 4.2 a and Table C.4) systems, respectively. Particularly for 2-pentanol solvent, the 2-pentanol concentrations in the aqueous phase decrease considerably from 3-5 wt% to 0.8-1 wt%. While, for MIBK solvent, the concentrations of MIBK for both systems in the absence and presence of NaCl are below 1% over the whole range of initial HMF concentrations. Furthermore, the water contents in the organic phase reduce from 3-6 wt% in the absence of NaCl to around 2 wt% in the presence of NaCl for MIBK and reduce from 12-15 wt% to below 10 wt% for 2-pentanol over the whole range of initial HMF concentrations. Therefore, the following product purification and solvent recovery processes would need less energy and costs compared to the systems without salt. This advantage is also attributed to the salting-out effect of NaCl, in which the mutual solubility between the organic solvent and water decrease, because of the strong interaction of water and salt ions.

In addition, the concentrations of DES and NaCl in the organic phase are very low for both systems using MIBK and 2-pentanol solvents which are below 1% for the whole range of initial HMF concentrations, as listed in Table C.6. Particularly for MIBK, the DES and NaCl contents in MIBK phase are almost zero. These results illustrate that DES and NaCl have very low solubility in organic solvent, mainly in MIBK solvent. This is beneficial for the HMF separation process, as the low DES and NaCl contents in the organic phase make the recovery and product purification easier and more efficient. Overall, from comparing Figure 4.5 with Figure 4.6 and as seen in Table C.6, the LLE system of MIBK-HMF-water-DES-NaCl represents lower organic solvent concentrations in the aqueous phase and lower DES and water contents in the organic phase than the 2-pentanol-HMF-water-DES-NaCl system, generating a better extraction and purification of HMF. Hence, from all the obtained results, it can be concluded that MIBK showed better extraction performance with higher separation factors than 2-pentanol and sufficiently high (>1.8) HMF distribution coefficients for the whole range of initial HMF concentrations. Furthermore, the negative effect of DES on the extraction performance can be improved with the introduction of NaCl into aqueous DES solution. Taking the benefit of DES as stabilizing agent for HMF, the combined effect of aqueous DES (ChCl-urea) with salt (NaCl) can enhance both the separation factor and the distribution coefficient of HMF which makes the HMF extraction more favorable.

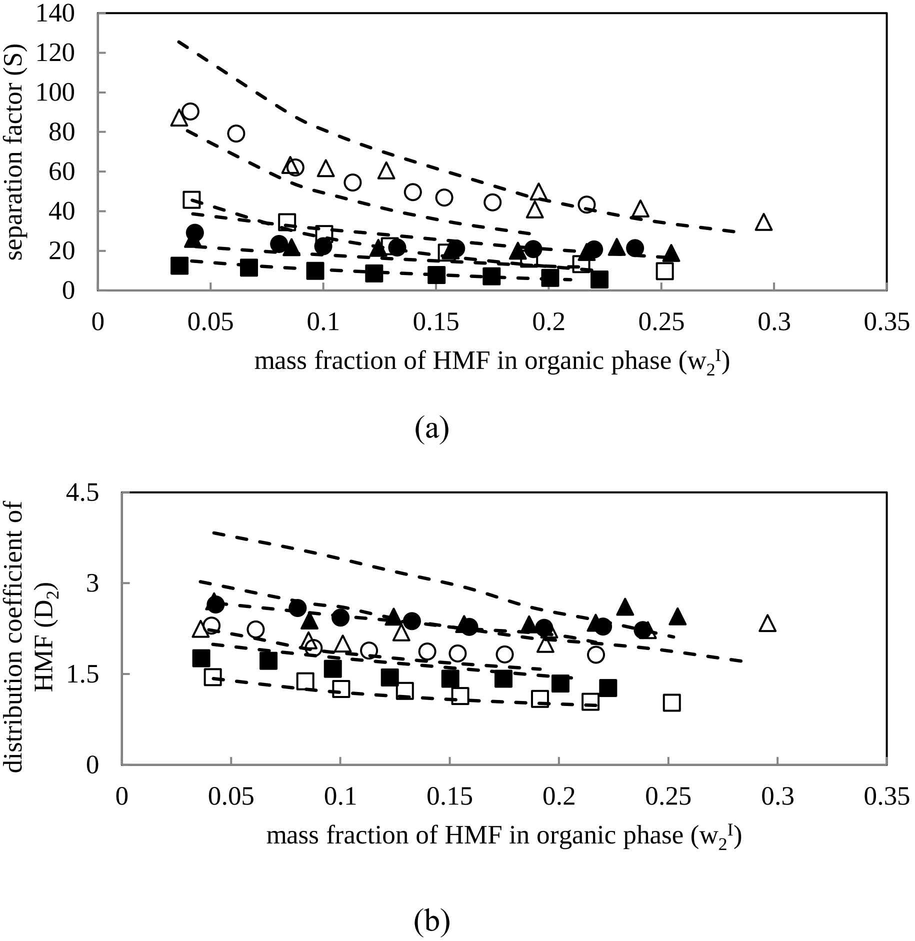


**Figure 4.7** (a) Separation factor (S) and (b) distribution coefficient of HMF (D2) for organic solvent-HMF-water-DES (ChCl-urea) systems in the absence and presence of NaCl and organic solvent-HMF-water-NaCl systems at T= 313.15 K and atmospheric pressure (0.1 MPa); □ : MIBK-HMF-water-DES (10 wt% DES);■ :2-pentanol-HMF-water-DES (10 wt% DES); ○ : MIBK-HMF-water-DES-NaCl; ● : 2-pentanol-HMF-water-DES-NaCl; Δ : MIBK-HMF-water-NaCl [22] ; ▲ : 2-pentanol-HMF-water-NaCl [22]; —·—· : NRTL model.

### 4.3.3 LLE correlation for organic solvent-HMF-water-DES in the absence and presence of NaCl

The Non-Random Two-Liquid (NRTL) model [35] is an activity coefficient model that is applied to correlate the phase equilibria. This model is also able to calculate the multicomponent LLE compositions by only using the constituent binary parameters. In this study, the LLE experimental data for the systems containing organic solvent (MIBK or 2-pentanol)-HMF-water-DES (ChCl-urea) in the absence and presence of NaCl were correlated by NRTL model at $T$=313.15 K using Aspen Plus V8.8. For the LLE systems of organic solvent-HMF-water-DES, the nonrandomness parameter ($\alpha_{ij}$) was set at 0.2 for each pair ($i$-$j$). The binary interaction parameters ($b_{ij}$ and $b_{ji}$) among organic solvents (MIBK and 2-pentanol), HMF, and water were fixed based on the ternary LLE correlation results of organic solvent-HMF-water systems [Chapter 2]. The $b_{ij}$ and $b_{ji}$ for the interactions of DES with organic solvents, HMF, and water were derived from regression of the experimental LLE data in this study, as presented in Table C.9. Furthermore, for the LLE of organic solvent-HMF-water-DES-NaCl systems, the $\alpha_{ij}$, $b_{ij}$ and $b_{ji}$ parameters were regressed for the interaction of NaCl with DES, as listed in Table C.10. Whereas, the interactions of organic solvent-HMF, organic solvent-water, organic solvent-DES, HMF-water, HMF-DES, and water-DES were fixed from the obtained binary interaction parameters in Table C.9. In the correlation, NaCl was assumed as one molecular species. While, the $\alpha_{ij}$, $b_{ij}$ and $b_{ji}$ for the interactions of NaCl with organic solvents (MIBK and 2-pentanol), HMF, and water were fixed from the determined optimal values in the quaternary LLE correlation results of organic solvent-HMF-water-NaCl [Chapter 2]. The

$b_{ij}$ and $b_{ji}$ among organic solvents, HMF, water, and DES for the LLE of organic solvent-HMF-water-DES in the presence of NaCl were taken from the obtained results in Table C.9. In this study, although negative values are obtained for $\alpha_{ij}$, it is allowed to give more flexibility to the NRTL correlation model enabling negative values of $\alpha_{ij}$ which leave any supposed physical meaning. Besides, the $\alpha_{ij}$ parameter also plays an important role in generating good correlation results for the LLE systems containing salt [36,37].

Furthermore, the experimental and calculated LLE tie-line data from the NRTL model are compared in Figures 4.1-4.2 for organic solvent-HMF-water-DES and Figures 4.5-4.6 for organic solvent-HMF-water-DES-NaCl systems. The closed and open symbols denote the LLE tie-lines from experimental data and NRTL model, respectively. The calculated results show good agreement with the experimental LLE tie-line data of the investigated systems. The RMSD of organic solvent-HMF-water-DES systems are 0.88% and 1.98% for MIBK and 2-pentanol solvents, respectively, as listed in Table C.9. While the RMSD of the LLE systems containing salt are 0.55% for MIBK – HMF – water – DES – NaCl and 1.44% for 2-pentanol – HMF – water – DES – NaCl system, as listed in Table C.10. In addition, it can be shown in Figures 4.3 and 4.7 that the NRTL model also gives good description of the separation factor and the distribution coefficient of HMF. However, it shows larger deviation in higher DES and HMF concentrations which is also visible from the correlated tie-lines in Figures 4.1-4.2 and 4.5-4.6. Overall, the NRTL model can correlate the experimental LLE data satisfactorily for all LLE systems studied.

## 4.4 Conclusions

The choline chloride urea effect on the LLE systems containing HMF, water, organic solvent (MIBK or 2-pentanol), water in the absence and presence of NaCl were investigated at 313.15 K and atmospheric pressure (0.1 MPa). The extraction performance was determined from the separation factor and the distribution coefficient of HMF obtained from LLE data. The results in this study indicated that the slope of tie-lines decreased with increasing DES (ChCl-urea) concentration, demonstrating lower separation factor and distribution coefficient of HMF as well. However, with the comparison of the LLE systems without DES/ IL, the DES (ChCl-urea) reduced the extraction performance much less than IL ([EMIM][$BF_4$]), which confirmed that the HMF extraction from aqueous DES showed better extraction performance. Besides, the addition of NaCl into HMF aqueous DES solution enhanced the extraction performance, enabling compensation of the DES effect. The separation factors and the distribution coefficients of HMF increased around 2.7 and 1.6 times, respectively. Taking the benefit of DES as stabilizing agent for HMF, the combination of aqueous DES with NaCl made the HMF extraction more favorable. Furthermore, from comparing MIBK with 2-pentanol, it can be inferred that MIBK was more selective as extraction solvent for HMF extraction in the presence of DES and NaCl with the separation factors 2.6 times higher than those of 2-pentanol. The experimental LLE tie-line data were correlated well using NRTL model. The RMSD of the LLE systems containing organic solvent-HMF-water-DES were 0.88% and 1.98% for MIBK and 2-pentanol solvents, respectively. While, the RMSD of the LLE systems in the presence of NaCl were 0.55% for MIBK – HMF –

water – DES – NaCl and 1.44% for 2-pentanol – HMF – water – DES – NaCl system.

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# Chapter 5

# Fructose effect on the extraction performance of 5-hydroxymethylfurfural in aqueous 1-ethyl-3-methylimidazolium tetrafluoroborate or choline chloride urea solution with the aid of sodium chloride using methyl isobutyl ketone solvent

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# ABSTRACT

Carbohydrates are the renewable feedstocks to produce 5-Hydroxymethylfurfural (HMF) through hexose dehydration. Fructose is widely applied as the raw material in the formation of HMF due to its high rate and selectivity of conversion to HMF. In HMF production process, the liquid-liquid extraction is essentially used to extract HMF from reaction medium. The use of ionic liquid (IL) and deep eutectic solvent (DES) have been recognized to increase the yield of HMF by suppressing the formation of side-products. The aim of this study is to systematically study the effect of fructose on the extraction performance of HMF in water-1-ethyl-3-methylimidazolium tetrafluoroborate ([EMIM][$BF_4$]) or choline chloride urea (ChCl-urea)-sodium chloride (NaCl) solution at 313.15 K and atmospheric pressure (0.1 MPa). Methyl isobutyl ketone (MIBK) was used as a selective extraction solvent. The separation factor and the distribution coefficient of HMF were obtained from liquid-liquid equilibrium (LLE) data to interpret the extraction performance. According to the results in this study, fructose had minimal effect on the extraction performance of HMF. For the LLE system using [EMIM][$BF_4$], the HMF distribution coefficient values showed comparable values to the LLE system without fructose. While the separation factors decreased around 1.1 times. Furthermore, fructose decreased the separation factors around 1.3 times and distribution coefficients of HMF around 1.1 times for the LLE system using ChCl-urea. Comparison of IL and DES used, indicated that HMF extraction from aqueous DES (ChCl-urea) demonstrated better extraction performance with the separation factor and the HMF distribution coefficient values 1.4 and 1.2 times higher than those for HMF extraction from aqueous IL ([EMIM][$BF_4$]), respectively. The experimental LLE data were correlated well using the Non-Random Two-Liquid (NRTL) model. The reliability of the experimental LLE data was also satisfactorily ascertained by the Hand and Othmer-Tobias correlations.

*Keywords*: Extraction performance; Fructose; 5-Hydroxymethylfurfural; Liquid-liquid equilibrium; MIBK

## 5.1 Introduction

The utilization of bio renewable feedstocks to produce fuels and chemicals has increased immensely [1-3]. Expansion of the worldwide population will also increase the world energy consumption and petroleum demand. Hence, biomass needs to be used as a potential material which is sustainable and biodegradable [3,4]. 5-Hydroxymethylfurfural (HMF) is a versatile platform chemical that can be converted to biofuels and various chemical products. HMF can be synthesized by a triple dehydration of hexose feedstocks such as fructose or glucose [3]. The use of fructose as the starting reactant gives the high yield of HMF formation. Fructose was first used as the model C6 sugar for the dehydration process, due to its higher reactivity which required lower temperature and shorter reaction time compared to glucose. The rate of fructose conversion and selectivity to HMF are higher than with glucose [3]. Therefore, the studies which examined the formation of HMF from fructose have significant improvement in the catalytic system and reaction engineering studies [5-9]. Besides, HMF can also be formed by integrating glucose isomerization with fructose dehydration in a “one-pot” reactor configuration in biphasic system to achieve high yield of HMF [3]. Liquid-liquid extraction can be applied in the HMF production process to enhance the yield and selectivity of HMF. HMF can be extracted from reaction medium into the organic solvent phase, which prevents the degradation of HMF.

Recently, many researchers have investigated the dehydration process of carbohydrates into HMF using ionic liquid (IL) or deep eutectic solvent (DES) [9-15]. It is recognized that IL and DES can be used in HMF production as stabilizing agent. IL and DES can also improve the HMF yield by suppressing the formation of undesirable by-products. IL is a green chemical solvent that has been applied in chemical industries. This compound is a salt which is liquid at room temperature. Because of the unique structure and physico-chemical properties, IL has been used in many applications [16]. Like IL, Abbott *et al.* [17-19] have indicated that solid organic salt and complexing agent mixtures can also form a liquid at temperatures below 100 ºC, which is called DES. The DES is also a green solvent which can be prepared easily from low-cost and non-toxic chemicals [20]. However, the separation of HMF from pure IL or DES is challenging due to the strong hydrogen bonding interactions between IL or DES with HMF molecules and its high viscosity resulting in a low HMF distribution coefficient [15,21]. The presence of water in the mixture is essential to improve the extraction efficiency and reduce the viscosity of the solution [22-24]. In the present study, an extraction of HMF using aqueous IL or DES was provided in which hydrophilic IL and DES were preferably used because their high solubility in water. Furthermore, the distribution coefficient of HMF can also be enhanced with the addition of salt into the aqueous solution [23-29] which also improves yield in the HMF synthesis [25]. Hence, the combination of aqueous IL or DES with sodium chloride (NaCl) was also applied in this study.

Few researchers have systematically investigated the thermodynamics of HMF extraction [23,24,28-31]. There is still a great need for the thermodynamic data, such as partitioning of HMF into the organic solvent phase and the liquid-liquid equilibria (LLE) of systems containing HMF with their correlations which are required as basis for the extraction process design. The effect of biphasic system constituents on the LLE is also essential to study. Our previous works have investigated the effect of salt and the presence of IL and DES on the LLE [23,24,29]. In the HMF production process, the conversion from sugar (fructose) to HMF is not always 100%. It is therefore crucial to investigate the extraction of HMF in the presence of unreacted fructose. In the present study, we systematically investigated the effect of reactant (fructose) on the extraction performance of HMF in water-IL or DES-NaCl solution at 313.15 K and atmospheric pressure (0.1 MPa). Methyl isobutyl ketone (MIBK) was used as the selective extraction solvent for HMF extraction [23,24]. 1-ethyl-3-methylimidazolium tetrafluoroborate ([EMIM][$BF_4$]) and choline chloride urea (ChCl-urea) which are the hydrophilic IL and DES were also applied in this work, respectively. The extraction performance was evaluated based on the values of the separation factor and the HMF distribution coefficient which were obtained from the LLE data. Additionally, the reliability of the experimental LLE data was ascertained by the Hand and Othmer-Tobias correlations. The experimental LLE data were also correlated using the Non-Random Two-Liquid (NRTL) thermodynamic model and the binary interaction parameters were generated in this study. The NRTL model is an appropriate correlation model to describe the LLE data in various systems including the LLE systems containing salts which is also available in Aspen Plus and can be applied easily for process simulation. The present study also introduces new biphasic systems containing HMF and expands the scope for the thermodynamics studies of HMF extraction.

## 5.2 Experimental Section

### 5.2.1 Chemicals

The description of chemicals used in this study are listed in Table D.1. Deionized ultrapure water was used for the experiments and analysis with resistance of 18.2 MΩ.cm. All the chemicals were used without further purification.

### 5.2.2 Tie-line measurements

The experimental LLE tie-lines of MIBK, HMF, water, [EMIM][$BF_4$] or ChCl-urea, and NaCl in the presence of fructose were measured using jacketed equilibrium cell at 313.15 K (40 °C) and atmospheric pressure (0.1 MPa). The thermostated water from water bath (Tamson-instruments TC 6B, Holland) was circulated to control the equilibrium cell at constant temperature with the standard uncertainty u($T$) of 0.02 K. The ChCl-urea was prepared by heating choline chloride and urea with a molar ratio of 1:2 at 80°C and stirring for 1 hour until a homogeneous liquid was formed [17]. In general, feed containing aqueous solutions of HMF-water-[EMIM][$BF_4$] or ChCl-urea-NaCl in the presence of fructose were prepared and weighed on an analytical balance Mettler Toledo (MS 304S/01, Switzerland) with a precision of ± 0.0001 g. The initial HMF concentration was varied in the range of 5 wt% to 35 wt% while keeping the [EMIM][$BF_4$] or ChCl-urea, NaCl, and fructose at constant concentrations. Subsequently, MIBK as extraction solvent was added into the mixtures with a mass ratio of 1:1 between MIBK and aqueous feed solution. The mixture was stirred in the equilibrium cell for 2.5 hours and allowed to settle for 20 hours for low HMF concentrations and at least 22 hours for high HMF concentrations at 313.15 K until the two liquid phases were completely separated and reached equilibrium. Then, approximately 5 mL of sample was required for analytical measurements which was taken from organic and aqueous phases, respectively. The organic and aqueous samples were placed in an oven at 40 $^{o}$C before further sample preparation for analytical measurements.

### 5.2.3 Analytical measurements

The concentrations of HMF, MIBK, and fructose from organic and aqueous phases were analysed using High-performance liquid chromatography (HPLC). The HPLC equipped with a reversed phase column C18 Zorbax ODS was applied to determine HMF and MIBK using UV/VIS (ultraviolet–visible) detector at a UV-wavelength of 278 nm and 42 $^{o}$C. Whereas, for fructose, the HPLC was equipped with Rezex RPM-Monosaccharide column at 75 $^{o}$C using RI (refractive index) detector. The HPLC analysis method was according to our previous studies using water and methanol as eluent to detect the peak area of HMF and MIBK [23,24]. Furthermore, the peak area of fructose was detected with peak maxima at 6.3 min using water as eluent with a flowrate of 1.5 mL/min. The Karl Fischer titration (Metrohm 756 KF) was used to analyse the water content in the organic phase. While the amount of water in the aqueous phase was determined by subtracting the sum of the other mass fractions from a value of 1. The concentrations of salt in the organic and aqueous phases were analysed by ICP-OES (Inductively Coupled Plasma Optical Emission Spectroscopy, Spectro Arcos EOP) using 3% of nitric acid ($HNO_3$) as diluent. In addition, the IL and DES concentrations in both phases were also analysed based on our previous studies method by ICP-OES and IC (ion exchange chromatography) performed with Dionex DX-120 Ion Chromatograph using aqueous methane sulfonic acid as eluent, respectively [23,24]. The mass fractions of each component in both phases were averaged from three replicated samples. The standard uncertainties u($w_i$) of MIBK, HMF, water, [EMIM][$BF_4$], ChCl-urea, NaCl, and fructose were estimated to be 0.0004, 0.0005, 0.0009, 0.0006, 0.0002, 0.0007, and 0.0004 in mass fraction, respectively.

## 5.3 Results and discussion

### 5.3.1 Effect of fructose on the extraction performance of HMF

The experimental LLE tie-line data for the systems containing MIBK – HMF – water – [EMIM][$BF_4$] – NaCl – fructose and MIBK – HMF – water – ChCl-urea – NaCl – fructose are presented in Tables D.2-D.3 and Figures 5.1-5.2 (on IL/DES, salt, and sugar free basis). The initial HMF concentration ranged from 5 wt% to 35 wt% with constant amount of [EMIM][$BF_4$] or ChCl-urea, NaCl, and fructose. The concentrations of [EMIM][$BF_4$] and ChCl-urea were selected at 10 wt%. Taking the benefit of IL and DES as stabilizing agent for HMF, the presence of 10 wt% of [EMIM][$BF_4$] or ChCl-urea in the solution is appropriate which generated better extraction performance compared to the ones with higher IL or DES concentration [23,24]. The NaCl concentration was fixed at 10 wt% which is near the maximum NaCl solubility in the highest HMF concentration used in our previous study (40 wt% of HMF) [29]. Additionally, we provided the LLE data when fructose and HMF both were present in the mixture. Thus, the presence of fructose in the aqueous solution indicated the unreacted fructose. In this case the fructose content should be less, therefore 10 wt% of fructose was adequate to be selected in this study. As it will be more difficult to observe fructose effect at lower concentration.

From Tables D.2-D.3, it is evident that the ChCl-urea contents in the organic phase are much lower than the [EMIM][$BF_4$] contents, which are below 0.05 wt% for all initial HMF concentrations. It also indicates that ChCl-urea has limited solubility in the MIBK solvent which is lower than that of [EMIM][$BF_4$] in MIBK. This has advantages of cost-saving and energy-saving for the further product purification and solvent recycling processes. From Tables D.2-D.3, it can also be seen that the concentrations of NaCl and fructose in the organic phase are very low. The NaCl concentrations range from 0.01-0.1 wt% and the fructose concentrations are below 0.1 wt% over the whole range of initial HMF concentrations for both LLE systems using [EMIM][$BF_4$] and ChCl-urea. The low NaCl and fructose contents in the organic phase demonstrate good extraction and simplify the further product purification process.

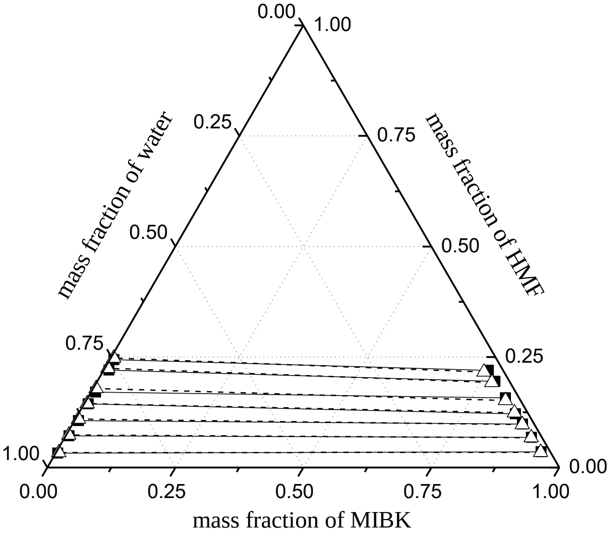


**Figure 5.1** Phase diagram of the experimental and calculated LLE tie-line data for MIBK-HMF-water-[EMIM][$BF_4$]-NaCl-fructose system on IL, salt, and sugar free basis at *T*= 313.15 K and atmospheric pressure (0.1 MPa) for 10 wt% [EMIM][$BF_4$], 10 wt% NaCl, and 10 wt% fructose using NRTL model; —■— : experimental data; ---△--- : NRTL model.

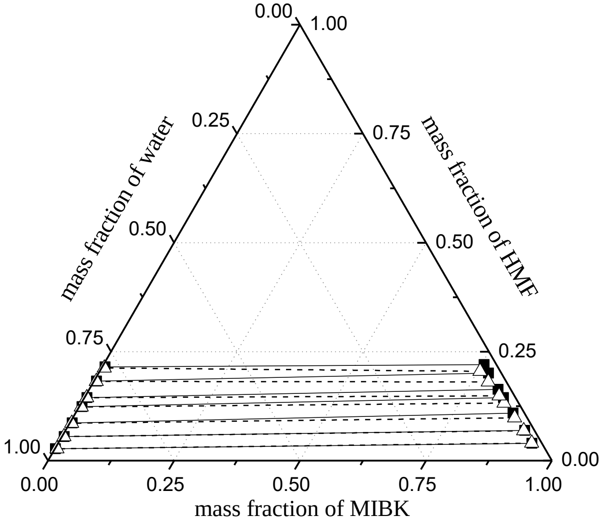
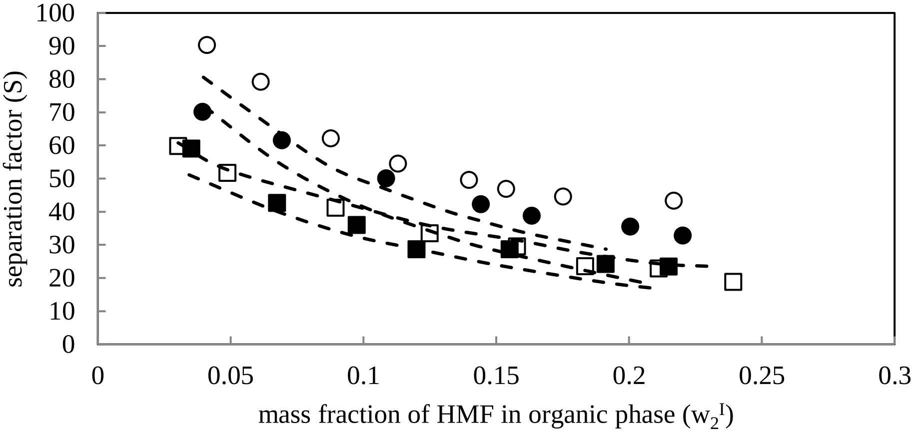


**Figure 5.2** Phase diagram of the experimental and calculated LLE tie-line data for MIBK-HMF-water-ChCl-urea-NaCl-fructose system on DES, salt, and sugar free basis at *T*= 313.15 K and atmospheric pressure (0.1 MPa) for 10 wt% ChCl-urea, 10 wt% NaCl, and 10 wt% fructose using NRTL model; —■— : experimental data; - - -△- - - : NRTL model.

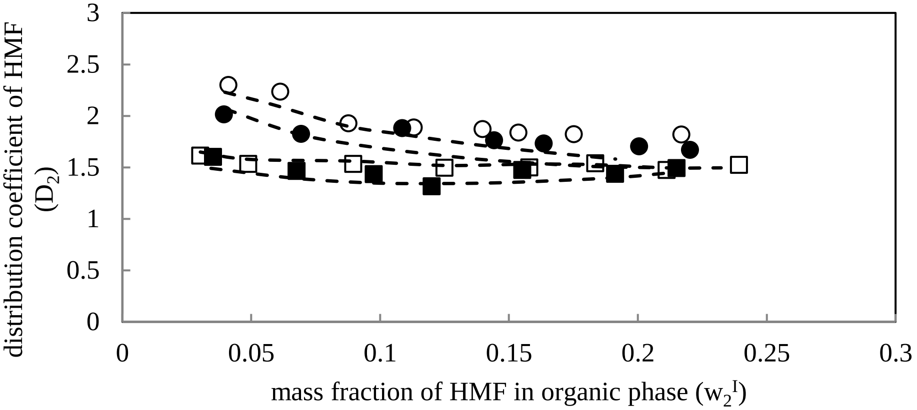
The separation factors and the distribution coefficients for the LLE of MIBK – HMF – water – [EMIM][BF$_4$] – NaCl – fructose and MIBK – HMF – water – ChCl-urea – NaCl – fructose are shown in Table D.4 and Figure 5.3. It illustrates that with the increase of HMF (solute) mass fraction in the solution at the same amount of extraction solvent, the solution becomes more concentrated, which causes the distribution coefficient of HMF (solute) and the separation factor decrease. The reason is with increasing HMF (solute) mass fraction at the same amount of extraction solvent, the solvent molecules are unable to bind and take all the HMF (solute) molecules from aqueous solution to organic phase, there are some HMF (solute) molecules that are trapped in the aqueous solution which also interact with water molecules. The greater the HMF (solute) mass fraction in the solution, the more HMF (solute) molecules interact with water molecules causing lower in HMF distribution coefficient, thus the separation factor decreases as well. Furthermore, it can be seen in Table D.4 and Figure 5.3 that the separation factors are much higher than 1 for all initial concentrations of HMF reaching up to 59.3 for the LLE system with [EMIM][$BF_4$] and up to 69.7 for the LLE system with ChCl-urea. Besides, both systems also exhibit sufficiently high HMF distribution coefficients, which are above 1.3 over the whole range of initial HMF concentrations. These results confirm that the extraction of HMF from an aqueous solution containing water-[EMIM][$BF_4$] or ChCl-urea-NaCl in the presence of fructose using MIBK extraction solvent is favorable over the whole range of initial HMF concentrations. A ketone is a polar compound in which oxygen is a relatively electronegative atom and it can form a strong dipole when it is bound to hydrogen and carbon covalently. The dipole can allow this compound to take part in strong hydrogen bonding interactions with HMF as hydrogen bond donor molecule. In addition, MIBK solvent has limited solubility in water, as illustrated by the low MIBK concentrations in aqueous phase for both systems using [EMIM][$BF_4$] and ChCl-urea which are all below 1%, as seen in Tables D.2-D.3 and Figures 5.1-5.2. This can minimize the solvent losses which is good for the extraction process. The water contents in organic phase are also sufficiently low ranging from 2-3 wt% over the whole range of initial HMF concentrations for both systems. From the energy efficiency point of view, the low water content in organic phase can also minimize the energy demand in the following product purification and solvent recycling processes.

Furthermore, from Table D.4 and Figure 5.3, it can be inferred that the HMF extraction from aqueous IL or DES also demonstrates much a better distribution coefficient of HMF compared to that from pure IL or DES with the HMF distribution coefficient reaching up to 0.287 using pure IL [21] and up to 0.45 using pure DES [15]. The IL and DES can interact with HMF molecule through hydrogen bonding interactions. Therefore, IL or DES and extraction solvent compete each other to make hydrogen bonding interaction with HMF which cause the extraction of HMF by extraction solvent more difficult. In this case, the presence of water as a hydrogen bond donor molecule in the solution is beneficial for HMF extraction process. As it can interact with IL or DES which reduces the interactions between IL or DES and HMF. With the presence of water in the solution, the HMF molecule is more easily extracted and the HMF distribution coefficient considerably increases as well.

The effect of fructose on the extraction performance of HMF in water-[EMIM][$BF_4$] or ChCl-urea-NaCl solution using MIBK solvent can also be observed in Figure 3 by comparing to the LLE systems in the absence of fructose [23,24]. It indicates that fructose has minimal effect on the separation factor and the HMF distribution coefficient. In the LLE system using [EMIM][$BF_4$], the separation factors decrease around 1.1 times. While the distribution coefficients of HMF are comparable with the LLE system in the absence of fructose. Furthermore, in the LLE system using ChCl-urea, fructose reduces the extraction performance around 1.3 times for the separation factors and 1.1 times for the HMF distribution coefficients. In the HMF production process, small amount of fructose is usually present in the solution after reaction indicating unreacted fructose. Therefore, this study confirms that the presence of fructose in the solution does not significantly affect the extraction performance. A good separation factor and HMF distribution coefficient can be achieved in both biphasic systems in the presence and absence of fructose. Additionally, from comparing IL and DES in Table D.4 and Figure 5.3, it demonstrates that the extraction of HMF from aqueous DES (ChCl-urea) exhibits better extraction performance with HMF separation factor and distribution coefficient values 1.4 and 1.2 times higher than those of HMF extraction from aqueous IL ([EMIM][$BF_4$]), respectively. Hence, DES can be used as a potential stabilizing agent alternative to IL in the HMF production which also shows sufficiently high extraction performance in the HMF extraction process with the presence of water.



(a)



(b)

**Figure 5.3** (a) Separation factor (S) and (b) distribution coefficient of HMF ($D_2$) for MIBK – HMF – water – [EMIM][$BF_4$] or ChCl-urea – NaCl systems in the absence and presence of fructose at *T*= 313.15 K and atmospheric pressure (0.1 MPa); □ : MIBK – HMF – water – [EMIM][$BF_4$] – NaCl [23]; ○ : MIBK – HMF – water - ChCl-urea – NaCl [24]; ■ : MIBK – HMF – water – [EMIM][$BF_4$] – NaCl – fructose; ● : MIBK – HMF – water – ChCl-urea – NaCl – fructose; − − − : NRTL model.

### 5.3.2 LLE correlation for MIBK-HMF-water-IL or DES-salt-sugar systems

The Non-Random Two-Liquid (NRTL) model [32] is used in the present study to correlate the experimental LLE data of the investigated systems by Aspen Plus V8.8. This activity coefficient model is able to calculate the multicomponent LLE compositions only using the constituent binary parameters. The nonrandomness parameters ($\alpha_{ij}$) among MIBK, HMF, water, [EMIM][$BF_4$], ChCl-urea, and fructose were set at 0.2. In the correlation, NaCl was considered as one molecular species. The $\alpha_{ij}$ parameters for the interactions of NaCl with MIBK, HMF, water, [EMIM][$BF_4$], and ChCl-urea were determined, instead of setting it to the default value, from the correlation results in the MIBK-HMF-water-NaCl and MIBK-HMF-water-[EMIM][BF$_4$] or ChCl-urea-NaCl systems [Chapters 2,3,4]. The $\alpha_{ij}$ parameter of NRTL model plays an important role in obtaining a good correlation in the experimental LLE systems containing salt [33,34]. The NRTL correlation model gives more flexibility to allow negative values for the $\alpha_{ij}$ parameter, leaving any supposed physical meaning. In addition, the binary interaction parameters ($b_{ij}$ and $b_{ji}$) among MIBK, HMF, water, and NaCl were fixed from the determined values in the ternary and quaternary LLE correlation results of MIBK-HMF-water and MIBK-HMF-water-NaCl systems [Chapter 2]. The $b_{ij}$ and $b_{ji}$ for the interactions of [EMIM][BF$_4$] or ChCl-urea with MIBK, HMF, water, and NaCl were taken from the correlation results obtained in the LLE of MIBK – HMF – water – [EMIM][BF$_4$] or ChCl-urea and MIBK – HMF – water – [EMIM][BF$_4$] or ChCl-urea – NaCl systems [Chapters 3,4]. While, the $b_{ij}$ and $b_{ji}$ parameters for the interactions of fructose with other components investigated and $\alpha_{ij}$ of fructose with NaCl were regressed in this study, as listed in Table D.5.

The comparison of the calculated LLE data from the NRTL model with the experimental LLE data are shown in Figures 5.1 and 5.2. The open and closed symbols denote the calculated and experimental LLE data, respectively. The NRTL model shows good agreement with the experimental LLE data with the root mean square deviations (RMSD) 0.37% for MIBK-HMF-water-[EMIM][BF$_4$]-NaCl-fructose and 0.71% for MIBK-HMF-water-ChCl-urea-NaCl-fructose systems, as presented in Table D.5. Furthermore, it can be seen in Figure 5.3 that the NRTL model also provides good description of separation factor and HMF distribution coefficient, except at some points, it shows larger deviation. However, overall the NRTL model correlates well the experimental LLE data with the RMSD below 1% for the investigated LLE systems.

### 5.3.3 The consistency of LLE tie-line data

The Hand [35] and Othmer-Tobias [36] correlations were used to ascertain the consistency of the experimental LLE tie-line data. The equations of Hand and Othmer-Tobias are defined in Eqs. (1) and (2), respectively.

$$ln\left(\frac{w_2^I}{w_1^I}\right) = a^* + b^*\, ln\left(\frac{w_2^{II}}{w_3^{II}}\right) \tag{1}$$

$$ln\left(\frac{1-w_1^I}{w_1^I}\right) = a + b\, ln\left(\frac{1-w_3^{II}}{w_3^{II}}\right) \tag{2}$$

where $w_1$, $w_2$, and $w_3$ are the mass fraction of MIBK, HMF, and water, respectively. While the superscripts $I$ and $II$ demonstrate the organic and aqueous phases, respectively. The optimal values of $a*$ and $b*$ for the Hand correlation and $a$ and $b$ for the Othmer-Tobias correlation are determined by fitting the LLE tie-line data to Eqs. (1) and (2), respectively as listed in Table D.6, in which the square of correlation coefficient ($R^2$) is a measure of the consistency of the LLE tie-line data. The correlated results of the Hand and Othmer-Tobias equations are compared to the experimental values in Figures 5.4 and 5.5, respectively. As seen from the graphs and the tabulated values of $R^2$, a high degree of consistency is obtained between the experimental data and both correlations, ascertaining the reliability of the experimental data.

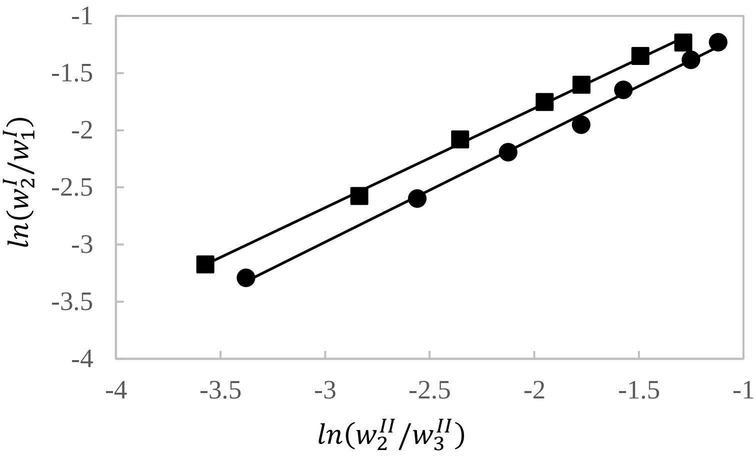


**Figure 5.4** Hand plots for LLE data of MIBK – HMF – water – [EMIM][BF$_4$] or ChCl-urea – NaCl systems in the presence of fructose at *T*= 313.15 K and atmospheric pressure (0.1 MPa); ● : MIBK – HMF – water – [EMIM][BF$_4$] – NaCl – fructose; ■ : MIBK – HMF – water – ChCl-urea – NaCl – fructose; ——— : Hand correlation.

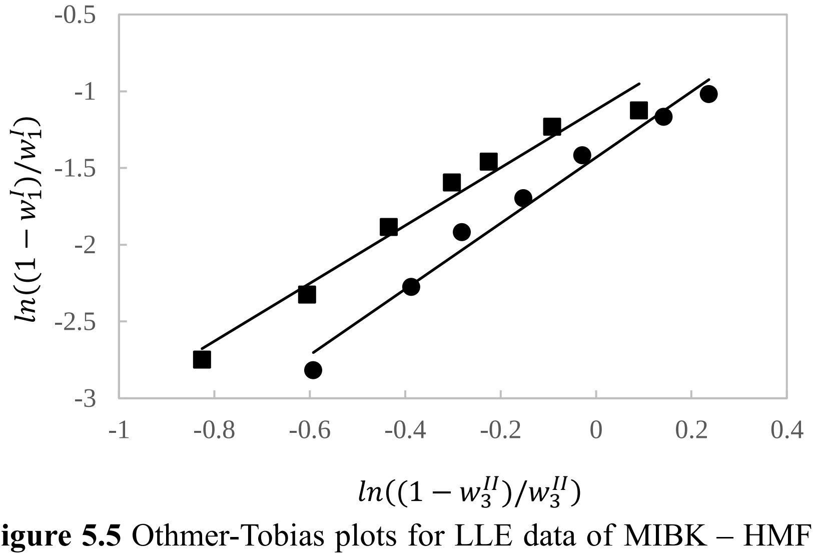


**Figure 5.5** Othmer-Tobias plots for LLE data of MIBK – HMF – water – [EMIM][BF$_4$] or ChCl-urea – NaCl systems in the presence of fructose at *T*= 313.15 K and atmospheric pressure (0.1 MPa); ● : MIBK – HMF – water – [EMIM][BF$_4$] – NaCl – fructose; ■ : MIBK – HMF – water – ChCl-urea – NaCl – fructose; ——— : Othmer-Tobias correlation.

## 5.4 Conclusions

The effect of fructose on the extraction performance of HMF in water-IL ([EMIM][$BF_4$]) or DES (ChCl-urea)-NaCl solution were studied at 313.15 K and atmospheric pressure (0.1 MPa) using MIBK as a selective extraction solvent. The separation factor and the distribution coefficient of HMF were determined from the LLE data investigated to evaluate the extraction performance. The results showed that fructose had limited effect on the separation factor and the HMF distribution coefficient. The extraction performance for the LLE systems of MIBK-HMF-water-[EMIM][$BF_4$] or ChCl-urea-NaCl in the presence of fructose was compared to the one without. It demonstrated that for the LLE system using [EMIM][$BF_4$], the separation factors decreased around 1.1 times. Whereas the distribution coefficients of HMF were comparable with the LLE system in the absence of fructose. For the LLE system using ChCl-urea, the extraction performance with the presence of fructose decreased around 1.3 and 1.1 times for the separation factors and the HMF distribution coefficients, respectively. In addition, from comparing IL ([EMIM][$BF_4$]) and DES (ChCl-urea), it can be inferred that the extraction of HMF from aqueous DES (ChCl-urea) generated better extraction performance with the values of the separation factor and the HMF distribution coefficient 1.4 and 1.2 times higher than those of HMF extraction from aqueous IL ([EMIM][$BF_4$]), respectively. The NRTL activity coefficient model was also used to correlate the experimental LLE of the investigated systems. The correlation model provided good agreement with the experimental data with the RMSD for the LLE systems of MIBK-HMF-water-[EMIM][$BF_4$]-NaCl-fructose and MIBK-HMF-water-ChCl-urea-NaCl-fructose 0.37% and 0.71%, respectively. The consistency of the LLE tie-line data measured in this study was also satisfactorily ascertained by the Hand and Othmer-Tobias correlations.

## 5.5 References

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# Chapter 6

# Liquid - liquid equilibrium data for 5-hydroxymethylfurfural separation from aqueous solution using tributyl phosphate as extraction solvent

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# ABSTRACT

5-hydroxymethylfurfural (HMF) is a bio renewable material used as an important platform chemical to produce biofuel and various chemical products. HMF is formed through hexose dehydration process. Fructose is commonly used as the raw material for HMF production, because of its high conversion rate and high yield and selectivity for HMF. Liquid-liquid extraction is beneficially applied in HMF production to separate HMF from reaction medium to prevent the degradation of HMF. Furthermore, ionic liquid (IL) and deep eutectic solvent (DES) can be applied as stabilizing agent in HMF production. The objective of this study is to investigate the liquid-liquid equilibrium (LLE) data of systems containing HMF in aqueous solution using tributyl phospate (TBP) as an extraction solvent at constant temperature (313.15 K) and atmospheric pressure (0.1 MPa). The effect of biphasic system constituents on the LLE phase diagram and extraction performance were also studied. We used aqueous-organic biphasic systems, and also added DES ChCl-urea (choline chloride-urea), salt (NaCl), and sugar (fructose) in the aqueous phase. The separation factor and HMF distribution coefficient were determined from LLE data to interpret the extraction performance. The performance of TBP solvent was also compared to that of MIBK and 2-pentanol extraction solvents. According to the results, the slope of tie-lines in the LLE of TBP-HMF-water-ChCl-urea system decreased compared to those in the ternary LLE system with the absence of ChCl-urea, demonstrating lower extraction performance. Both the separation factors and the HMF distribution coefficients reduced around 1.3 times in the presence of ChCl-urea. However, the addition of NaCl enhanced the separation factors and the distribution coefficients of HMF around 2.0 and 1.7 times, respectively, enabling compensation of the DES effects. The presence of fructose in the aqueous solution had limited effect on the extraction performance. Furthermore, for the solvent effect, it can be inferred that TBP is more selective as extraction solvent and also superior in terms of HMF distribution coefficient than the other two solvents (MIBK and 2-pentanol). Overall, by using TBP solvent, it showed a very good HMF extraction performance from aqueous ChCl-urea solution in the presence of NaCl and fructose. The experimental LLE data were also correlated well with the thermodynamic models for the investigated systems in this study.

*Keywords*: Distribution coefficient; 5-Hydroxymethylfurfural; Liquid-liquid equilibrium; Separation factor; Tributyl phospate

## 6.1 Introduction

5-Hydroxymethylfurfural (HMF) has been known as a promising product from hexose dehydration for biofuels and chemicals [1]. The use of this versatile platform chemical may overcome the problem of the dependence on fossil resources. Fructose, glucose, sucrose, cellulose, and inulin can be arranged as bio renewable feedstocks which are abundantly available. Recently, various studies in the process of the HMF formation have been conducted in order to get more effective method for the transformation of carbohydrates into HMF [1-13]. The formation of HMF using fructose as a raw material is widely applied and get significant improvement in the catalytic system and reaction engineering studies. High yield and selectivity of HMF can be achieved with the use of fructose [1,2]. HMF production is also possible by integrating glucose isomerization with fructose dehydration in a "one-pot" reactor configuration in biphasic system to achieve high yield of HMF [1]. Researchers indicated that carbohydrates can be converted to HMF with high yield in biphasic aqueous-organic systems [1-6]. The organic solvent is used as an extraction solvent to extract HMF from its aqueous solution which prevents the HMF degradation or side products formation. The selection of organic solvent in liquid-liquid extraction of HMF also plays an important role in obtaining good distribution and separation of HMF. Methyl isobutyl ketone (MIBK) and 2-pentanol were used as extraction solvents in our previous studies [14-17] due to their strong hydrogen bonding interactions with HMF. It was found that MIBK was more selective as an extraction solvent for HMF which is less miscible with water. In the present study, we try to use tributyl phosphate (TBP) solvent for the comparison with the two previously studied solvents. TBP is a very effective extraction solvent for HMF and also has low solubility in water [18]. However, TBP is a high boiling organic solvent, hence the separation of HMF from this solvent should be conducted by back-extraction instead of distillation.

Furthermore, ionic liquid (IL) and deep eutectic solvent (DES) have been recognized as stabilizing agent in HMF production by suppressing the formation of side products which generated high yield of HMF [5,7,9-12,19-22]. Nevertheless, the interactions between IL/DES and HMF are mainly controlled by the strong hydrogen bonding interactions. This phenomenon leads to the difficulty in the HMF separation from pure IL/DES, resulting in a reduced distribution coefficient of HMF [22,23]. Therefore, the presence of water in the mixture proved advantageous through a higher separation factor and distribution coefficient of HMF [15-17]. Water as a hydrogen bond donor molecule can decrease the interaction between IL/DES and HMF. Our previous studies [16,17] also indicated that the use of aqueous DES ChCl-urea (choline chloride-urea) generated better extraction performance of HMF compared to that of aqueous IL [EMIM][$BF_4$] (1-ethyl-3-methylimidazolium tetrafluoroborate). The DES can be used as an alternative to IL which is also a green solvent and can be prepared easily from cheaper and non-toxic materials [24,25]. Additionally, the addition of NaCl in the aqueous phase can favor the partitioning of HMF into organic phase that increases the yield of HMF as well [14-17,26-29].

The objective of the present study is to investigate the liquid-liquid equilibrium (LLE) data of systems containing HMF in aqueous solution using TBP as an extraction solvent at constant temperature (313.15 K) and atmospheric pressure (0.1 MPa). We added DES (ChCl-urea) in the aqueous phase. Then, the combined effect of aqueous ChCl-urea with salt (NaCl) in the absence and presence of sugar (fructose) were also studied. To our best knowledge, there is no phase equilibrium data available for these systems. The LLE data are essential information as basis in the HMF extraction process design. The separation factor and distribution coefficient of HMF were determined from the LLE data to interpret the extraction performance. The extraction performance of the LLE using TBP solvent in this study were also compared to that of the LLE using MIBK and 2-pentanol extraction solvents [14,16,17]. Furthermore, the NRTL (Non-Random Two-Liquid) and UNIQUAC (Universal Quasi-Chemical) thermodynamic models were applied to correlate the ternary experimental LLE data, while the experimental LLE data containing ChCl-urea, NaCl, and fructose were correlated using the NRTL model. This study also introduces new biphasic systems and expands the scope for the thermodynamics studies on liquid-liquid extraction of HMF.

## 6.2 Experimental Section

### 6.2.1 Chemicals

All the chemicals used in this study are described in Table E.1. The water used for the LLE experiments and analysis was deionized ultrapure water with resistance of 18.2 MΩ.cm. All the chemicals were used without further purification.

### 6.2.2 Tie-line measurements

The experimental LLE tie-lines of the investigated systems were measured with a jacketed equilibrium cell at constant temperature (313.15 K) and atmospheric pressure (0.1 MPa) using the same procedure reported in our previous studies [14-17]. The thermostatic water from a heating circulator bath (Tamson-instruments TC 6B, Holland) was used to maintain the temperature of the equilibrium cell with a standard uncertainty u($T$) of 0.02 K. Feed containing known quantities of HMF aqueous solutions were prepared and weighed on an analytical balance Mettler Toledo (MS 304S/01, Switzerland) with a precision of ± 0.0001 g. Subsequently, TBP extraction solvent was added into the mixtures with a mass ratio of 1:1 between TBP and aqueous solution. For the TBP-HMF-water system, the LLE tie-line experiments were carried out at two different temperatures, i.e. 298.15 and 313.15 K. Then, the LLE of TBP – HMF – water – ChCl-urea and TBP – HMF – water – ChCl-urea – NaCl in the absence and presence of fructose were also measured at 313.15 K with the same procedure. The ChCl-urea was prepared prior to the tie-line measurements by mixing and heating choline chloride and urea with a molar ratio of 1:2 at 80°C for 1 hour until a homogeneous liquid was formed [24]. In the LLE tie-line experiments, HMF feed concentration was varied with constant ChCl-urea, NaCl, and fructose concentrations. In general, the mixture in the equilibrium cell was stirred for 2.5 hours for the LLE of multicomponent system of TBP-HMF-water-ChCl-urea-NaCl-fructose, while for the ternary system of TBP-HMF-water 1.5 hours was adequate for the stirring time. Afterwards, the mixture was left at rest for 20 hours for low HMF concentrations and at least 22 hours for high HMF concentrations at operating temperature studied until the aqueous-organic phases were completely separated and reached equilibrium. Approximately 5 mL of sample was taken from each phase to analyse the concentrations of each component. The samples were placed in an oven at 40°C before further sample preparation for analytical measurements. Additionally, the LLE experiments for MIBK – HMF – water – [EMIM][$BF_4$] – NaCl – fructose and MIBK – HMF – water – ChCl-urea – NaCl – fructose with the addition of TBP in the organic phase and constant HMF concentration (10 wt%) were also measured at 313.15 K and atmospheric pressure (0.1 MPa). The TBP concentration in the organic phase was varied from 0 wt% to 100 wt% which also resulted in a decrease of the MIBK concentration from 100 wt% to 0 wt%. These experiments were carried out prior to the LLE experiments of the investigated systems in this study (using 100% TBP as an extraction solvent).

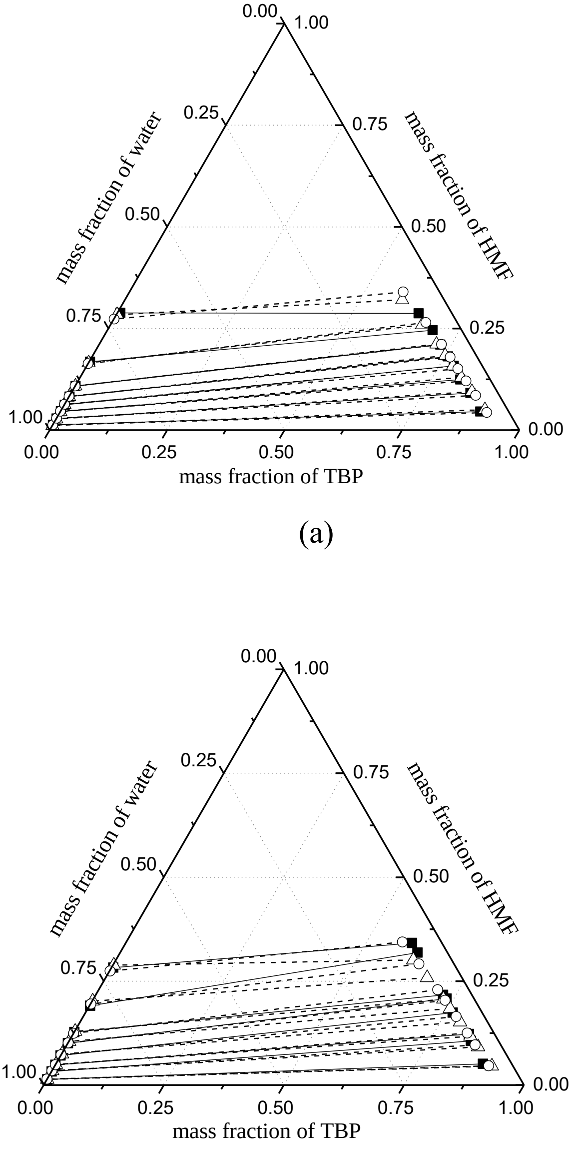
### 6.2.3 Analytical measurements

The equilibrium concentrations of HMF, MIBK, and fructose in the aqueous and organic phases were analysed using the same method in our previous study [17] by high-performance liquid chromatography (HPLC). The HPLC was equipped with a reversed phase column C18 Zorbax ODS at 42°C using UV/VIS (ultraviolet–visible) detector at a UV-wavelength of 278 nm for HMF and MIBK analyses. A mixture of water and methanol with volume ratio of 95:5 and 60:40 was prepared as eluent with flowrate of 1 and 0.6 mL/min. The peak area of HMF and MIBK were detected with peak maxima at 6.7 and 15.5 mins, respectively. While, for fructose concentration, the HPLC was equipped with Rezex RPM-Monosaccharide column at 75°C using RI (refractive index) detector. Water with a flowrate of 1.5 mL/min was used as eluent to detect the peak area of fructose with peak maxima at 6.3 min. Calibration curves were made prior to the analysis. The concentration of analyte in weight% was plotted versus the peak area of analyte. The DES concentrations in both phases were analysed based on our previous study method by IC (ion exchange chromatography) performed with Dionex DX-120 Ion Chromatograph using aqueous methane sulfonic acid as eluent [16]. Furthermore, ICP-OES (Inductively Coupled Plasma Optical Emission Spectroscopy, Spectro Arcos EOP) was also applied based on our previous studies method to analyse salt, IL, and TBP concentrations in the aqueous and organic phases using 3% of nitric acid ($HNO_3$) as diluent [14,15]. The water content in the organic phase was analysed using Karl Fischer titration (Metrohm 756 KF). Whereas, the water content in the aqueous phase was determined by subtracting the sum of the other mass fractions from a value of 1. The mass fractions of each component in both phases were averaged from three replicated samples. For the experimental LLE of the investigated systems, the standard uncertainties u($w_i$) of TBP, HMF, water, ChCl-urea, NaCl, and fructose were estimated to be 0.0012, 0.0010, 0.0009, 0.0004, 0.0009, and 0.0007 in mass fraction, respectively.

## 6.3 Results and discussion

### 6.3.1 LLE of TBP-HMF-water and TBP-HMF-water-ChCl-urea systems

The ternary and quaternary experimental LLE tie-lines for TBP-HMF-water and TBP-HMF-water-ChCl-urea systems are shown in Tables E.2-E.3 and Figures 6.1-6.2 (on DES-free basis), respectively. The LLE of TBP-HMF-water were measured at 298.15 and 313.15 K and atmospheric pressure (0.1 MPa) for the HMF feed concentrations in aqueous solution ranging from 5 wt% to 50 wt%. Furthermore, the LLE data of TBP-HMF-water-ChCl-urea system were measured at 313.15 K for the HMF feed concentrations ranging from 5 wt% to 40 wt% while keeping the ChCl-urea concentration constant. The ChCl-urea concentration was fixed at 10 wt% which generated better extraction performance compared to the higher ChCl-urea concentration reported in our previous study [16]. The effect of ChCl-urea on the LLE phase diagram is represented from the tie-lines slope that also indicates the extraction performance, as seen in Figures 6.1 and 6.2. From comparing Figure 6.1 (b) with Figure 6.2, it becomes evident that the tie-lines slope are more pronounced positive for the ternary LLE system in the absence of ChCl-urea, indicating more HMF molecules can be extracted from aqueous solution by TBP solvent. In this case, the presence of ChCl-urea in the HMF aqueous solution has a negative effect on the LLE phase diagram.



(a)

(b)

**Figure 6.1** Phase diagram of the experimental and calculated LLE tie-line data for TBP-HMF-water systems at (a) *T*= 298.15 and (b) *T*= 313.15 K and atmospheric pressure (0.1 MPa) using NRTL and UNIQUAC models; —■— : experimental data; --△--- : NRTL model; --○--- : UNIQUAC model.

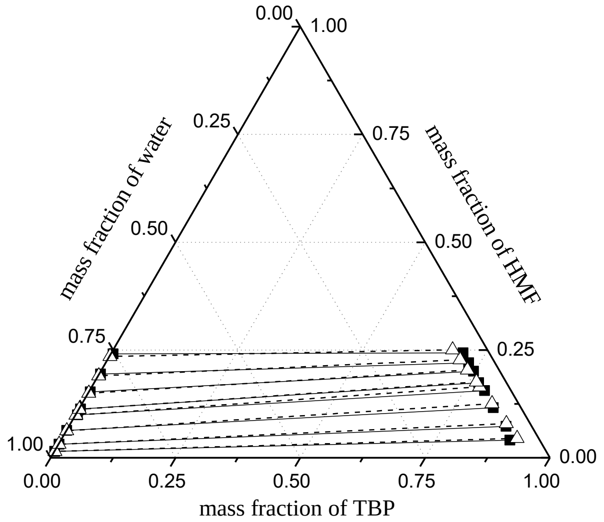
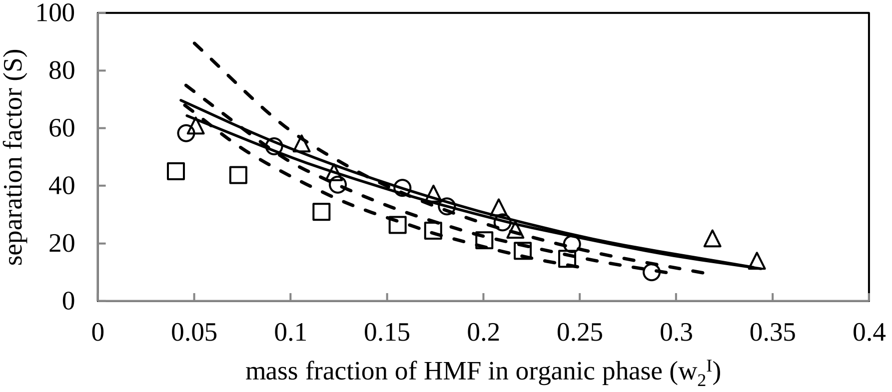


**Figure 6.2** Phase diagram of the experimental and calculated LLE tie-line data for TBP-HMF-water-ChCl-urea system on DES-free basis at *T*= 313.15 K and atmospheric pressure (0.1 MPa) using NRTL model; —■— : experimental data; - - -△- - - : NRTL model.

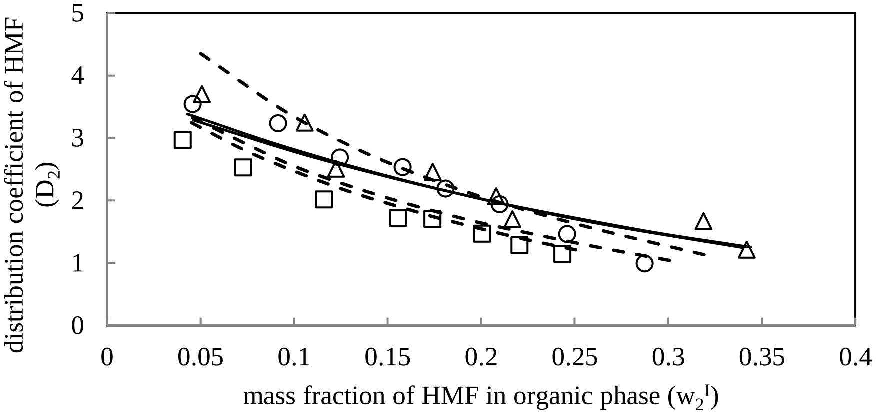
The effect of the addition of TBP in the LLE containing MIBK – HMF – water – [EMIM][BF$_4$] – NaCl – fructose and MIBK – HMF – water – ChCl-urea – NaCl – fructose at constant HMF feed concentration were also tested at 313.15 K and atmospheric pressure (0.1 MPa) prior to the LLE experiments of the investigated systems in this study, as seen in Figure E.1. The 10 wt% HMF in aqueous solution containing 10 wt% [EMIM][BF$_4$] (or ChCl-urea), 10 wt% NaCl, and 10 wt% fructose were prepared. Then, the TBP was added in the organic phase ranging from 0 wt% to 100 wt%, while the MIBK concentration was reduced from 100 wt% to 0 wt%. It is shown in Figure E.1 that the distribution coefficients of HMF can be enhanced from 1.46 to 3.55 and from 1.83 to 4.25 with the increase of TBP concentration from 0-100 wt% for the LLE systems with IL ([EMIM][$BF_4$]) and DES (ChCl-urea), respectively. While, the separation factors increase up to 1.2 times higher than the LLE systems in the absence of TBP (100 wt% MIBK). These results demonstrate that with the addition of TBP solvent up to 100 wt%, the distribution coefficients of HMF can be improved considerably while maintaining the separation factor at high values. Hence, for the LLE experiments of the investigated systems in this study, we used 100 wt% TBP as an extraction solvent and aqueous DES (ChCl-urea) which generates better extraction performance compared to that of aqueous IL ([EMIM][$BF_4$]).

The values of the separation factors and the HMF distribution coefficients for TBP-HMF-water and TBP-HMF-water-ChCl-urea systems are listed in Table E.4 and shown in Figure 6.3. It represents that the separation factors are much higher than 1 and the distribution coefficients of HMF are also higher than 1 over the whole range of HMF feed concentrations, demonstrating a favourable HMF extraction. The separation factor and HMF distribution coefficient can reach up to 60.7 and 3.70 for the ternary LLE system of TBP-HMF-water at 313.15 K, respectively. These results indicate that TBP is very good solvent for HMF extraction with high extraction performance. The TBP contents in the aqueous phase are very low ranging from 0.02-0.6 wt%, as seen in Tables E.2-E.3 for TBP-HMF-water and TBP-HMF-water-ChCl-urea systems, indicating low solubility of TBP in water. Additionally, the concentrations of ChCl-urea in the organic phase are also very low (almost zero) over the whole range of HMF feed concentrations, as listed in Table E.3. It illustrates that ChCl-urea has very low solubility in TBP solvent, which is good for extraction and solvent recovery processes.

Furthermore, from Table E.4 and Figure 6.3, it shows that the separation factors and HMF distribution coefficients for TBP-HMF-water at 313.15 K slightly increase compared to those for TBP-HMF-water at 298.15 K. Overall, there is no significant influence of operating temperature on the extraction performance in this system. For further LLE experiments in this study, 313.15 K was selected as a moderate operating temperature for the extraction of HMF by TBP solvent. Besides, Table E.4 and Figure 6.3 represent that the extraction performance for the LLE system in the presence of 10 wt% of ChCl-urea are lower than those for the LLE system in the absence of ChCl-urea at the same temperature (313.15 K). Both the separation factors and the distribution coefficients of HMF decrease around 1.3 times in the LLE of TBP-HMF-water-ChCl-urea system. The strong hydrogen bonding interactions between HMF and ChCl-urea cause the HMF extraction by TBP solvent more difficult in the presence of ChCl-urea. The ChCl-urea and TBP compete each other to make hydrogen bonding interaction with HMF, result in lower extraction performance. These results are in agreement with the previous study [16] which used other extraction solvents (MIBK and 2-pentanol).



(a)

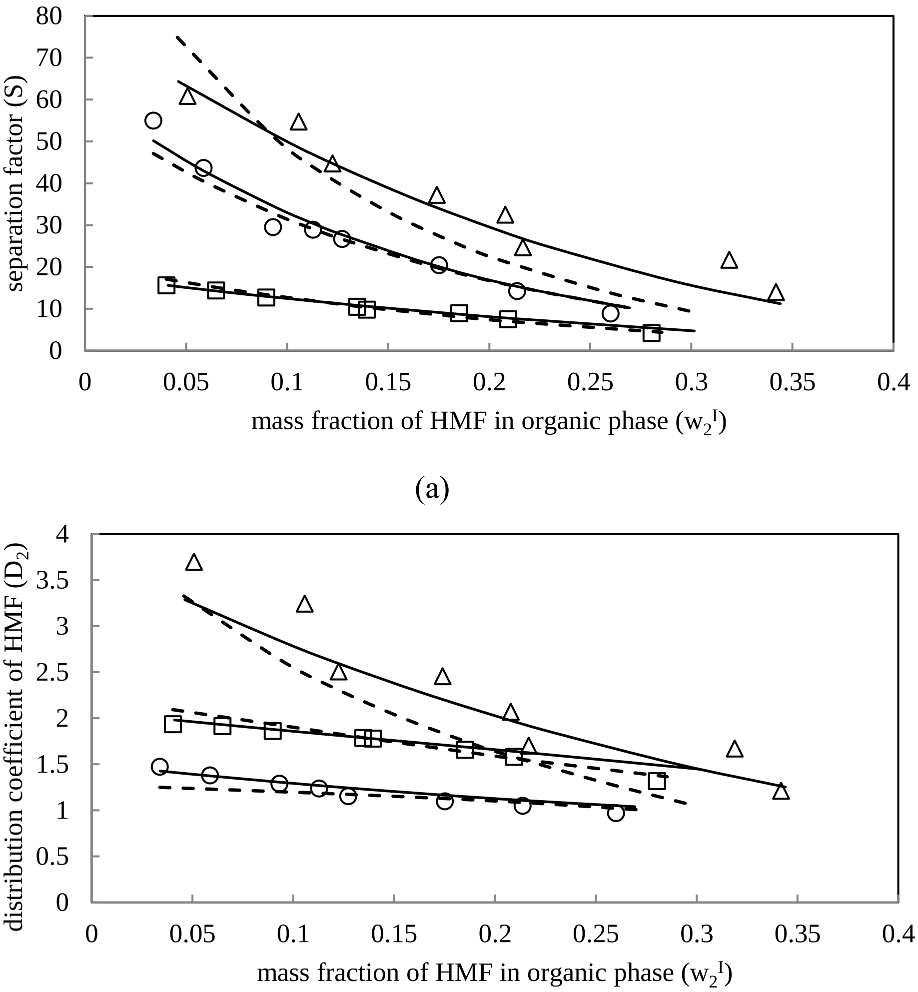


(b)

**Figure 6.3** (a) Separation factor (S) and (b) distribution coefficient of HMF ($D_2$) for TBP-HMF-water and TBP-HMF-water-ChCl-urea systems at *T*= 298.15 and 313.15 K and atmospheric pressure (0.1 MPa); ○ : TBP-HMF-water (298.15 K); △ : TBP-HMF-water (313.15 K); □ : TBP-HMF-water-ChCl-urea (313.15 K); − − − : NRTL model; ——— : UNIQUAC model.

The comparison of the solvent effect on the extraction performance of the organic solvent-HMF-water and organic solvent-HMF-water-ChCl-urea systems can also be observed from

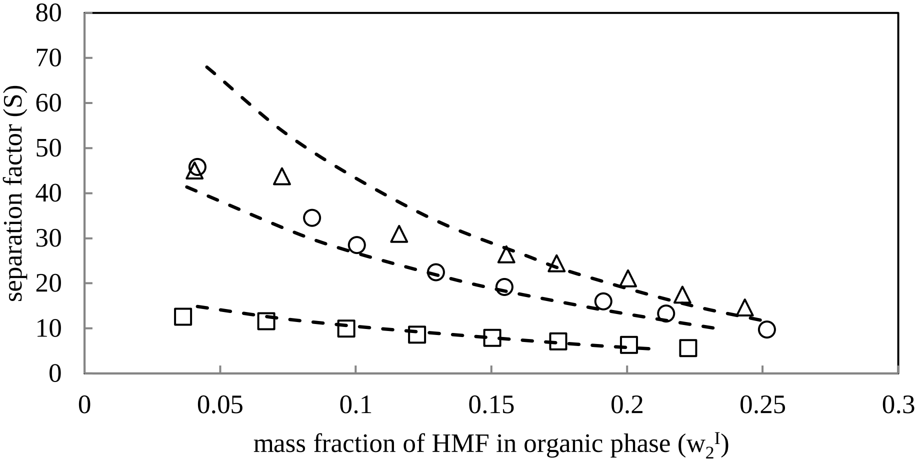
Figures 6.4 and 6.5. It represents in Figure 6.4 that the separation factors and HMF distribution coefficients of the ternary system using TBP extraction solvent are higher 1.3 and 1.9 times than those of the ternary systems using MIBK solvent [14], respectively. Whereas, the extraction performance of TBP-HMF-water can be enhanced around 3.4 and 1.3 times for the separation factors and distribution coefficients of HMF, respectively compared to those of 2-pentanol-HMF-water system [14]. Furthermore, from Figure 6.5 it also exhibits that the extraction performance using TBP solvent is superior to the other two solvents for the quaternary LLE systems in the presence of ChCl-urea. The quaternary LLE system with TBP increases both the separation factors and the distribution coefficients of HMF about 1.2 and 1.5 times relative to those with MIBK solvent [16]. Besides, the TBP can be more selectively extracted HMF with 3.1 times higher separation factors than 2-pentanol solvent [16] for the organic solvent-HMF-water-ChCl-urea systems. The HMF distribution coefficients also increase about 1.2 times higher than those for the 2-pentanol-HMF-water-ChCl-urea. The TBP is a very effective solvent for HMF with a good free energy of transfer of the solute (HMF) from water to organic solvent [18]. Nevertheless TBP has higher boiling point than MIBK and 2-pentanol. Therefore, the following product purification process to separate HMF from TBP requires back-extraction method, instead of distillation.



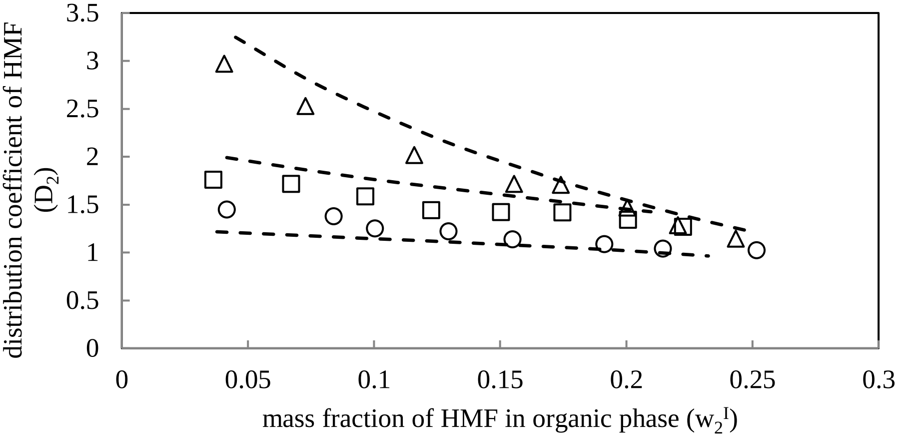
(a)

(b)

**Figure 6.4** (a) Separation factor (S) and (b) distribution coefficient of HMF ($D_2$) for organic solvent-HMF-water systems at *T*= 313.15 K and atmospheric pressure (0.1 MPa); △ : TBP-HMF-water; ○ : MIBK-HMF-water [14]; □ : 2-pentanol-HMF-water [14]; − − − : NRTL model; ——— : UNIQUAC model.



(a)



(b)

**Figure 6.5** (a) Separation factor (S) and (b) distribution coefficient of HMF ($D_2$) for organic solvent-HMF-water-ChCl-urea systems at *T*= 313.15 K and atmospheric pressure (0.1 MPa); △ : TBP-HMF-water-ChCl-urea; ○ : MIBK – HMF – water – ChCl-urea [16]; □ : 2-pentanol-HMF-water-ChCl-urea [16]; – – – : NRTL model.

### 6.3.2 LLE of TBP-HMF-water-ChCl-urea-NaCl in the absence and presence of fructose

The experimental LLE tie-lines for TBP – HMF – water – ChCl-urea – NaCl and TBP – HMF – water – ChCl-urea – NaCl – fructose systems were investigated at 313.15 K and atmospheric pressure (0.1 MPa), as seen in Tables E.5-E.6 and Figures 6.6-6.7 (on DES, salt, and sugar free basis). The HMF feed concentrations differed from 5 wt% to 40 wt% for the LLE of TBP-HMF-water-ChCl-urea-NaCl system with constant amount of ChCl-urea and NaCl. The NaCl feed concentration was fixed at 10 wt% which is near the maximum solubility of NaCl in a 40 wt% HMF aqueous solution [14]. In addition, for the LLE of TBP – HMF – water – ChCl-urea – NaCl – fructose, the HMF feed concentrations were varied from 5 wt% to 35 wt% and kept the ChCl-urea, NaCl, and fructose at constant concentrations. In the HMF production process, the sugar (fructose) conversion to HMF is not always 100%, therefore in the present study we also investigated the LLE system containing HMF in the presence of fructose. A small amount of fructose present in the aqueous solution indicates the unreacted fructose. In this study, the concentration of fructose was selected at 10 wt% which was adequate for the measurement, as the effect of fructose will be more difficult to be observed at lower concentration.

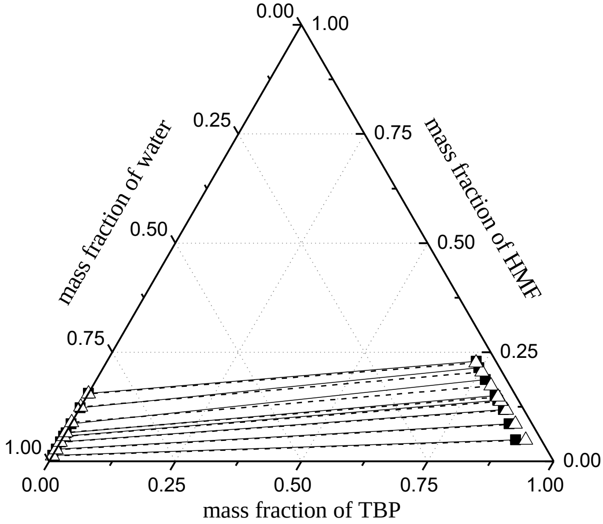


**Figure 6.6** Phase diagram of the experimental and calculated LLE tie-line data for TBP-HMF-water-ChCl-urea-NaCl system on DES and salt free basis at *T*= 313.15 K and atmospheric pressure (0.1 MPa) using NRTL model; —■—: experimental data; - - △- - - : NRTL model.

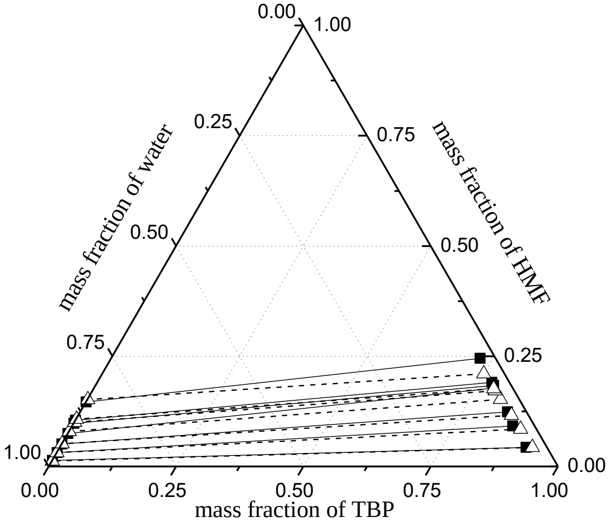
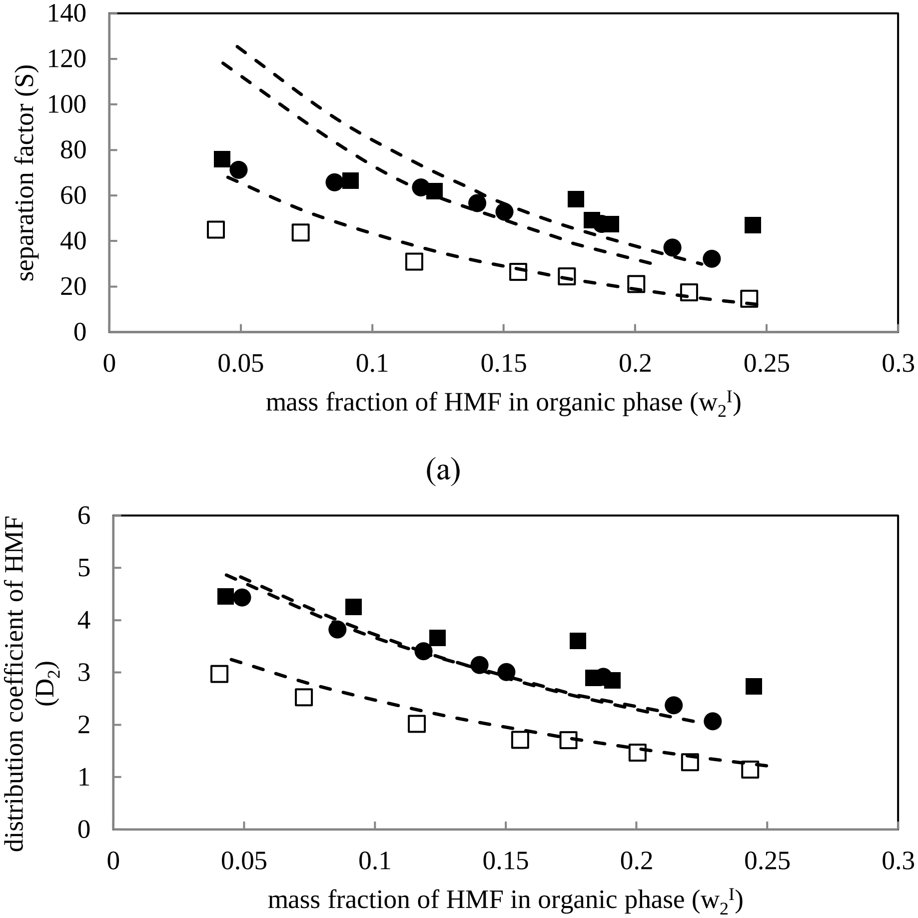


**Figure 6.7** Phase diagram of the experimental and calculated LLE tie-line data for TBP-HMF-water-ChCl-urea-NaCl-fructose system on DES, salt, and sugar free basis at *T*= 313.15 K and atmospheric pressure (0.1 MPa) using NRTL model; —■— : experimental data; - - -△- - - : NRTL model.

The comparison of the LLE phase diagram for the systems containing TBP-HMF-water-ChCl-urea in the absence and presence of NaCl are represented in Figures 6.2 and 6.6. It exhibits that the tie-line slopes increase with the addition of NaCl in the aqueous ChCl-urea solution. The steeper tie-line slopes demonstrate the increase of HMF distribution coefficient by the salting-out effect of NaCl. The interaction between ions from salt (NaCl) and water molecules induce strongly the HMF separation from the aqueous solution into the TBP solvent phase. This salting out effect significantly improves the extraction performance, as compared in Figure 6.8 and Tables E.4 and E.7 for the TBP-HMF-water-ChCl-urea and TBP-HMF-water-ChCl-urea-NaCl systems, respectively. It can be observed that the separation factors and

HMF distribution coefficients of the LLE system with NaCl are higher than those of the LLE system without NaCl over the whole range of HMF feed concentrations. By introducing NaCl into the aqueous ChCl-urea solution, the separation factors and the distribution coefficients of HMF can be enhanced around 2.0 and 1.7 times, respectively. The values of HMF distribution coefficient in the presence of NaCl can also reach up to 4.43 and improve above 2 over the whole range of HMF feed concentrations. Besides, the TBP concentrations in the aqueous phase decrease gradually from 0.09-0.4 wt% (Table E.3) to 0.01-0.08 wt% (Table E.5). The low extraction solvent content in the aqueous phase is beneficial for HMF extraction as the potential solvent losses and the energy consumption for solvent recovery can be reduced as well.

The extraction performance of the TBP – HMF – water – ChCl-urea – NaCl and TBP – HMF – water – ChCl-urea – NaCl – fructose systems is compared in Figure 6.8 and listed in Table E.7. It demonstrates that fructose has minimal effect on the extraction performance. The separation factors for the LLE of TBP-HMF-water-ChCl-urea-NaCl in the absence and presence of fructose are comparable. While the distribution coefficients of HMF are slightly higher for the LLE system with fructose. Hence, it can be inferred that high extraction performance can be attained in both LLE systems using TBP solvent in the absence and presence of fructose. Furthermore, it is observed in Tables E.5 and E.6 that the NaCl and fructose concentrations in the TBP solvent phase are very low which are almost zero over the whole range of HMF feed concentrations. The low amount of NaCl and fructose in the organic phase generate good extraction and solvent recovery processes.

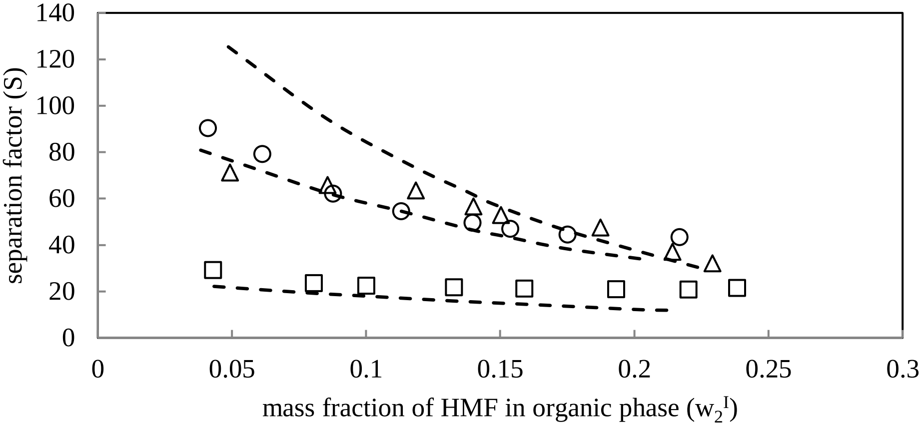


(a)

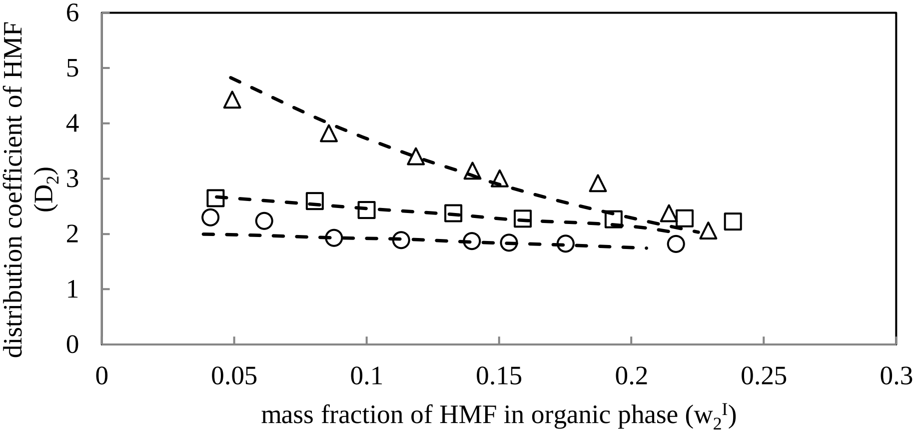
(b)

**Figure 6.8** (a) Separation factor (S) and (b) distribution coefficient of HMF ($D_2$) for TBP – HMF – water - ChCl-urea and TBP – HMF – water – ChCl-urea – NaCl in the absence and presence of fructose at *T*= 313.15 K and atmospheric pressure (0.1 MPa); □ : TBP – HMF – water – ChCl-urea; ● : TBP – HMF – water – ChCl-urea – NaCl; ■ : TBP – HMF – water – ChCl-urea – NaCl – fructose; – – – : NRTL model.

Furthermore, the ability of solvent in the extraction of HMF from water-ChCl-urea-NaCl solution in the absence and presence of fructose are also compared in Figures 6.9 and 6.10. In Figure 6.9, it can be seen that the separation factors of TBP-HMF-water-ChCl-urea-NaCl are 2.3 times higher than those of 2-pentanol-HMF-water-ChCl-urea-NaCl [16]. However, there is no significant effect on the separation factors between TBP and MIBK solvents. Whereas, the HMF distribution coefficients with TBP solvent can be enhanced around 1.6 and 1.3 times compared to those with MIBK and 2-pentanol [16], respectively. In addition, it exhibits that the HMF extraction from water-ChCl-urea-NaCl solution in the presence of fructose with TBP solvent generates around 1.3 and 1.9 times higher separation factors and HMF distribution coefficients than those with MIBK solvent [17], respectively as shown in Figure 6.10. Overall, TBP is more selective as extraction solvent and also superior in terms of HMF distribution coefficient than the other two solvents (MIBK and 2-pentanol).

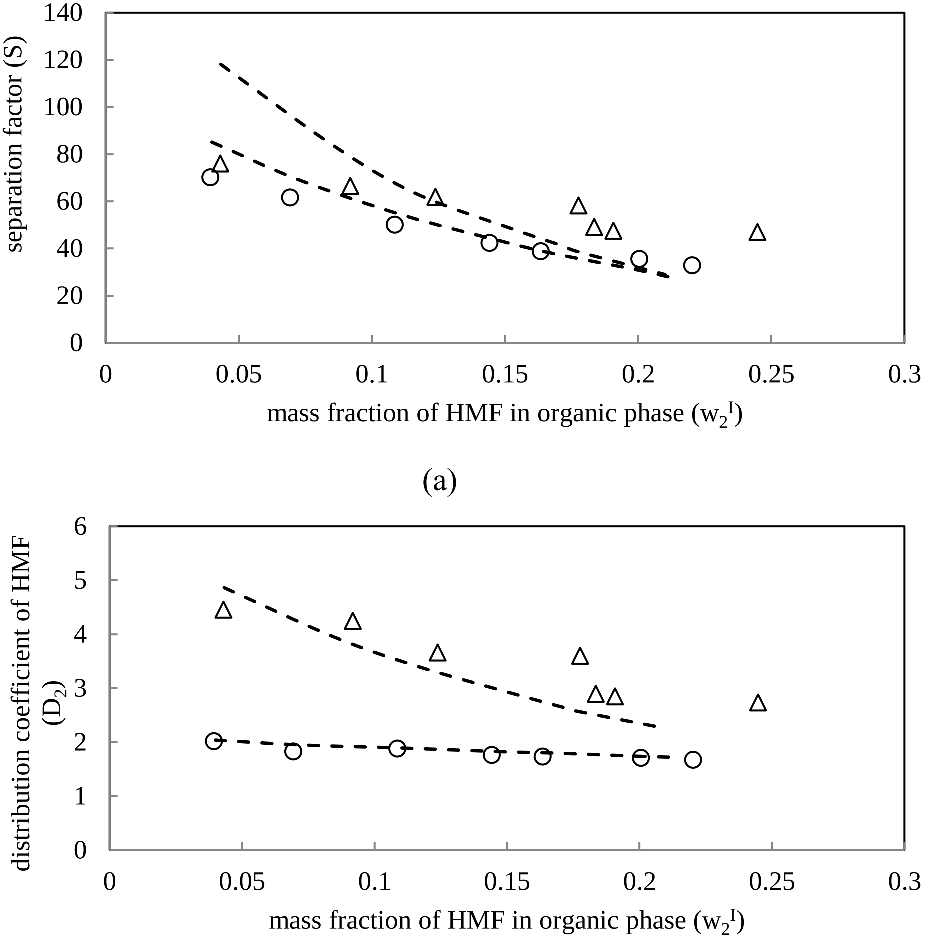


(a)



(b)

**Figure 6.9** (a) Separation factor (S) and (b) distribution coefficient of HMF ($D_2$) for organic solvent-HMF-water-ChCl-urea-NaCl systems at $T$= 313.15 K and atmospheric pressure (0.1 MPa); △ : TBP – HMF – water – ChCl-urea – NaCl; ○ : MIBK – HMF – water - ChCl-urea – NaCl [16]; □ : 2-pentanol – HMF – water – ChCl-urea – NaCl [16]; – – – : NRTL model.



(a)

(b)

**Figure 6.10** (a) Separation factor (S) and (b) distribution coefficient of HMF ($D_2$) for organic solvent-HMF-water-ChCl-urea-NaCl-fructose systems at *T*= 313.15 K and atmospheric pressure (0.1 MPa); △ : TBP-HMF-water-ChCl-urea-NaCl-fructose; ○ : MIBK – HMF – water – ChCl-urea – NaCl – fructose [17]; – – – : NRTL model.

### 6.3.3 Correlation of the experimental LLE tie-line data

The experimental LLE tie-line data for the ternary system of TBP-HMF-water at 298.15 and 313.15 K were correlated using the NRTL (Non-Random Two-Liquid) [30] and UNIQUAC (Universal

Quasi-Chemical) [31] activity coefficient models. These models are able to calculate the multicomponent LLE phase compositions only using the constituent binary parameters. The LLE tie-line data of MIBK-HMF-water at 298.15 K [29] and 313.15 K [14] were also correlated with these models. The binary interaction parameters $b_{ij}$ and $b_{ji}$ among MIBK, HMF, water were regressed, then the $b_{ij}$ and $b_{ji}$ parameters between HMF and water obtained from the regression results of the MIBK-HMF-water were fixed in the correlation of the TBP-HMF-water system. While, the $b_{ij}$ and $b_{ji}$ were regressed in the LLE of TBP-HMF-water for the interactions of TBP with HMF and water. The nonrandomness parameters ($\alpha_{ij}$) among MIBK, TBP, HMF, and water were set at 0.2. The determined parameters of the NRTL and UNIQUAC models for these systems are listed in Table E.8. The van der Waals volume ($r_i$) and surface area ($q_i$) parameters of the UNIQUAC model were estimated by Bondi method [32], as shown in Table E.9.

Furthermore, the quaternary LLE of MIBK-HMF-water-ChCl-urea [16] and TBP-HMF-water-ChCl-urea were also correlated using the NRTL model. The binary interaction parameters $b_{ij}$ and $b_{ji}$ among organic solvent (MIBK or TBP), HMF, and water were taken from the regression results in the ternary LLE systems. While the $b_{ij}$ and $b_{ji}$ for the interactions of ChCl-urea with MIBK, HMF, and water were regressed. Afterwards, the $b_{ij}$ and $b_{ji}$ for the interactions of ChCl-urea with HMF and water were fixed in the LLE system containing ChCl-urea using TBP solvent. The $b_{ij}$ and $b_{ji}$ were regressed only for the interactions of ChCl-urea with TBP. The $\alpha_{ij}$ values were also fixed at 0.2 for all components interactions with ChCl-urea. The NRTL parameters obtained for these quaternary systems can be seen in Table E.10.

In the LLE systems containing ChCl-urea and NaCl using MIBK [16] and TBP solvents, the $b_{ij}$, $b_{ji}$, and $\alpha_{ij}$ parameters for the interactions of NaCl with MIBK, TBP, HMF, water, and ChCl-urea were regressed together, as listed in Table E.11. In this case, NaCl was considered as one molecular species. Whereas, the $b_{ij}$ and $b_{ji}$ among organic solvent (MIBK or TBP), HMF, water, and ChCl-urea were fixed from the determined parameters in the ternary and quaternary LLE systems. In addition, for the experimental LLE of MIBK – HMF – water – ChCl-urea – NaCl – fructose [17] and TBP – HMF – water – ChCl-urea – NaCl – fructose were also correlated using NRTL model. The $b_{ij}$ and $b_{ji}$ parameters among MIBK or TBP, HMF, water, ChCl-urea, and NaCl were taken from the regressed parameters in the previous correlations (Table E.8 and Tables E.10-E.11). The $\alpha_{ij}$ values for the interactions with NaCl were also fixed from the correlation results in the LLE systems with the presence of ChCl-urea and NaCl (Table E.11). Whilst, the $b_{ij}$ and $b_{ji}$ for the interactions of fructose with other components studied and $\alpha_{ij}$ of fructose with NaCl were regressed in these correlations, as listed in Table E.12. In the NRTL model, the $\alpha_{ij}$ plays an important role in obtaining a good correlation of the LLE systems with the presence of salt [33,34]. The NRTL model provides more flexibility enabling negative values for the $\alpha_{ij}$ which leave any supposed physical meaning.

The experimental and calculated LLE tie-line data with the NRTL and UNIQUAC models for the investigated systems in this study are compared in Figures 6.1-6.2 and Figures 6.6-6.7. The closed and open symbols denote the experimental and calculated tie-lines, respectively. The correlations show good agreement with the experimental LLE data with the root mean square deviations (RMSD) presented in Table E.8

and Tables E.10-E.12. Additionally, it can be seen in Figures 6.3 and 6.8 that the correlation models also give good description of separation factor and distribution coefficient of HMF, except at some points, it shows larger deviation which is also visible from the calculated tie-lines in Figures 6.1-6.2 and Figures 6.6-6.7. Nevertheless, overall the NRTL and UNIQUAC models correlate the experimental LLE data of the investigated systems in this study well.

## 6.4 Conclusions

The LLE data of systems containing HMF in the aqueous solution using TBP as an extraction solvent were investigated at constant temperature (313.15 K) and atmospheric pressure (0.1 MPa). The separation factor and the distribution coefficient of HMF were determined from the LLE data to evaluate the extraction performance. The results in the present study indicated that the tie-lines slope decreased with the presence of ChCl-urea in the TBP-HMF-water system, demonstrating lower performance of extraction. The separation factors and HMF distribution coefficients of the TBP-HMF-water-ChCl-urea system were about 1.3 times lower than those of the system without ChCl-urea, respectively. However, the introduction of NaCl enhanced the extraction performance about 2.0 times for the separation factors and 1.7 times for the distribution coefficients of HMF compared to the one without, enabling compensation of the ChCl-urea effect. While, the presence of fructose in the aqueous solution had minimal effect on the extraction performance. In general, it can be concluded that TBP is more selective as extraction solvent and also superior in terms of HMF distribution coefficient compared to MIBK and 2-pentanol. By using TBP solvent, it showed a very good extraction performance of HMF from aqueous ChCl-urea solution in the presence of NaCl and fructose. Furthermore, the thermodynamic models correlated well the experimental LLE data of the investigated systems in this study.

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# Chapter 7

# Conclusions and Recommendations

In this study, liquid-liquid equilibrium (LLE) data for multicomponent systems containing 5-hydroxymethylfurfural (HMF) in aqueous solution were measured at constant temperature (313.15 K) and atmospheric pressure (0.1 MPa) using three different extraction solvents, i.e. methyl isobutyl ketone (MIBK), 2-pentanol, and tributyl phosphate (TBP). We also added IL [EMIM][$BF_4$] (1-ethyl-3-methylimidazolium tetrafluoroborate) or DES ChCl-urea (choline chloride-urea) in the aqueous solution. The effect of the addition of sugar (fructose) and salt in the variety of cation ($Na^+$, $K^+$) and anion ($Cl^-$, $SO_4^{2-}$) were also investigated. The experimental LLE data of the investigated systems were correlated well using thermodynamics models. The NRTL and UNIQUAC models were applied for correlating the ternary experimental LLE data, whereas the experimental LLE data containing salt, IL, DES, and sugar were correlated using the NRTL model. The thermodynamic data, such as LLE data and partitioning of HMF into organic phase are required as basis for a rational design and optimal HMF extraction operation.

The results in this study indicated that the HMF distribution coefficient of the LLE systems using 2-pentanol is up to 1.4 times higher than that of the LLE systems using MIBK. Besides, MIBK has a 2-3 times higher separation factor than 2-pentanol. While, TBP is more selective as extraction solvent and also superior in terms of HMF distribution coefficient than MIBK and 2-pentanol. The order of salting-out strength was NaCl > $Na_2SO_4$ > KCl > $K_2SO_4$ for the LLE of organic solvent (MIBK or 2-pentanol)-HMF-water-salt systems. The addition of NaCl in the HMF aqueous solution showed better extraction performance compared to the other salts studied. Furthermore, the presence of IL [EMIM][$BF_4$] and DES (ChCl-urea) caused negative effect on the LLE phase diagram, separation factor, and HMF distribution coefficient. However, DES (ChCl-urea) reduced the separation factor and the distribution coefficient of HMF less than IL [EMIM][$BF_4$]. The addition of salt (NaCl) increased the extraction performance, enabling compensation of the IL and DES effects. The presence of salt can enhance the HMF distribution coefficient as well as the separation factor up to 2-4 times for all the investigated systems studied using three different organic solvents and also in the presence of IL or DES. Whereas, the presence of fructose in the aqueous solution had minimal effect on the extraction performance. In general, it can be inferred that by taking the advantage of IL/DES as stabilizing agent, the combination of aqueous IL/DES with salt (NaCl) can be used to improve the extraction performance in the HMF extraction process.

Although knowledge was developed through this study, there is still room for improvement and for new findings. It is advisable for the further studies to investigate the mass transfer of HMF at the aqueous-organic interface in the presence of IL or DES, salt, and fructose using several extraction solvents. These in order to improve mass transfer of HMF more efficiently, hence the HMF can be extracted more optimally as well. HMF is very useful as intermediate not only for the production of the next generation of plant-based polyester building block, but also for the production of potential biofuel candidates and other various chemical products. Thus, research on the HMF production needs to be developed continuously in various engineering studies. The efficient and favorable approach which can achieve high yield of HMF is still needed to be developed, especially the implementation in the industrial scale.

The simulation work can also be conducted for biphasic HMF production process. The LLE data obtained in this research provide the basis for the further application of the HMF production process design. Hence, the conceptual design for the production of HMF in biphasic systems with fructose as the starting reactant using three different extraction solvents studied (MIBK, 2-pentanol, or TBP) in the presence of IL or DES and salt can be further developed in several process conditions and designs to achieve the most efficient and economic design. The results in this study showed that the TBP solvent can give high extraction performance for HMF with the separation factors up to 75 and the distribution coefficients of HMF reaching higher than 4 in the presence of DES, salt, and fructose. TBP is a very effective extraction solvent for HMF and also has low solubility in water. The extraction performance using TBP solvent is superior compared to the other two solvents (MIBK and 2-pentanol). However, TBP has high boiling point which is the drawback of this solvent, therefore it is more difficult to separate HMF in the TBP phase. While, HMF is relatively easier to be separated from MIBK or 2-pentanol phase by simple distillation which is volatile polar compound. Hence the separation of HMF from TBP should be conducted by back-extraction instead of distillation. These processes can be further evaluated to address the best one.

# APPENDIX

## Appendix A

**Table A.1** List of chemicals used in this study

| Name | Chemical formula | Source | Purity (wt%) |
|---|---|---|---|
| Methyl isobutyl ketone | $C_6H_{12}O$ | Thermo Fisher Scientific (France) | ≥99% |
| 2-Pentanol | $C_5H_{12}O$ | Thermo Fisher Scientific (Germany) | 99% |
| 5-hydroxymethylfurfural | $C_6H_6O_3$ | Nanjing Zelang Medical Technology (China) | 99% |
| Butylated hydroxyanisole | $C_{11}H_{16}O_2$ | Sigma-Aldrich (India) | 99% |
| Dimethylformamide | $C_3H_7NO$ | Sigma-Aldrich (Germany) | 99.8% |
| Sodium chloride | NaCl | Sigma-Aldrich (USA) | ≥99% |
| Potassium chloride | KCl | Sigma-Aldrich (USA) | ≥99% |
| Sodium sulfate | $Na_2SO_4$ | Sigma-Aldrich (India) | ≥99% |
| Potassium sulfate | $K_2SO_4$ | Sigma-Aldrich (Germany) | ≥99% |
| Nitric acid | $HNO_3$ | Thermo Fisher Scientific (USA) | 70% |
| Water | $H_2O$ | Available in our Lab. | Deionized ultrapure water |

**Table A.2** Experimental LLE tie-line data of the MIBK (1)-HMF (2)-water (3) system in mass fraction ($w_i$) at temperature $T$= 313.15 K and atmospheric pressure[a]

| Organic Phase | | | Aqueous Phase | | |
|---|---|---|---|---|---|
| $w_1^{I}$ | $w_2^{I}$ | $w_3^{I}$ | $w_1^{II}$ | $w_2^{II}$ | $w_3^{II}$ |
| 0.9403 | 0.0339 | 0.0258 | 0.0135 | 0.0230 | 0.9636 |
| 0.9115 | 0.0587 | 0.0298 | 0.0142 | 0.0426 | 0.9432 |
| 0.8670 | 0.0931 | 0.0398 | 0.0157 | 0.0722 | 0.9121 |
| 0.8491 | 0.1128 | 0.0382 | 0.0166 | 0.0911 | 0.8923 |
| 0.8351 | 0.1272 | 0.0377 | 0.0194 | 0.1102 | 0.8705 |
| 0.7809 | 0.1752 | 0.0439 | 0.0233 | 0.1596 | 0.8171 |

| Organic Phase | | | Aqueous Phase | | |
|---|---|---|---|---|---|
| $w_1^{I}$ | $w_2^{I}$ | $w_3^{I}$ | $w_1^{II}$ | $w_2^{II}$ | $w_3^{II}$ |
| 0.7297 | 0.2138 | 0.0566 | 0.0312 | 0.2037 | 0.7650 |
| 0.6633 | 0.2601 | 0.0766 | 0.0313 | 0.2688 | 0.6999 |

[a] Standard uncertainties are $u(T)$ = 0.02 K and $u(w_i)$ = 0.0006 (MIBK), 0.0008 (HMF), and 0.0006 (water)

**Table A.3** Experimental LLE tie-line data of the 2-Pentanol (1)-HMF (2)-water (3) system in mass fraction ($w_i$) at temperature $T$= 313.15 K and atmospheric pressure[a]

| Organic Phase | | | Aqueous Phase | | |
|---|---|---|---|---|---|
| $w_1^{I}$ | $w_2^{I}$ | $w_3^{I}$ | $w_1^{II}$ | $w_2^{II}$ | $w_3^{II}$ |
| 0.8419 | 0.0403 | 0.1178 | 0.0306 | 0.0208 | 0.9486 |
| 0.8110 | 0.0649 | 0.1242 | 0.0339 | 0.0339 | 0.9323 |
| 0.7757 | 0.0898 | 0.1345 | 0.0352 | 0.0482 | 0.9165 |
| 0.7144 | 0.1347 | 0.1510 | 0.0407 | 0.0754 | 0.8839 |
| 0.7003 | 0.1394 | 0.1603 | 0.0425 | 0.0783 | 0.8791 |
| 0.6589 | 0.1852 | 0.1559 | 0.0437 | 0.1117 | 0.8446 |
| 0.6179 | 0.2095 | 0.1726 | 0.0490 | 0.1326 | 0.8184 |
| 0.4850 | 0.2803 | 0.2347 | 0.0337 | 0.2127 | 0.7536 |

[a] Standard uncertainties are $u(T)$ = 0.02 K and $u(w_i)$ = 0.0007 (2-Pentanol), 0.0008 (HMF), and 0.0006 (water)

**Table A.4** NRTL and UNIQUAC parameters for the ternary system organic solvent (1)-HMF (2)-water (3) at temperature $T$= 313.15 K

| System | Model | *i-j* | $\alpha_{ij}$ | $b_{ij}{}^{a}(K)$ | $b_{ji}{}^{a}(K)$ | RMSD (%) |
|---|---|---|---|---|---|---|
| MIBK-HMF-water | NRTL | 1-2 | 0.20 | 483.26 | -738.00 | 0.4188 |
| | | 1-3 | 0.20 | 199.41 | 1722.53 | |
| | | 2-3 | 0.20 | -379.83 | 310.86 | |
| MIBK-HMF-water | UNIQUAC | 1-2 | - | -72.93 | 165.13 | 0.4760 |
| | | 1-3 | - | -416.64 | -127.71 | |
| | | 2-3 | - | -136.38 | 326.25 | |
| 2-pentanol-HMF-water | NRTL | 1-2 | 0.20 | 911.98 | -754.74 | 0.7610 |
| | | 1-3 | 0.20 | -205.68 | 1777.28 | |
| | | 2-3 | 0.20 | -379.83 | 310.86 | |

| System | Model | $i$-$j$ | $\alpha_{ij}$ | $b_{ij}{}^{a}(K)$ | $b_{ji}{}^{a}(K)$ | RMSD (%) |
|---|---|---|---|---|---|---|
| 2-pentanol-HMF-water | UNIQUAC | 1-2 | - | -14.13 | 92.99 | 0.7482 |
| | | 1-3 | - | -79.60 | -188.64 | |
| | | 2-3 | - | -136.38 | 326.25 | |

[a] $\tau_{ij} = \frac{b_{ij}}{T}$ for NRTL; $\tau_{ij} = exp\left(\frac{b_{ij}}{T}\right)$ for UNIQUAC

**Table A.5** Van der Waals volume and surface area parameters for the UNIQUAC model

| Parameter | HMF | MIBK | 2-Pentanol | Water |
|---|---|---|---|---|
| $r_i$ | 4.2235 | 4.5959 | 4.2835 | 0.9200 |
| $q_i$ | 3.3280 | 3.9520 | 3.5556 | 1.4000 |

**Table A.6** Separation factor (S) and distribution coefficients ($D_i$) for the organic solvent (1)-HMF (2)-water (3) systems at temperature $T$= 313.15 K and atmospheric pressure

| MIBK (1)-HMF (2)-water (3) | | | | 2-pentanol (1)-HMF (2)-water (3) | | | |
|---|---|---|---|---|---|---|---|
| $w_2{}^{II}$ | $D_2$ | $D_3$ | S | $w_2{}^{II}$ | $D_2$ | $D_3$ | S |
| 0.0230 | 1.47 | 0.027 | 54.4 | 0.0208 | 1.94 | 0.124 | 15.6 |
| 0.0426 | 1.38 | 0.032 | 43.1 | 0.0339 | 1.92 | 0.133 | 14.4 |
| 0.0722 | 1.29 | 0.044 | 29.3 | 0.0482 | 1.86 | 0.147 | 12.7 |
| 0.0911 | 1.24 | 0.043 | 28.8 | 0.0754 | 1.79 | 0.171 | 10.5 |
| 0.1102 | 1.15 | 0.043 | 26.7 | 0.0783 | 1.78 | 0.182 | 9.8 |
| 0.1596 | 1.10 | 0.054 | 20.4 | 0.1117 | 1.66 | 0.185 | 9.0 |
| 0.2037 | 1.05 | 0.074 | 14.2 | 0.1326 | 1.58 | 0.211 | 7.5 |
| 0.2688 | 0.97 | 0.110 | 8.8 | 0.2127 | 1.32 | 0.311 | 4.2 |

**Table A.7** Experimental LLE tie-line data of the MIBK (1)-HMF (2)-water (3)-salt (4) systems in mass fraction ($w_i$) at temperature $T$= 313.15 K and atmospheric pressure[a]

| Salt | Organic Phase | | | | Aqueous Phase | | | |
|---|---|---|---|---|---|---|---|---|
| | $w_1{}^{I}$ | $w_2{}^{I}$ | $w_3{}^{I}$ | $w_4{}^{I}$ | $w_1{}^{II}$ | $w_2{}^{II}$ | $w_3{}^{II}$ | $w_4{}^{II}$ |
| NaCl | 0.9405 | 0.0361 | 0.0231 | 0.0002 | 0.0052 | 0.0161 | 0.9016 | 0.0771 |
| | 0.8857 | 0.0854 | 0.0287 | 0.0001 | 0.0041 | 0.0415 | 0.8851 | 0.0693 |

| Salt | Organic Phase | | | | Aqueous Phase | | | |
|---|---|---|---|---|---|---|---|---|
| | $w_1^{I}$ | $w_2^{I}$ | $w_3^{I}$ | $w_4^{I}$ | $w_1^{II}$ | $w_2^{II}$ | $w_3^{II}$ | $w_4^{II}$ |
| | 0.8705 | 0.1011 | 0.0283 | 0.0001 | 0.0034 | 0.0505 | 0.8728 | 0.0732 |
| | 0.8418 | 0.1279 | 0.0299 | 0.0003 | 0.0040 | 0.0584 | 0.8277 | 0.1099 |
| | 0.7668 | 0.1939 | 0.0388 | 0.0005 | 0.0040 | 0.0970 | 0.7953 | 0.1037 |
| | 0.7687 | 0.1956 | 0.0353 | 0.0004 | 0.0039 | 0.0876 | 0.7915 | 0.1170 |
| | 0.7176 | 0.2407 | 0.0414 | 0.0002 | 0.0036 | 0.1083 | 0.7717 | 0.1164 |
| | 0.6538 | 0.2955 | 0.0497 | 0.0010 | 0.0038 | 0.1262 | 0.7376 | 0.1323 |
| KCl | 0.9379 | 0.0386 | 0.0233 | 0.0002 | 0.0062 | 0.0190 | 0.8942 | 0.0805 |
| | 0.9018 | 0.0709 | 0.0272 | 0.0001 | 0.0033 | 0.0466 | 0.8660 | 0.0842 |
| | 0.8482 | 0.1201 | 0.0317 | 0.0001 | 0.0048 | 0.0681 | 0.8318 | 0.0953 |
| | 0.8292 | 0.1380 | 0.0324 | 0.0005 | 0.0060 | 0.0779 | 0.8240 | 0.0921 |
| | 0.7841 | 0.1806 | 0.0350 | 0.0003 | 0.0036 | 0.1210 | 0.7791 | 0.0963 |
| | 0.7565 | 0.2054 | 0.0378 | 0.0003 | 0.0027 | 0.1245 | 0.7661 | 0.1067 |
| | 0.7183 | 0.2351 | 0.0462 | 0.0003 | 0.0049 | 0.1324 | 0.7455 | 0.1172 |
| | 0.6388 | 0.3169 | 0.0440 | 0.0003 | 0.0018 | 0.2152 | 0.6691 | 0.1140 |
| $Na_2SO_4$ | 0.9139 | 0.0593 | 0.0267 | 0.0002 | 0.0009 | 0.0252 | 0.9512 | 0.0227 |
| | 0.8856 | 0.0848 | 0.0294 | 0.0002 | 0.0027 | 0.0388 | 0.9369 | 0.0216 |
| | 0.8582 | 0.1097 | 0.0318 | 0.0003 | 0.0079 | 0.0636 | 0.8989 | 0.0296 |
| | 0.8386 | 0.1239 | 0.0374 | 0.0001 | 0.0051 | 0.0752 | 0.8904 | 0.0293 |
| | 0.8049 | 0.1534 | 0.0416 | 0.0001 | 0.0095 | 0.0870 | 0.8714 | 0.0321 |
| | 0.7387 | 0.2115 | 0.0497 | 0.0001 | 0.0071 | 0.1154 | 0.8521 | 0.0254 |
| | 0.7083 | 0.2338 | 0.0575 | 0.0004 | 0.0087 | 0.1336 | 0.8132 | 0.0445 |
| | 0.6990 | 0.2430 | 0.0573 | 0.0007 | 0.0081 | 0.1304 | 0.8100 | 0.0514 |
| $K_2SO_4$ | 0.9266 | 0.0472 | 0.0262 | 0.0000 | 0.0049 | 0.0208 | 0.9604 | 0.0139 |
| | 0.8943 | 0.0753 | 0.0304 | 0.0000 | 0.0070 | 0.0456 | 0.9332 | 0.0142 |
| | 0.8642 | 0.1013 | 0.0346 | 0.0000 | 0.0085 | 0.0599 | 0.9165 | 0.0151 |
| | 0.8185 | 0.1407 | 0.0407 | 0.0000 | 0.0065 | 0.0934 | 0.8851 | 0.0151 |
| | 0.8046 | 0.1618 | 0.0336 | 0.0000 | 0.0102 | 0.1110 | 0.8505 | 0.0283 |
| | 0.7618 | 0.1963 | 0.0418 | 0.0000 | 0.0106 | 0.1375 | 0.8216 | 0.0304 |
| | 0.7494 | 0.2013 | 0.0493 | 0.0000 | 0.0096 | 0.1389 | 0.8173 | 0.0342 |
| | 0.6952 | 0.2528 | 0.0520 | 0.0000 | 0.0157 | 0.1870 | 0.7652 | 0.0321 |

[a] Standard uncertainties are $u(T)$ = 0.02 K and $u(w_i)$ = 0.0006 (MIBK), 0.0008 (HMF), 0.0006 (water), 0.0004 (NaCl), 0.0004 (KCl), 0.0002 ($Na_2SO_4$), and 0.0001 ($K_2SO_4$)

**Table A.8** Experimental LLE tie-line data of the 2-pentanol (1)-HMF (2)-water (3)-salt (4) systems in mass fraction ($w_i$) at temperature $T$= 313.15 K and atmospheric pressure[a]

| Salt | Organic Phase | | | | Aqueous Phase | | | |
|---|---|---|---|---|---|---|---|---|
| | $w_1^{I}$ | $w_2^{I}$ | $w_3^{I}$ | $w_4^{I}$ | $w_1^{II}$ | $w_2^{II}$ | $w_3^{II}$ | $w_4^{II}$ |
| NaCl | 0.8666 | 0.0423 | 0.0905 | 0.0006 | 0.0025 | 0.0156 | 0.8716 | 0.1103 |
| | 0.8213 | 0.0859 | 0.0925 | 0.0003 | 0.0019 | 0.0360 | 0.8461 | 0.1160 |
| | 0.7788 | 0.1244 | 0.0961 | 0.0007 | 0.0019 | 0.0509 | 0.8460 | 0.1013 |
| | 0.7486 | 0.1566 | 0.0943 | 0.0006 | 0.0019 | 0.0673 | 0.8226 | 0.1082 |
| | 0.7203 | 0.1863 | 0.0925 | 0.0010 | 0.0027 | 0.0803 | 0.8013 | 0.1157 |
| | 0.6900 | 0.2169 | 0.0921 | 0.0010 | 0.0019 | 0.0925 | 0.7646 | 0.1410 |
| | 0.6777 | 0.2303 | 0.0910 | 0.0010 | 0.0024 | 0.0883 | 0.7721 | 0.1373 |
| | 0.6502 | 0.2544 | 0.0936 | 0.0019 | 0.0016 | 0.1038 | 0.7228 | 0.1719 |
| KCl | 0.8595 | 0.0387 | 0.1017 | 0.0002 | 0.0045 | 0.0197 | 0.8793 | 0.0965 |
| | 0.8238 | 0.0739 | 0.1021 | 0.0002 | 0.0040 | 0.0385 | 0.8558 | 0.1018 |
| | 0.7932 | 0.1015 | 0.1047 | 0.0005 | 0.0048 | 0.0555 | 0.8413 | 0.0984 |
| | 0.7548 | 0.1382 | 0.1064 | 0.0007 | 0.0060 | 0.0705 | 0.7865 | 0.1369 |
| | 0.7329 | 0.1595 | 0.1068 | 0.0008 | 0.0063 | 0.0828 | 0.7698 | 0.1411 |
| | 0.6925 | 0.1983 | 0.1079 | 0.0012 | 0.0046 | 0.0950 | 0.7460 | 0.1544 |
| | 0.6717 | 0.2209 | 0.1059 | 0.0015 | 0.0049 | 0.1057 | 0.7171 | 0.1722 |
| | 0.6473 | 0.2457 | 0.1052 | 0.0018 | 0.0038 | 0.1172 | 0.6922 | 0.1868 |
| $Na_2SO_4$ | 0.8537 | 0.0290 | 0.1171 | 0.0002 | 0.0067 | 0.0154 | 0.9427 | 0.0351 |
| | 0.8125 | 0.0635 | 0.1238 | 0.0001 | 0.0066 | 0.0314 | 0.9241 | 0.0378 |
| | 0.7768 | 0.0897 | 0.1333 | 0.0001 | 0.0081 | 0.0452 | 0.9078 | 0.0390 |
| | 0.7261 | 0.1309 | 0.1428 | 0.0001 | 0.0061 | 0.0595 | 0.8911 | 0.0433 |
| | 0.7018 | 0.1489 | 0.1491 | 0.0001 | 0.0053 | 0.0669 | 0.8802 | 0.0475 |
| | 0.6585 | 0.1857 | 0.1556 | 0.0001 | 0.0031 | 0.0763 | 0.8724 | 0.0481 |
| | 0.6349 | 0.2014 | 0.1635 | 0.0002 | 0.0037 | 0.0824 | 0.8711 | 0.0428 |
| | 0.6074 | 0.2237 | 0.1687 | 0.0002 | 0.0027 | 0.0815 | 0.8602 | 0.0556 |
| $K_2SO_4$ | 0.8461 | 0.0312 | 0.1227 | 0.0000 | 0.0064 | 0.0142 | 0.9653 | 0.0141 |
| | 0.8005 | 0.0663 | 0.1331 | 0.0001 | 0.0060 | 0.0300 | 0.9483 | 0.0157 |
| | 0.7563 | 0.1022 | 0.1415 | 0.0000 | 0.0056 | 0.0433 | 0.9339 | 0.0171 |
| | 0.7208 | 0.1339 | 0.1452 | 0.0000 | 0.0055 | 0.0572 | 0.9148 | 0.0225 |
| | 0.6943 | 0.1498 | 0.1560 | 0.0000 | 0.0058 | 0.0733 | 0.8985 | 0.0224 |
| | 0.6636 | 0.1746 | 0.1618 | 0.0000 | 0.0062 | 0.0783 | 0.8865 | 0.0290 |
| | 0.6292 | 0.2009 | 0.1699 | 0.0000 | 0.0065 | 0.0944 | 0.8690 | 0.0301 |
| | 0.5995 | 0.2246 | 0.1759 | 0.0000 | 0.0063 | 0.0982 | 0.8589 | 0.0366 |

[a] Standard uncertainties are $u(T)$ = 0.02 K and $u(w_i)$ = 0.0007 (2-pentanol), 0.0008 (HMF), 0.0006 (water), 0.0004 (NaCl), 0.0004 (KCl), 0.0002 ($Na_2SO_4$), and 0.0001 ($K_2SO_4$)

**Table A.9** Regressed parameters from NRTL model for the quaternary systems of organic solvent (1)-HMF (2)-water (3)-salt (4) at $T$= 313.15 K

| System | *i-j* | $b_{ij}$ [a]($K$) | $b_{ji}$ [a]($K$) | $\alpha_{ij}$ | RMSD (%) |
|---|---|---|---|---|---|
| MIBK-HMF-water-NaCl | 1-4 | -9044.68 | 4925.37 | -0.0532 | 1.0899 |
| | 2-4 | -1776.15 | 1987.56 | -0.3133 | |
| | 3-4 | -13345.69 | 5478.59 | -0.0456 | |
| MIBK-HMF-water-KCl | 1-4 | -1101.96 | -3654.22 | 0.0085 | 0.8333 |
| | 2-4 | 9170.39 | 2529.49 | 0.1391 | |
| | 3-4 | -7002.91 | -3893.26 | -0.0885 | |
| MIBK-HMF-water-$Na_2SO_4$ | 1-4 | 1794.74 | -1596.15 | 0.1570 | 1.4425 |
| | 2-4 | 809.33 | 9317.72 | 0.8138 | |
| | 3-4 | -9277.54 | -2550.14 | -0.1036 | |
| MIBK-HMF-water-$K_2SO_4$ | 1-4 | -1508.00 | 3193.86 | 0.0179 | 1.5421 |
| | 2-4 | 4712.56 | 819.70 | 0.6543 | |
| | 3-4 | -4277.54 | -527.59 | -0.3727 | |
| 2-pentanol-HMF-water- NaCl | 1-4 | 366.82 | 4479.63 | 0.5220 | 0.9796 |
| | 2-4 | -1776.15 | 1987.56 | -0.3133 | |
| | 3-4 | -13345.69 | 5478.59 | -0.0456 | |
| 2-pentanol-HMF-water- KCl | 1-4 | 1041.50 | -4956.73 | 0.0090 | 0.6314 |
| | 2-4 | 9170.39 | 2529.49 | 0.1391 | |
| | 3-4 | -7002.91 | -3893.26 | -0.0885 | |
| 2-pentanol-HMF-water- $Na_2SO_4$ | 1-4 | -1709.93 | -799.68 | -0.0140 | 0.6408 |
| | 2-4 | 809.33 | 9317.72 | 0.8138 | |
| | 3-4 | -9277.54 | -2550.14 | -0.1036 | |
| 2-pentanol-HMF-water- $K_2SO_4$ | 1-4 | -707.33 | 815.31 | -0.0116 | 0.5032 |
| | 2-4 | 4712.56 | 819.70 | 0.6543 | |
| | 3-4 | -4277.54 | -527.59 | -0.3727 | |

[a] $\tau_{ij} = \frac{b_{ij}}{T}$

**Table A.10** Separation factor (S) and distribution coefficients ($D_i$) for the MIBK (1)-HMF (2)-water (3)-salt (4) systems at temperature *T*= 313.15 K and atmospheric pressure

| MIBK (1)-HMF (2)-water (3)-NaCl (4) | | | | MIBK (1)-HMF (2)-water (3)-KCl (4) | | | |
|---|---|---|---|---|---|---|---|
| $w_2^{II}$ | $D_2$ | $D_3$ | S | $w_2^{II}$ | $D_2$ | $D_3$ | S |
| 0.0161 | 2.24 | 0.026 | 86.2 | 0.0190 | 2.03 | 0.026 | 78.1 |
| 0.0415 | 2.06 | 0.032 | 64.4 | 0.0466 | 1.52 | 0.031 | 49.0 |
| 0.0505 | 2.00 | 0.032 | 62.5 | 0.0681 | 1.76 | 0.038 | 46.3 |
| 0.0584 | 2.19 | 0.036 | 60.8 | 0.0779 | 1.77 | 0.039 | 45.4 |
| 0.0876 | 2.23 | 0.045 | 49.6 | 0.1210 | 1.49 | 0.045 | 33.1 |
| 0.0970 | 2.00 | 0.049 | 40.8 | 0.1245 | 1.65 | 0.049 | 33.7 |
| 0.1083 | 2.22 | 0.054 | 41.1 | 0.1324 | 1.78 | 0.062 | 28.7 |
| 0.1262 | 2.34 | 0.067 | 34.9 | 0.2152 | 1.47 | 0.066 | 22.3 |

| MIBK (1)-HMF (2)-water (3)-$Na_2SO_4$ (4) | | | | MIBK (1)-HMF (2)-water (3)-$K_2SO_4$ (4) | | | |
|---|---|---|---|---|---|---|---|
| $w_2^{II}$ | $D_2$ | $D_3$ | S | $w_2^{II}$ | $D_2$ | $D_3$ | S |
| 0.0252 | 2.35 | 0.028 | 83.9 | 0.0208 | 2.26 | 0.027 | 83.7 |
| 0.0388 | 2.18 | 0.031 | 70.3 | 0.0456 | 1.65 | 0.033 | 50.0 |
| 0.0636 | 1.73 | 0.035 | 49.4 | 0.0599 | 1.69 | 0.038 | 44.5 |
| 0.0752 | 1.65 | 0.042 | 39.3 | 0.0934 | 1.51 | 0.046 | 32.8 |
| 0.0870 | 1.76 | 0.048 | 36.7 | 0.1110 | 1.46 | 0.040 | 36.5 |
| 0.1154 | 1.83 | 0.058 | 31.6 | 0.1375 | 1.43 | 0.051 | 28.0 |
| 0.1304 | 1.86 | 0.071 | 26.2 | 0.1389 | 1.45 | 0.060 | 24.2 |
| 0.1336 | 1.75 | 0.071 | 24.6 | 0.1870 | 1.35 | 0.068 | 19.9 |

**Table A.11** Separation factor (S) and distribution coefficients ($D_i$) for the 2-pentanol (1)-HMF (2)-water (3)-salt (4) systems at temperature *T*= 313.15 K and atmospheric pressure

| 2-pentanol (1)-HMF (2)-water (3)-NaCl (4) | | | | 2-pentanol (1)-HMF (2)-water (3)-KCl (4) | | | |
|---|---|---|---|---|---|---|---|
| $w_2^{II}$ | $D_2$ | $D_3$ | S | $w_2^{II}$ | $D_2$ | $D_3$ | S |
| 0.0156 | 2.70 | 0.104 | 26.0 | 0.0197 | 1.96 | 0.116 | 16.9 |
| 0.0360 | 2.39 | 0.109 | 21.9 | 0.0385 | 1.92 | 0.119 | 16.1 |
| 0.0509 | 2.44 | 0.114 | 21.4 | 0.0555 | 1.83 | 0.124 | 14.8 |
| 0.0673 | 2.33 | 0.115 | 20.3 | 0.0705 | 1.96 | 0.135 | 14.5 |
| 0.0803 | 2.32 | 0.115 | 20.2 | 0.0828 | 1.93 | 0.139 | 13.9 |
| 0.0883 | 2.61 | 0.118 | 22.1 | 0.0950 | 2.09 | 0.145 | 14.4 |
| 0.0925 | 2.35 | 0.120 | 19.6 | 0.1057 | 2.09 | 0.148 | 14.1 |
| 0.1038 | 2.45 | 0.130 | 18.8 | 0.1172 | 2.10 | 0.152 | 13.8 |

| 2-pentanol (1)-HMF (2)-water (3)-$Na_2SO_4$ (4) | | | | 2-pentanol (1)-HMF (2)-water (3)-$K_2SO_4$ (4) | | | |
|---|---|---|---|---|---|---|---|
| $w_2^{II}$ | $D_2$ | $D_3$ | S | $w_2^{II}$ | $D_2$ | $D_3$ | S |
| 0.0154 | 1.88 | 0.124 | 15.2 | 0.0142 | 2.20 | 0.127 | 17.3 |
| 0.0314 | 2.02 | 0.134 | 15.1 | 0.0300 | 2.21 | 0.141 | 15.7 |
| 0.0452 | 1.99 | 0.147 | 13.5 | 0.0433 | 2.36 | 0.152 | 15.5 |
| 0.0595 | 2.20 | 0.160 | 13.8 | 0.0572 | 2.34 | 0.159 | 14.7 |
| 0.0669 | 2.22 | 0.169 | 13.1 | 0.0733 | 2.04 | 0.174 | 11.7 |
| 0.0763 | 2.43 | 0.178 | 13.7 | 0.0783 | 2.23 | 0.183 | 12.2 |
| 0.0815 | 2.75 | 0.196 | 14.0 | 0.0944 | 2.13 | 0.196 | 10.9 |
| 0.0824 | 2.44 | 0.188 | 13.0 | 0.0982 | 2.29 | 0.205 | 11.2 |

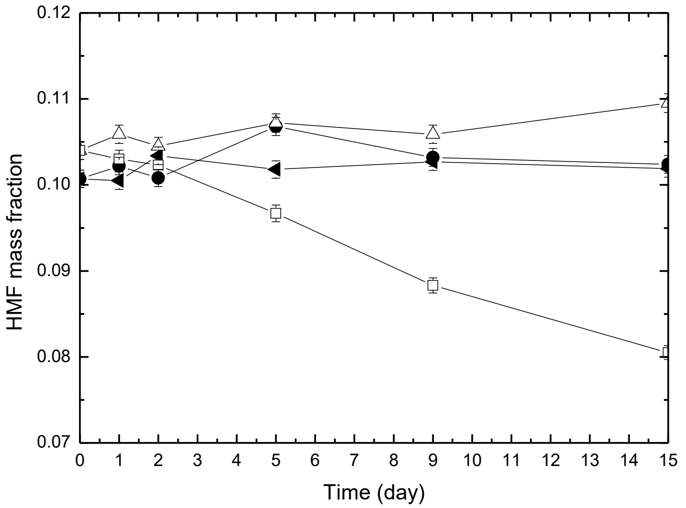


**Figure A.1** HMF stability validation at $T$= 313.15 K and atmospheric pressure; (—◀—) HMF in water with BHA; (—●—) HMF in water without BHA; (—△—) HMF in MIBK with BHA; (—□—) HMF in MIBK without BHA

## Topological analysis of the Gibbs energy of mixing function ($G^M$) for liquid-liquid equilibrium correlations

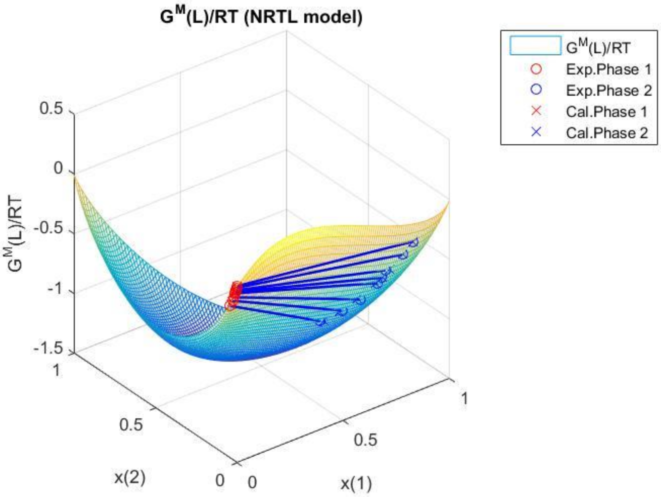
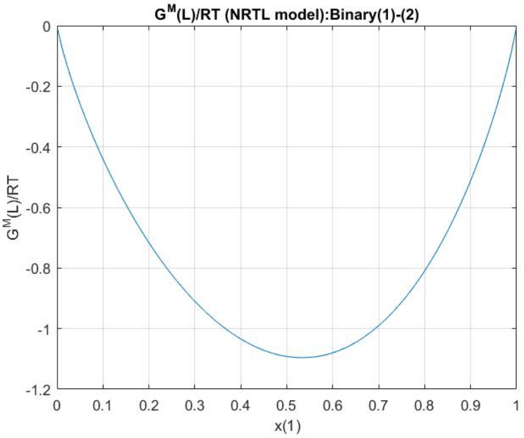
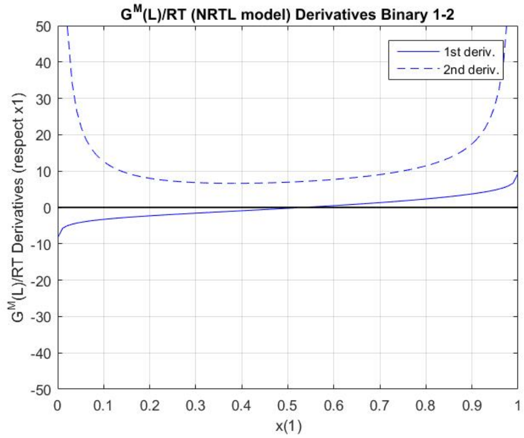
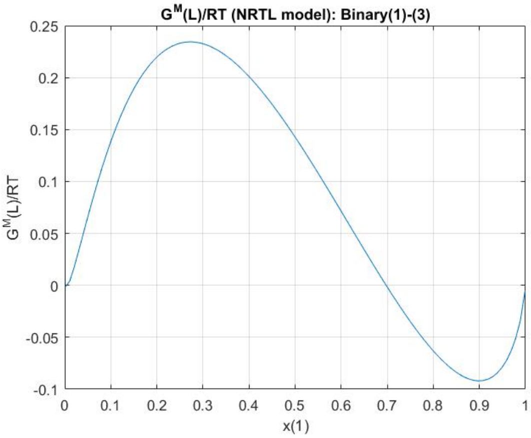
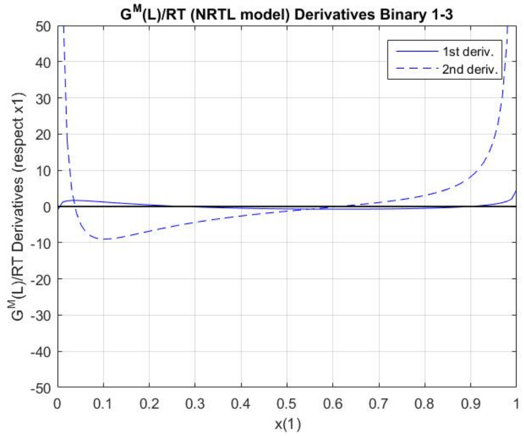


**Figure A.2** $G^M/RT$ surface of NRTL model with tie-lines for the ternary system of MIBK (1)-HMF (2)-water (3).




G$^{M}$(L)/RT (NRTL model) Derivatives Binary 1-2


G$^{M}$(L)/RT (NRTL model): Binary(1)-(3)


G$^{M}$(L)/RT (NRTL model) Derivatives Binary 1-3

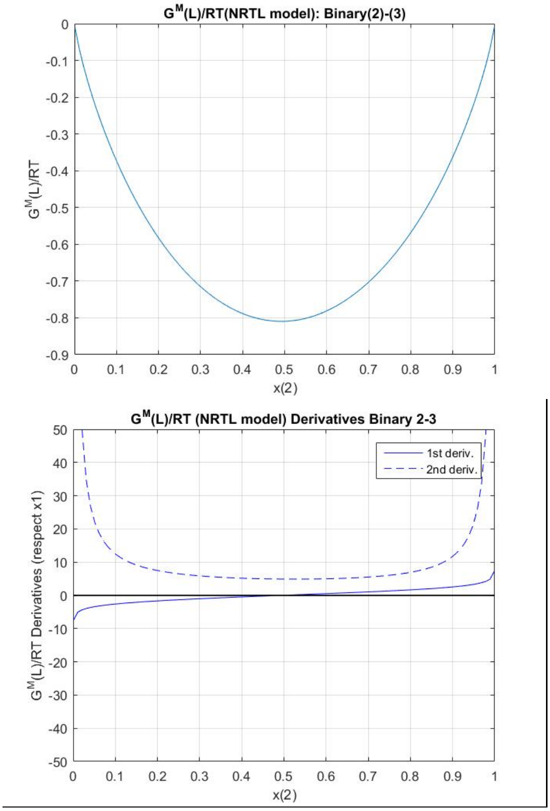


**Figure A.3** $G^M$/RT binary curves and the derivatives of NRTL model for the ternary system of MIBK (1)-HMF (2)-water (3).

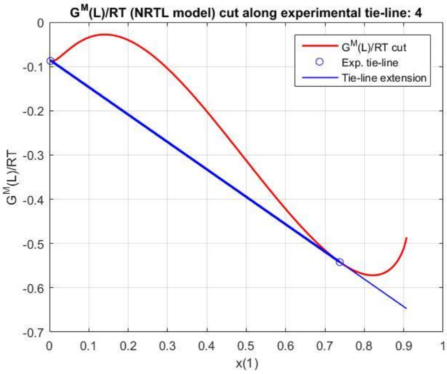


**Figure A.4** Shape of the $G^M$/RT curve (tie-line 4) of NRTL model for the ternary system of MIBK (1)-HMF (2)-water (3).

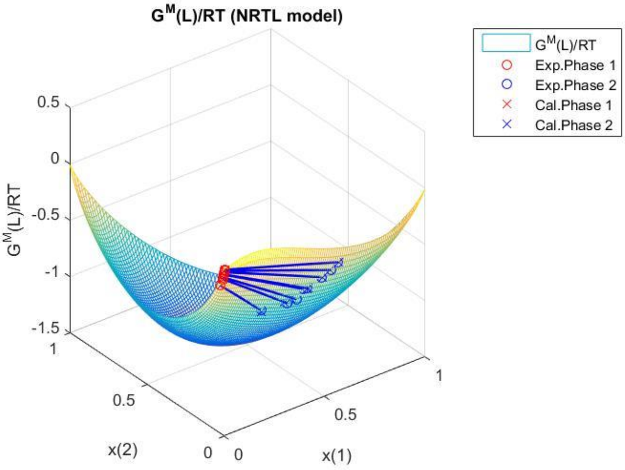
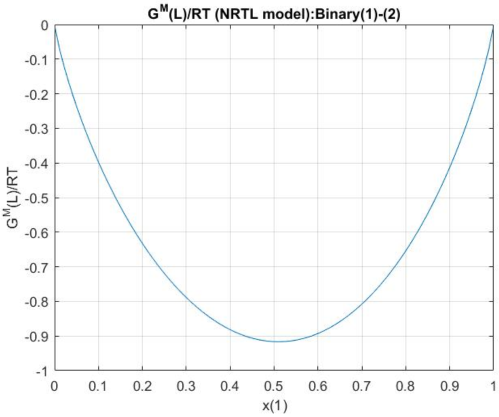
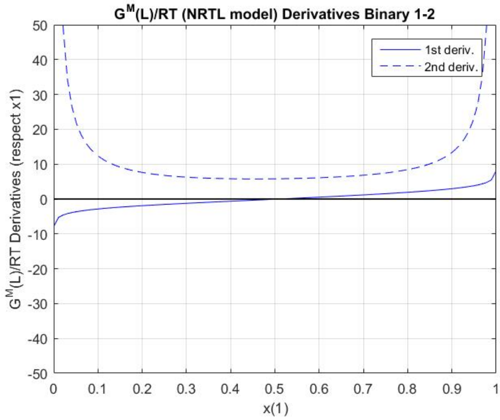
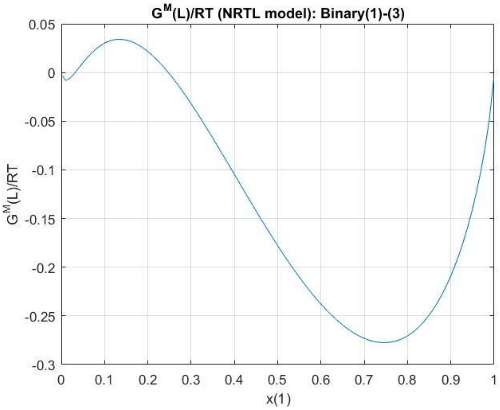


**Figure A.5** G$^{M}$/RT surface of NRTL model with tie-lines for the ternary system of 2-pentanol (1)-HMF (2)-water (3).

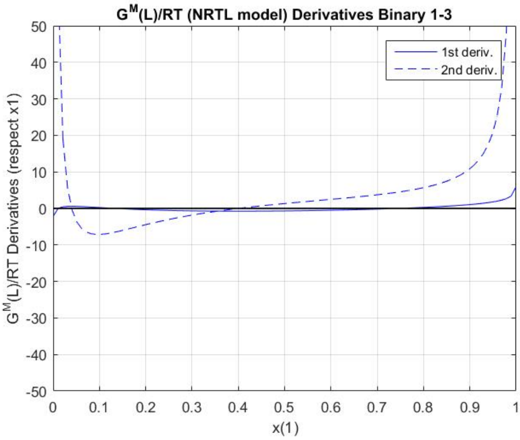




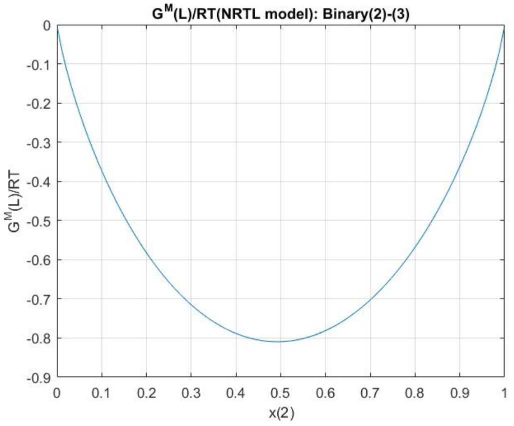
$G^M(L)/RT$ (NRTL model) Derivatives Binary 1-2
1st deriv.
2nd deriv.
$G^M(L)/RT$ Derivatives (respect x1)
x(1)
50
40
30
20
10
0
-10
-20
-30
-40
-50
0
0.1
0.2
0.3
0.4
0.5
0.6
0.7
0.8
0.9
1



$G^M(L)/RT$ (NRTL model): Binary(1)-(3)
$G^M(L)/RT$
x(1)
0.05
0
-0.05
-0.1
-0.15
-0.2
-0.25
-0.3
0
0.1
0.2
0.3
0.4
0.5
0.6
0.7
0.8
0.9
1



$G^M(L)/RT$ (NRTL model) Derivatives Binary 1-3
1st deriv.
2nd deriv.
$G^M(L)/RT$ Derivatives (respect x1)
x(1)
50
40
30
20
10
0
-10
-20
-30
-40
-50
0
0.1
0.2
0.3
0.4
0.5
0.6
0.7
0.8
0.9
1



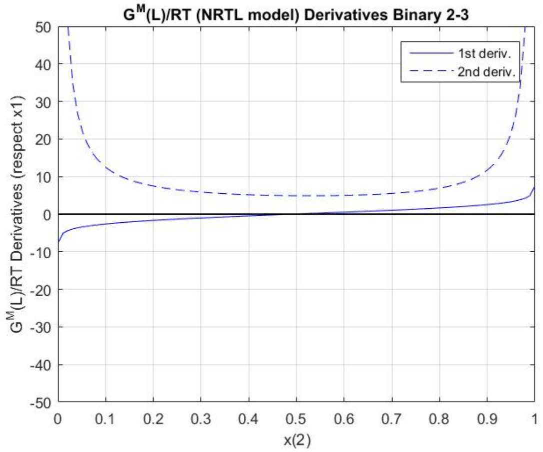


**Figure A.6** $G^M/RT$ binary curves and the derivatives of NRTL model for the ternary system of 2-pentanol (1)-HMF (2)-water (3).

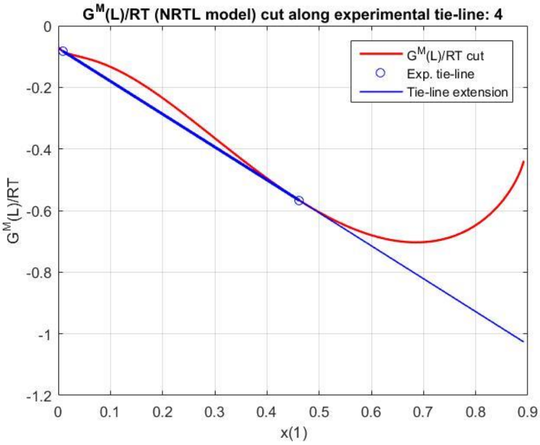


**Figure A.7** Shape of the $G^M/RT$ curve (tie-line 4) of NRTL model for the ternary system of 2-pentanol (1)-HMF (2)-water (3).

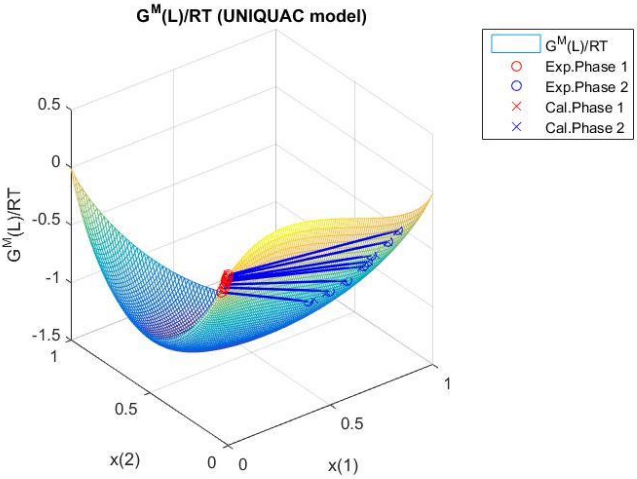
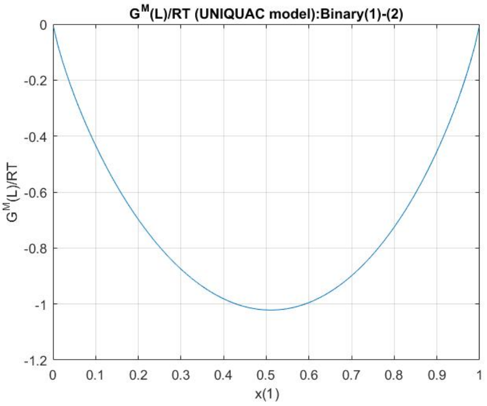
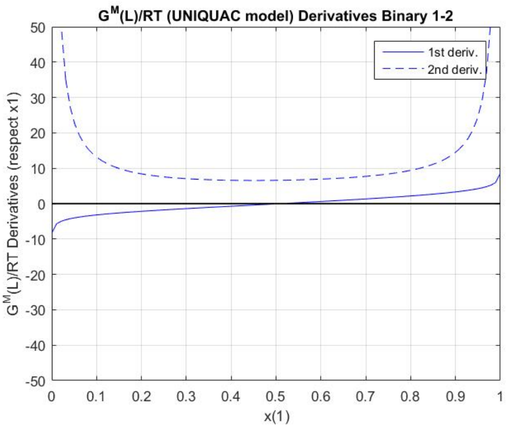
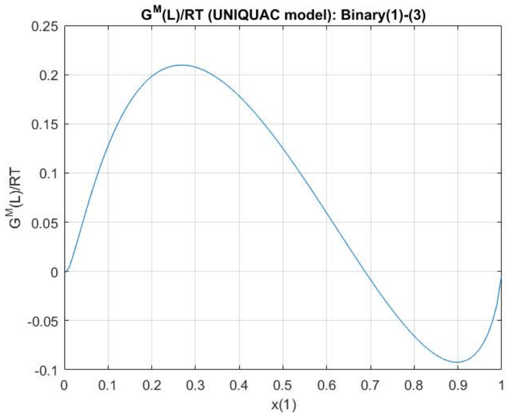


**Figure A.8** $G^M/RT$ surface of UNIQUAC model with tie-lines for the ternary system of MIBK (1)-HMF (2)-water (3).


$G^M(L)/RT$ (UNIQUAC model):Binary(1)-(2)
$G^M(L)/RT$
0
-0.2
-0.4
-0.6
-0.8
-1
-1.2
0
0.1
0.2
0.3
0.4
0.5
0.6
0.7
0.8
0.9
1
x(1)


$G^M(L)/RT$ (UNIQUAC model) Derivatives Binary 1-2
$G^M(L)/RT$ Derivatives (respect x1)
1st deriv.
2nd deriv.
50
40
30
20
10
0
-10
-20
-30
-40
-50
0
0.1
0.2
0.3
0.4
0.5
0.6
0.7
0.8
0.9
1
x(1)


$G^M(L)/RT$ (UNIQUAC model): Binary(1)-(3)
$G^M(L)/RT$
0.25
0.2
0.15
0.1
0.05
0
-0.05
-0.1
0
0.1
0.2
0.3
0.4
0.5
0.6
0.7
0.8
0.9
1
x(1)

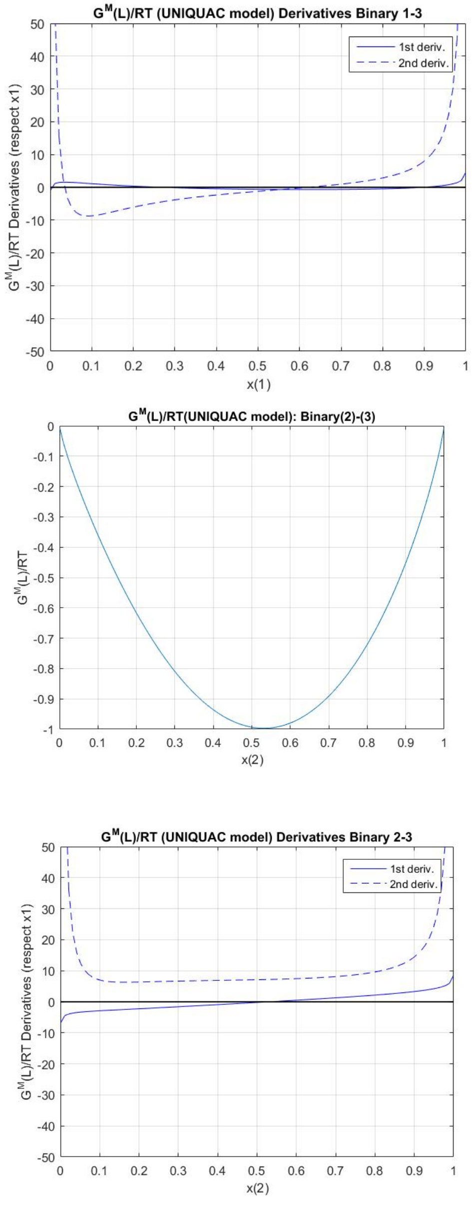


**Figure A.9** $G^M/RT$ binary curves and the derivatives of UNIQUAC model for the ternary system of MIBK (1)-HMF (2)-water (3).

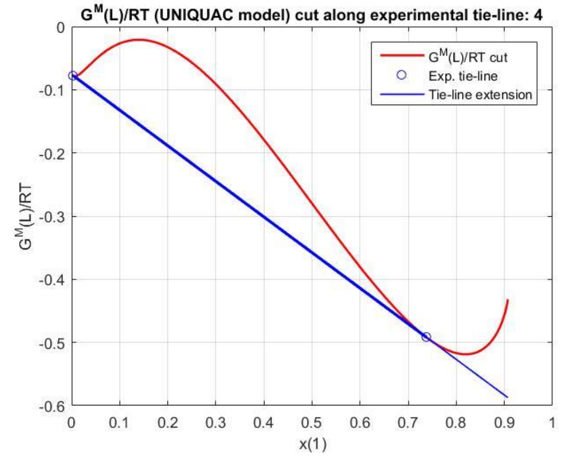


**Figure A.10** Shape of the G$^M$/RT curve (tie-line 4) of UNIQUAC model for the ternary system of MIBK (1)-HMF (2)-water (3).

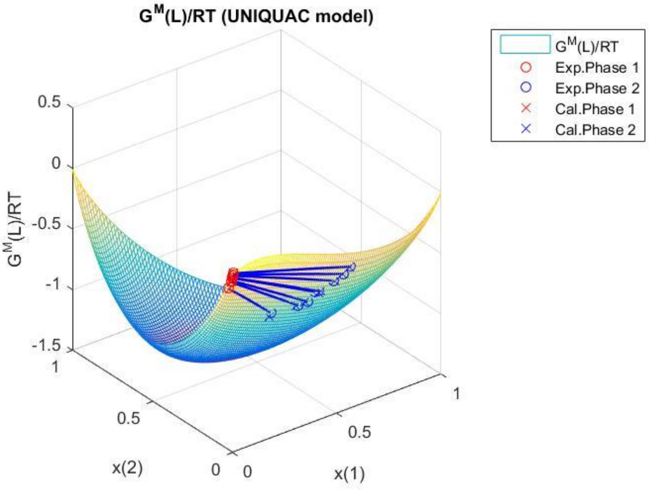
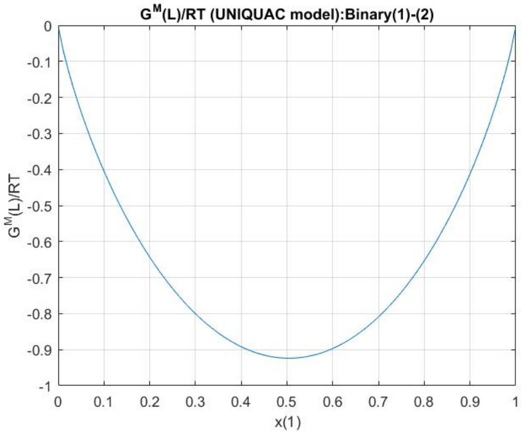
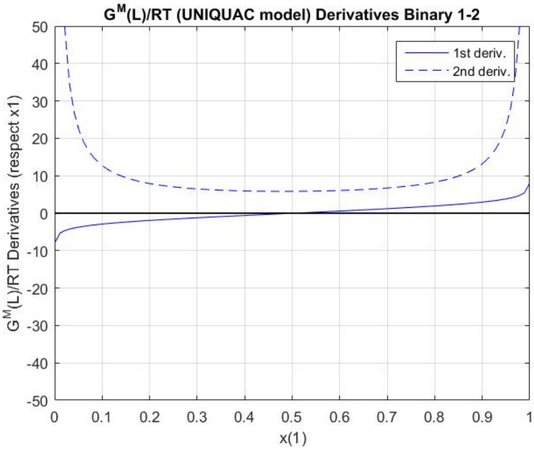
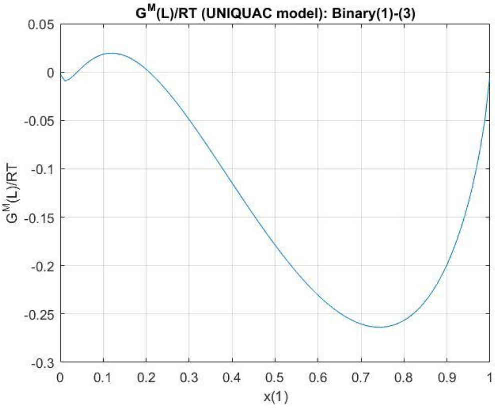


**Figure A.11** G$^M$/RT surface of UNIQUAC model with tie-lines for the ternary system of 2-pentanol (1)-HMF (2)-water (3).


G$^M$(L)/RT (UNIQUAC model):Binary(1)-(2)
G$^M$(L)/RT
x(1)
0
-0.1
-0.2
-0.3
-0.4
-0.5
-0.6
-0.7
-0.8
-0.9
-1
0
0.1
0.2
0.3
0.4
0.5
0.6
0.7
0.8
0.9
1


G$^M$(L)/RT (UNIQUAC model) Derivatives Binary 1-2
G$^M$(L)/RT Derivatives (respect x1)
x(1)
1st deriv.
2nd deriv.
50
40
30
20
10
0
-10
-20
-30
-40
-50
0
0.1
0.2
0.3
0.4
0.5
0.6
0.7
0.8
0.9
1


G$^M$(L)/RT (UNIQUAC model): Binary(1)-(3)
G$^M$(L)/RT
x(1)
0.05
0
-0.05
-0.1
-0.15
-0.2
-0.25
-0.3
0
0.1
0.2
0.3
0.4
0.5
0.6
0.7
0.8
0.9
1

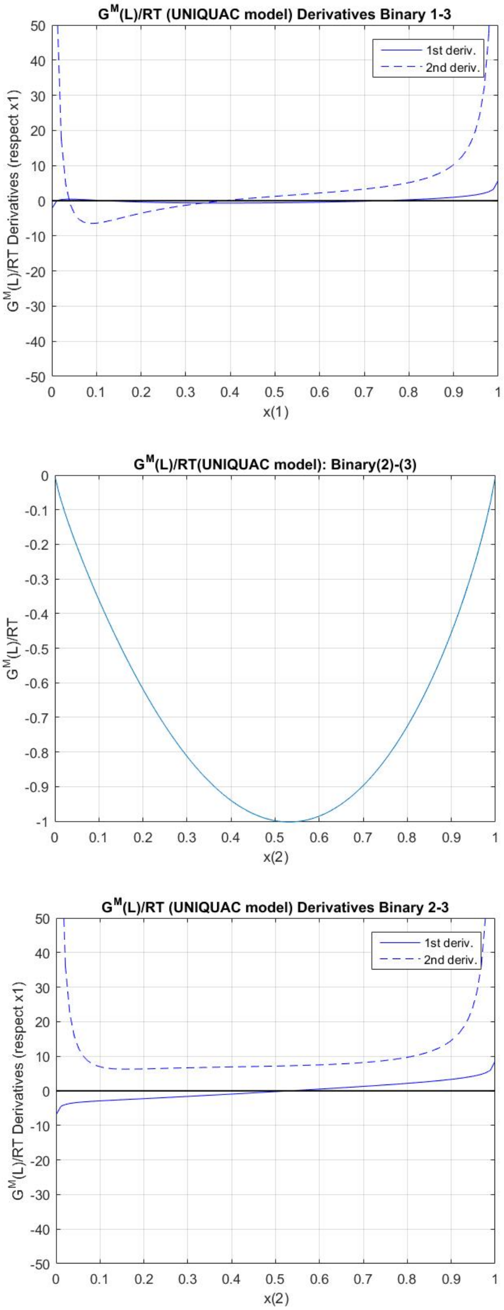


**Figure A.12** $G^M/RT$ binary curves and the derivatives of UNIQUAC model for the ternary system of 2-pentanol (1)-HMF (2)-water (3).

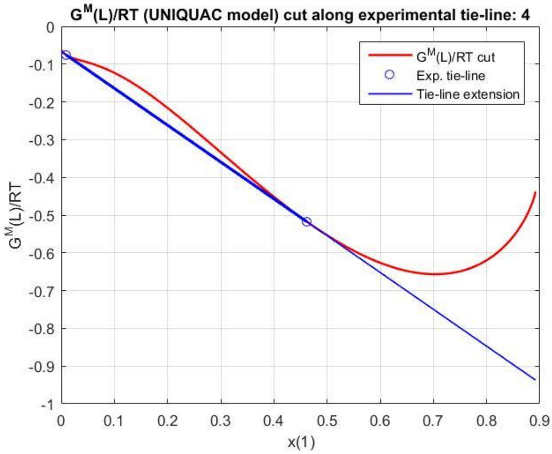


**Figure A.13** Shape of the $G^M/RT$ curve (tie-line 4) of UNIQUAC model for the ternary system of 2-pentanol (1)-HMF (2)-water (3).

## References

[A1] J.A. Reyes-Labarta, M.M. Olaya, A. Marcilla, Topological analysis of the GM function in liquid-liquid equilibrium correlation data (Thermodynamic Review), Institutional Repository RUA: http://hdl.handle.net/10045/51725.

[A2] A. Marcilla, J.A. Reyes-Labarta, M.M. Olaya, Should we trust all the published LLE correlation parameters in phase equilibria? Necessity of their assessment prior to publication, Fluid Phase Equilib. 433 (2017) 243–252.

## Appendix B

**Table B.1** Description of chemicals used in this study

| Chemical Name | Source | Mass Fraction Purity | Purification method |
|---|---|---|---|
| 5-hydroxymethylfurfural | AVA Biochem, Switzerland | ≥ 0.99 | No |
| Methyl isobutyl ketone | Thermo Fisher Scientific, France | ≥ 0.99 | No<br>No |
| 2-Pentanol | Thermo Fisher Scientific, Germany | 0.99 | No |
| Methanol | Honeywell, France | ≥ 0.999 | |
| Sodium chloride | Sigma-Aldrich, USA | ≥ 0.99 | No |
| 1-ethyl-3-methylimidazolium tetrafluoroborate | Sigma-Aldrich, USA | ≥ 0.98 | No |
| Nitric acid | Thermo Fisher Scientific, USA | 0.70 | No |
| Water | Available in our Lab. | Deionized ultrapure water | No |

**Table B.2** Experimental and literature values of densities (ρ) of chemicals used in this study at temperature *T*= 293.15 K and *P*= 0.1 MPa[a].

| Chemical Name | Chemical Formula | Molecular weight (g/mol) | $\rho$ (g/cm$^3$) | |
|---|---|---|---|---|
| | | | Expt. | Lit. |
| 5-hydroxymethylfurfural | $C_6H_6O_3$ | 126.11 | - | 1.2[b] |
| Methyl isobutyl ketone | $C_6H_{12}O$ | 100.16 | 0.8010 | 0.8010[c] |
| 2-Pentanol | $C_5H_{12}O$ | 88.15 | 0.8103 | 0.8090[d] |
| Methanol | $CH_4O$ | 32.04 | 0.7919 | 0.7914[e] |
| Sodium chloride | $NaCl$ | 58.44 | - | 2.17[f] |
| 1-ethyl-3-methylimidazolium tetrafluoroborate | $C_6H_{11}BF_4N_2$ | 197.97 | 1.2846 | 1.2844[g] |
| Nitric acid (70 wt%) | $HNO_3$ | 63.01 | 1.4128 | 1.4134[h] |
| Water | $H_2O$ | 18.02 | 0.9986 | 0.9982[h] |

[a] Standard uncertainties are $u(T)$ = 0.001 K, $u(P)$ = 5x10$^{-5}$ MPa, and $u(\rho)$ = 0.0008 g/cm$^3$, [b] Provided by AVA Biochem, [c] Ref. [B1], [d] Ref. [B2], [e] Ref. [B3], [f] Provided by Sigma-Aldrich, [g] Ref. [B4], [h] Ref. [B5].

**Table B.3** Experimental LLE tie-line data of MIBK (1)-HMF (2)-water (3)-[EMIM][BF$_4$] (4) systems in mass fraction ($w_i$) at temperature $T$= 313.15 K and $P$= 0.1 MPa[a]

| IL | Organic Phase | | | | Aqueous Phase | | | |
|---|---|---|---|---|---|---|---|---|
| | $w_1^{I}$ | $w_2^{I}$ | $w_3^{I}$ | $w_4^{I}$ | $w_1^{II}$ | $w_2^{II}$ | $w_3^{II}$ | $w_4^{II}$ |
| 5% | 0.9498 | 0.0284 | 0.0214 | 0.0004 | 0.0184 | 0.0248 | 0.9183 | 0.0386 |
| | 0.9154 | 0.0598 | 0.0241 | 0.0007 | 0.0197 | 0.0550 | 0.8864 | 0.0388 |
| | 0.8812 | 0.0861 | 0.0315 | 0.0011 | 0.0217 | 0.0824 | 0.8547 | 0.0411 |
| | 0.8680 | 0.0981 | 0.0326 | 0.0013 | 0.0235 | 0.0954 | 0.8401 | 0.0410 |
| | 0.8337 | 0.1273 | 0.0369 | 0.0021 | 0.0275 | 0.1377 | 0.7913 | 0.0435 |
| | 0.8167 | 0.1394 | 0.0413 | 0.0026 | 0.0338 | 0.1666 | 0.7560 | 0.0436 |
| | 0.7950 | 0.1582 | 0.0432 | 0.0036 | 0.0344 | 0.1892 | 0.7228 | 0.0536 |
| | 0.7548 | 0.1885 | 0.0518 | 0.0049 | 0.0424 | 0.2331 | 0.6721 | 0.0525 |
| 10% | 0.9424 | 0.0303 | 0.0259 | 0.0014 | 0.0129 | 0.0286 | 0.8759 | 0.0825 |
| | 0.9131 | 0.0561 | 0.0285 | 0.0023 | 0.0092 | 0.0546 | 0.8505 | 0.0857 |
| | 0.8774 | 0.0849 | 0.0347 | 0.0031 | 0.0160 | 0.0875 | 0.8135 | 0.0831 |
| | 0.8615 | 0.1018 | 0.0314 | 0.0053 | 0.0193 | 0.1235 | 0.7728 | 0.0844 |
| | 0.8455 | 0.1169 | 0.0336 | 0.0040 | 0.0354 | 0.1463 | 0.7340 | 0.0843 |
| | 0.8319 | 0.1270 | 0.0362 | 0.0048 | 0.0401 | 0.1639 | 0.7085 | 0.0875 |
| | 0.7924 | 0.1557 | 0.0442 | 0.0077 | 0.0585 | 0.2022 | 0.6357 | 0.1036 |
| | 0.7904 | 0.1609 | 0.0419 | 0.0068 | 0.0544 | 0.2427 | 0.6054 | 0.0975 |
| 30% | 0.9580 | 0.0198 | 0.0192 | 0.0030 | 0.0414 | 0.0343 | 0.6296 | 0.2947 |
| | 0.9365 | 0.0374 | 0.0223 | 0.0039 | 0.0490 | 0.0658 | 0.5789 | 0.3062 |
| | 0.9219 | 0.0502 | 0.0233 | 0.0046 | 0.0590 | 0.0946 | 0.5379 | 0.3085 |
| | 0.8762 | 0.0798 | 0.0335 | 0.0105 | 0.0634 | 0.1384 | 0.4856 | 0.3126 |
| | 0.8662 | 0.0867 | 0.0353 | 0.0119 | 0.0630 | 0.1661 | 0.4452 | 0.3257 |
| | 0.8586 | 0.0976 | 0.0329 | 0.0109 | 0.0665 | 0.1929 | 0.4274 | 0.3132 |
| | 0.7988 | 0.1378 | 0.0437 | 0.0198 | 0.0587 | 0.2577 | 0.3653 | 0.3183 |
| | 0.7514 | 0.1611 | 0.0556 | 0.0319 | 0.0612 | 0.2916 | 0.3333 | 0.3138 |

[a] Standard uncertainties are $u(T)$ = 0.02 K, $u(P)$ = 0.001 MPa, and $u(w_i)$= 0.0012 (MIBK), 0.0015 (HMF), 0.0015 (water), 0.0008 ([EMIM][BF$_4$]).

**Table B.4** Experimental LLE tie-line data of 2-pentanol (1)-HMF (2)-water (3)-[EMIM][$BF_4$] (4) systems in mass fraction ($w_i$) at temperature $T$= 313.15 K and $P$= 0.1 MPa[a]

| IL | Organic Phase | | | | Aqueous Phase | | | |
|---|---|---|---|---|---|---|---|---|
| | $w_1^{I}$ | $w_2^{I}$ | $w_3^{I}$ | $w_4^{I}$ | $w_1^{II}$ | $w_2^{II}$ | $w_3^{II}$ | $w_4^{II}$ |
| 10% | 0.8393 | 0.0293 | 0.1226 | 0.0088 | 0.0436 | 0.0213 | 0.8380 | 0.0971 |
| | 0.8084 | 0.0548 | 0.1273 | 0.0095 | 0.0477 | 0.0463 | 0.8084 | 0.0976 |
| | 0.7693 | 0.0812 | 0.1381 | 0.0114 | 0.0536 | 0.0723 | 0.7757 | 0.0984 |
| | 0.7303 | 0.1062 | 0.1484 | 0.0151 | 0.0636 | 0.0976 | 0.7331 | 0.1057 |
| | 0.6899 | 0.1313 | 0.1602 | 0.0186 | 0.0706 | 0.1222 | 0.7010 | 0.1063 |
| | 0.6401 | 0.1555 | 0.1789 | 0.0254 | 0.0848 | 0.1545 | 0.6563 | 0.1045 |
| | 0.6056 | 0.1778 | 0.1866 | 0.0301 | 0.1024 | 0.1843 | 0.6070 | 0.1063 |
| | 0.5412 | 0.2038 | 0.2140 | 0.0410 | 0.1163 | 0.2196 | 0.5447 | 0.1195 |
| 30% | 0.8446 | 0.0235 | 0.1193 | 0.0127 | 0.0709 | 0.0297 | 0.6127 | 0.2867 |
| | 0.8211 | 0.0427 | 0.1188 | 0.0174 | 0.0838 | 0.0616 | 0.5662 | 0.2885 |
| | 0.7842 | 0.0663 | 0.1269 | 0.0225 | 0.0955 | 0.0927 | 0.5250 | 0.2868 |
| | 0.7537 | 0.0803 | 0.1305 | 0.0355 | 0.1108 | 0.1203 | 0.4712 | 0.2977 |
| | 0.7178 | 0.0986 | 0.1371 | 0.0464 | 0.1340 | 0.1515 | 0.4149 | 0.2996 |
| | 0.6533 | 0.1485 | 0.1523 | 0.0459 | 0.1786 | 0.1909 | 0.3346 | 0.2958 |
| | 0.6239 | 0.1672 | 0.1458 | 0.0630 | 0.1914 | 0.2264 | 0.2661 | 0.3161 |

[a] Standard uncertainties are $u(T)$ = 0.02 K, $u(P)$ = 0.001 MPa, and $u(w_i)$ = 0.0008 (2-pentanol), 0.0015 (HMF), 0.0015 (water), 0.0008 ([EMIM][$BF_4$]).

**Table B.5** Separation factor (S) and distribution coefficients ($D_i$) for organic solvent (1)-HMF (2)-water (3)-[EMIM][$BF_4$] (4) systems at temperature $T$= 313.15 K and $P$= 0.1 MPa

| MIBK-HMF-water-[EMIM][$BF_4$] (5% IL) | | | | MIBK-HMF-water-[EMIM][$BF_4$] (10% IL) | | | |
|---|---|---|---|---|---|---|---|
| $w_2^{I}$ | $D_2$ | $D_3$ | S | $w_2^{I}$ | $D_2$ | $D_3$ | S |
| 0.0284 | 1.14 | 0.023 | 49.6 | 0.0303 | 1.06 | 0.030 | 35.3 |
| 0.0598 | 1.09 | 0.027 | 40.4 | 0.0561 | 1.03 | 0.034 | 30.3 |
| 0.0861 | 1.04 | 0.037 | 28.1 | 0.0849 | 0.97 | 0.043 | 22.6 |
| 0.0981 | 1.03 | 0.039 | 26.4 | 0.1018 | 0.82 | 0.041 | 20.0 |
| 0.1273 | 0.92 | 0.047 | 19.6 | 0.1169 | 0.80 | 0.046 | 17.4 |
| 0.1394 | 0.84 | 0.055 | 15.3 | 0.1270 | 0.78 | 0.051 | 15.3 |
| 0.1582 | 0.84 | 0.060 | 14.0 | 0.1557 | 0.77 | 0.070 | 11.0 |
| 0.1885 | 0.81 | 0.077 | 10.5 | 0.1609 | 0.66 | 0.069 | 9.6 |

| MIBK-HMF-water-[EMIM][BF$_4$] (30% IL) | | | | 2-pentanol-HMF-water-[EMIM][BF$_4$] (10% IL) | | | |
|---|---|---|---|---|---|---|---|
| $w_2^I$ | $D_2$ | $D_3$ | S | $w_2^I$ | $D_2$ | $D_3$ | S |
| 0.0198 | 0.58 | 0.031 | 18.7 | 0.0293 | 1.38 | 0.146 | 9.5 |
| 0.0374 | 0.57 | 0.038 | 15.0 | 0.0548 | 1.18 | 0.157 | 7.5 |
| 0.0502 | 0.53 | 0.043 | 12.3 | 0.0812 | 1.12 | 0.178 | 6.3 |
| 0.0798 | 0.58 | 0.069 | 8.4 | 0.1062 | 1.09 | 0.202 | 5.4 |
| 0.0867 | 0.52 | 0.079 | 6.6 | 0.1313 | 1.07 | 0.229 | 4.7 |
| 0.0976 | 0.51 | 0.077 | 6.6 | 0.1555 | 1.01 | 0.273 | 3.7 |
| 0.1378 | 0.53 | 0.120 | 4.4 | 0.1778 | 0.96 | 0.307 | 3.1 |
| 0.1611 | 0.55 | 0.167 | 3.3 | 0.2038 | 0.93 | 0.393 | 2.4 |

| 2-pentanol-HMF-water-[EMIM][BF$_4$] (30% IL) | | | |
|---|---|---|---|
| $w_2^I$ | $D_2$ | $D_3$ | S |
| 0.0235 | 0.79 | 0.195 | 4.1 |
| 0.0427 | 0.69 | 0.210 | 3.3 |
| 0.0663 | 0.72 | 0.242 | 3.0 |
| 0.0803 | 0.67 | 0.277 | 2.4 |
| 0.0986 | 0.65 | 0.330 | 2.0 |
| 0.1485 | 0.78 | 0.455 | 1.7 |
| 0.1672 | 0.74 | 0.548 | 1.4 |

**Table B.6** Parameters of NRTL model for organic solvent (1)-HMF (2)-water (3)-[EMIM][BF$_4$] (4) systems at temperature $T$= 313.15 K and $P$= 0.1 MPa

| System | *i-j* | $b_{ij}$[a]($K$) | $b_{ji}$[a]($K$) | $\alpha_{ij}$ | RMSD (%) |
|---|---|---|---|---|---|
| MIBK-HMF-water-[EMIM][BF$_4$] | 1-2 | 483.26[b] | -738.00[b] | 0.20 | 1.0317 |
| | 1-3 | 199.41[b] | 1722.53[b] | 0.20 | |
| | 1-4 | 290.07 | 8545.18 | 0.20 | |
| | 2-3 | -379.83[b] | 310.86[b] | 0.20 | |
| | 2-4 | -270.18 | -1282.76 | 0.20 | |
| | 3-4 | 3177.31 | -1492.19 | 0.20 | |

| System | $i$-$j$ | $b_{ij}$ [a]$(K)$ | $b_{ji}$ [a]$(K)$ | $\alpha_{ij}$ | RMSD (%) |
|---|---|---|---|---|---|
| 2-pentanol-HMF-water-[EMIM][$BF_4$] | 1-2 | 911.98 [b] | -754.74 [b] | 0.20 | 0.8614 |
| | 1-3 | -205.68 [b] | 1777.28 [b] | 0.20 | |
| | 1-4 | 116.74 | 3367.99 | 0.20 | |
| | 2-3 | -379.83 [b] | 310.86 [b] | 0.20 | |
| | 2-4 | -270.18 | -1282.76 | 0.20 | |
| | 3-4 | 3177.31 | -1492.19 | 0.20 | |

[a] $\tau_{ij} = \frac{b_{ij}}{T}$

[b] Fixed from the ternary LLE correlations of organic solvent-HMF-water [Chapter 2].

**Table B.7** Experimental LLE tie-line data of organic solvent (1)-HMF (2)-water (3)-[EMIM][BF$_4$] (4)-NaCl (5) systems in mass fraction ($x_i$) at temperature $T$= 313.15 K and $P$= 0.1 MPa[a]

| Organic solvent | Organic Phase | | | | | Aqueous Phase | | | | |
|---|---|---|---|---|---|---|---|---|---|---|
| | $w_1^{I}$ | $w_2^{I}$ | $w_3^{I}$ | $w_4^{I}$ | $w_5^{I}$ | $w_1^{II}$ | $w_2^{II}$ | $w_3^{II}$ | $w_4^{II}$ | $w_5^{II}$ |
| MIBK | 0.9457 | 0.0303 | 0.0214 | 0.0024 | 0.0002 | 0.0072 | 0.0187 | 0.7929 | 0.1106 | 0.0706 |
| | 0.9244 | 0.0489 | 0.0233 | 0.0032 | 0.0002 | 0.0040 | 0.0318 | 0.7854 | 0.1080 | 0.0708 |
| | 0.8773 | 0.0896 | 0.0280 | 0.0049 | 0.0002 | 0.0028 | 0.0584 | 0.7523 | 0.1118 | 0.0748 |
| | 0.8355 | 0.1250 | 0.0321 | 0.0071 | 0.0003 | 0.0023 | 0.0836 | 0.7193 | 0.1154 | 0.0794 |
| | 0.7953 | 0.1579 | 0.0358 | 0.0107 | 0.0004 | 0.0009 | 0.1053 | 0.7063 | 0.1083 | 0.0792 |
| | 0.7566 | 0.1835 | 0.0441 | 0.0153 | 0.0005 | 0.0008 | 0.1192 | 0.6769 | 0.1185 | 0.0846 |
| | 0.7292 | 0.2112 | 0.0418 | 0.0173 | 0.0005 | 0.0006 | 0.1433 | 0.6488 | 0.1172 | 0.0900 |
| | 0.6827 | 0.2393 | 0.0508 | 0.0263 | 0.0009 | 0.0003 | 0.1571 | 0.6302 | 0.1115 | 0.1009 |
| 2-pentanol | 0.8766 | 0.0343 | 0.0847 | 0.0038 | 0.0005 | 0.0151 | 0.0170 | 0.8012 | 0.1032 | 0.0635 |
| | 0.8469 | 0.0679 | 0.0798 | 0.0048 | 0.0005 | 0.0160 | 0.0349 | 0.7779 | 0.1042 | 0.0669 |
| | 0.8109 | 0.0968 | 0.0831 | 0.0060 | 0.0032 | 0.0144 | 0.0498 | 0.7795 | 0.0933 | 0.0629 |
| | 0.7828 | 0.1200 | 0.0862 | 0.0076 | 0.0034 | 0.0147 | 0.0612 | 0.7407 | 0.1072 | 0.0762 |
| | 0.7420 | 0.1510 | 0.0932 | 0.0094 | 0.0044 | 0.0154 | 0.0762 | 0.7328 | 0.1015 | 0.0741 |
| | 0.7107 | 0.1813 | 0.0923 | 0.0115 | 0.0042 | 0.0141 | 0.0898 | 0.7120 | 0.1057 | 0.0785 |
| | 0.7021 | 0.1963 | 0.0864 | 0.0140 | 0.0012 | 0.0123 | 0.0971 | 0.6641 | 0.1252 | 0.1012 |
| | 0.6519 | 0.2252 | 0.0924 | 0.0283 | 0.0022 | 0.0112 | 0.1070 | 0.6374 | 0.1288 | 0.1156 |

[a] Standard uncertainties are $u(T)$ = 0.02 K, $u(P)$ = 0.001 MPa, and $u(w_i)$ = 0.0012 (MIBK), 0.0008 (2-pentanol), 0.0015 (HMF), 0.0015 (water), 0.0008 ([EMIM][BF$_4$]), 0.0004 (NaCl)

**Table B.8** Separation factor (S) and distribution coefficients ($D_i$) for organic solvent (1)-HMF (2)-water (3)-[EMIM][$BF_4$] (4)-NaCl (5) systems at temperature $T$= 313.15 K and $P$= 0.1 MPa

| MIBK-HMF-water-[EMIM][$BF_4$]-NaCl | | | | 2-pentanol-HMF-water-[EMIM][$BF_4$]-NaCl | | | |
|---|---|---|---|---|---|---|---|
| $w_2^I$ | $D_2$ | $D_3$ | S | $w_2^I$ | $D_2$ | $D_3$ | S |
| 0.0303 | 1.61 | 0.027 | 59.6 | 0.0343 | 2.02 | 0.106 | 19.1 |
| 0.0489 | 1.53 | 0.030 | 51.0 | 0.0679 | 1.94 | 0.103 | 18.8 |
| 0.0896 | 1.53 | 0.037 | 41.4 | 0.0968 | 1.94 | 0.107 | 18.1 |
| 0.1250 | 1.49 | 0.045 | 33.1 | 0.1200 | 1.96 | 0.116 | 16.9 |
| 0.1579 | 1.50 | 0.051 | 29.4 | 0.1510 | 2.00 | 0.127 | 15.7 |
| 0.1835 | 1.54 | 0.065 | 23.7 | 0.1813 | 2.03 | 0.129 | 15.7 |
| 0.2112 | 1.47 | 0.064 | 23.0 | 0.1963 | 2.02 | 0.130 | 15.5 |
| 0.2393 | 1.52 | 0.081 | 18.8 | 0.2252 | 2.11 | 0.145 | 14.6 |

**Table B.9** Parameters of NRTL model for organic solvent (1)-HMF (2)-water (3)-[EMIM][$BF_4$] (4)- NaCl (5) systems at temperature $T$= 313.15 K and $P$= 0.1 MPa

| System | $i$-$j$ | $b_{ij}$ $^{a}$($K$) | $b_{ji}$ $^{a}$($K$) | $\alpha_{ij}$ | RMSD (%) |
|---|---|---|---|---|---|
| MIBK-HMF-water-[EMIM][$BF_4$]-NaCl | 1-5 | -9044.68$^{b}$ | 4925.37$^{b}$ | -0.0532$^{b}$ | 0.8189 |
| | 2-5 | -1776.15$^{b}$ | 1987.56$^{b}$ | -0.3133$^{b}$ | |
| | 3-5 | -13345.69$^{b}$ | 5478.59$^{b}$ | -0.0456$^{b}$ | |
| | 4-5 | 6449.31 | 1149.44 | 0.0640 | |
| 2-pentanol-HMF-water-[EMIM][$BF_4$]-NaCl | 1-5 | 366.82$^{b}$ | 4479.63$^{b}$ | 0.5220$^{b}$ | 1.6914 |
| | 2-5 | -1776.15$^{b}$ | 1987.56$^{b}$ | -0.3133$^{b}$ | |
| | 3-5 | -13345.69$^{b}$ | 5478.59$^{b}$ | -0.0456$^{b}$ | |
| | 4-5 | 6449.31 | 1149.44 | 0.0640 | |

[a] $\tau_{ij} = \frac{b_{ij}}{T}$

[b] Fixed from the quaternary LLE correlations of organic solvent-HMF-water-NaCl [Chapter 2].

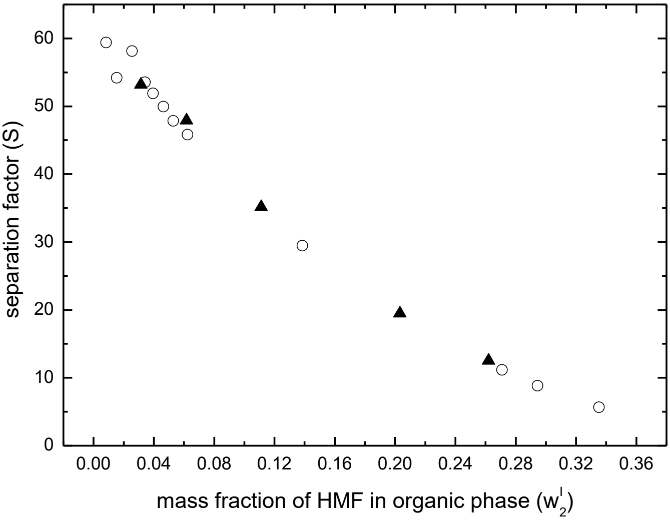


**Figure B.1** Separation factor (S) for MIBK-HMF-water system at *T*= 298.15 K and atmospheric pressure (0.1 MPa); ○ : from Mohammad *et al.* [8]; ▲ : from this study.

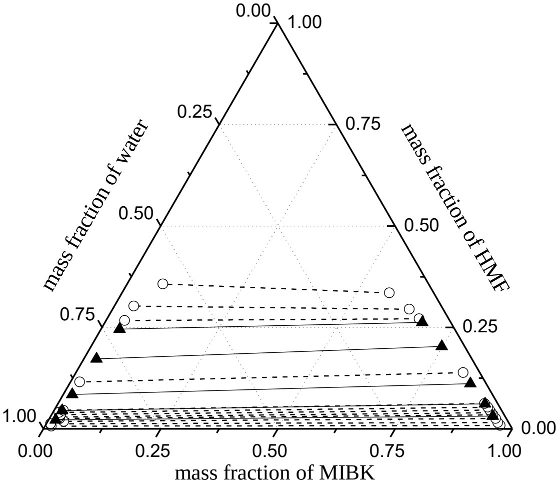
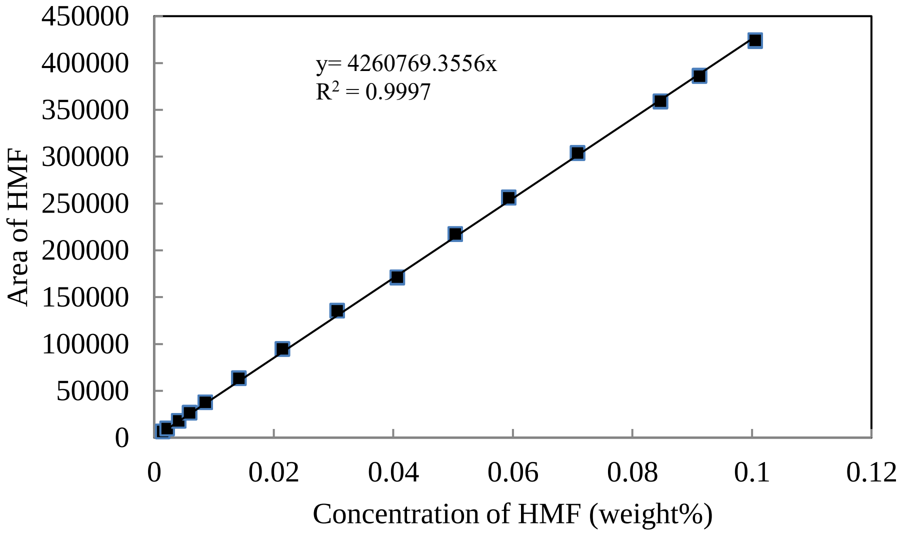
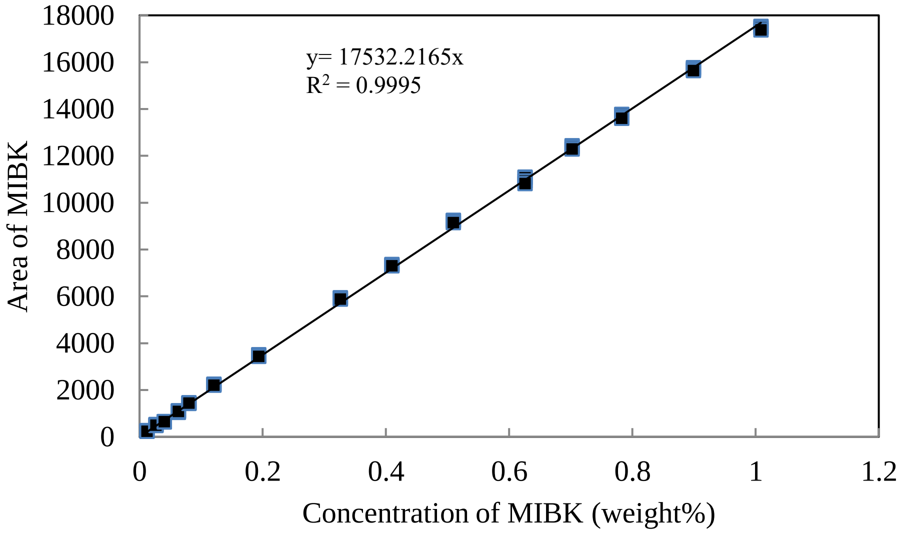


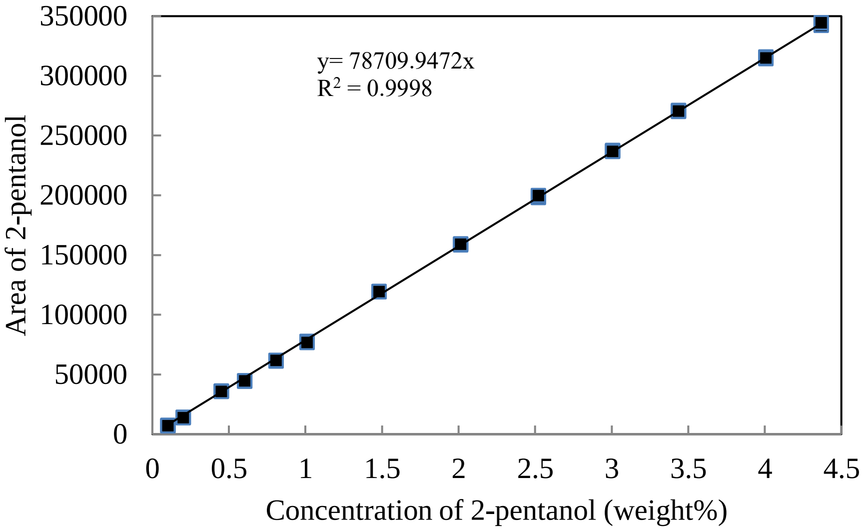
**Figure B.2** Phase diagram of the experimental LLE tie-line data for MIBK-HMF-water system at *T*= 298.15 K and atmospheric pressure (0.1 MPa); --○-- : LLE from Mohammad *et al.* [8]; —▲— : LLE from this study.


450000
400000
350000
300000
250000
200000
150000
100000
50000
0
Area of HMF
y= 4260769.3556x
R² = 0.9997
0
0.02
0.04
0.06
0.08
0.1
0.12
Concentration of HMF (weight%)

(a)


18000
16000
14000
12000
10000
8000
6000
4000
2000
0
Area of MIBK
y= 17532.2165x
R² = 0.9995
0
0.2
0.4
0.6
0.8
1
1.2
Concentration of MIBK (weight%)

(b)



(c)

**Figure B.3** Calibration curves of (a) HMF, (b) MIBK, and (c) 2-Pentanol by HPLC method.

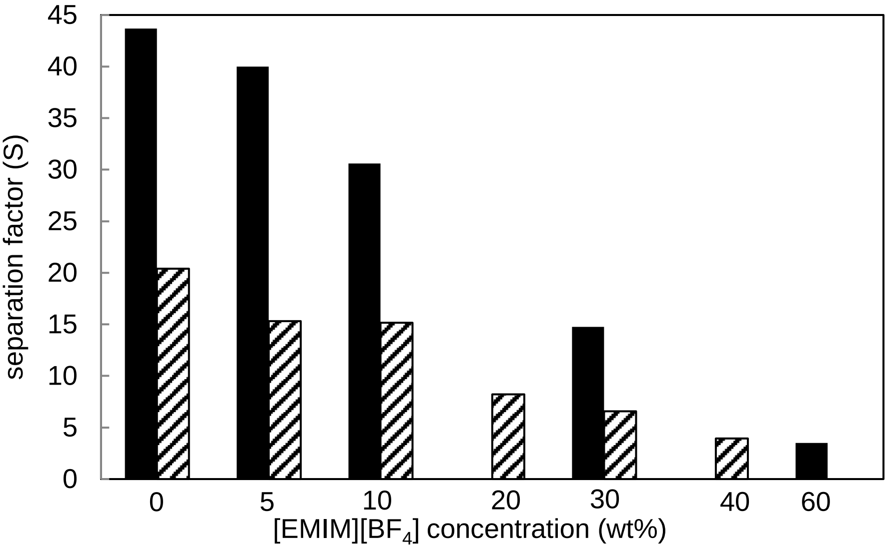


**Figure B.4** Relationship between separation factor (S) and [EMIM][BF$_4$] concentration (wt%) for MIBK-HMF-water-[EMIM][BF$_4$] systems at $T$= 313.15 K and atmospheric pressure (0.1 MPa); ■ : 10 wt% of initial HMF concentration; ▨ : 30 wt% of initial HMF concentration.

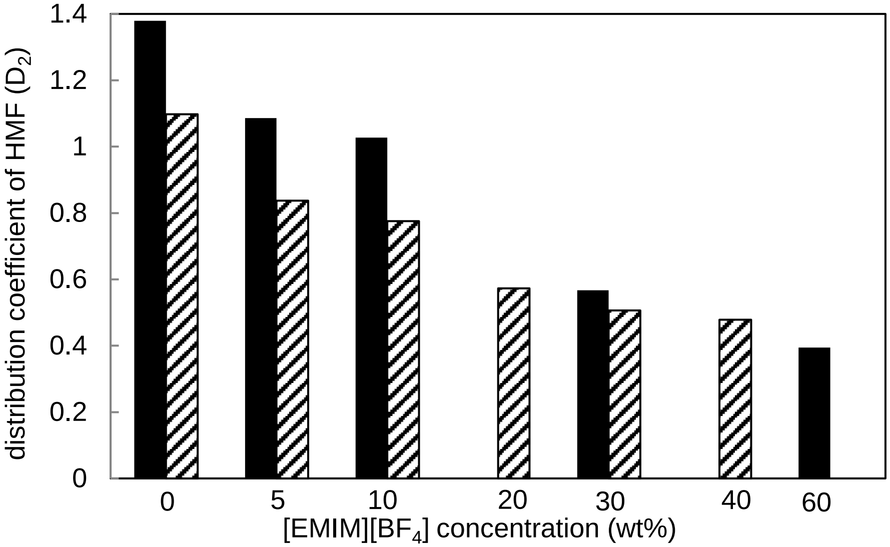


**Figure B.5** Relationship between distribution coefficient of HMF ($D_2$) and [EMIM][$BF_4$] concentration (wt%) for MIBK – HMF – water - [EMIM][$BF_4$] systems at *T*= 313.15 K and atmospheric pressure (0.1 MPa); ■ : 10 wt% of initial HMF concentration; ▨ : 30 wt% of initial HMF concentration.

## References

[B1] R. Riggio, M.H. Ubeda, J.F. Ramos, H.E. Martinez, Densities and refractive indexes of binary mixtures in the system methyl isobutyl ketone-2-butanol. Mathematical relations obtained, J. Chem. Eng. Data 25 (1980) 318–320.

[B2] B. Gonzalez, A. Dominguez, J. Tojo, Dynamic viscosities of 2-pentanol with alkanes (octane, decane, and dodecane) at three temperatures T = (293.15, 298.15, and 303.15) K. New UNIFAC-VISCO interaction parameters, J. Chem. Eng. Data 49 (2004) 1225–1230.

[B3] N. Wang, Q. Fu, G. Yang, Determination of the solubility, dissolution enthalpy and entropy of icariin in water, ethanol, and methanol, Fluid Phase Equilib. 324 (2012) 41–43.

[B4] R. Taguchi, H. Machida, Y. Sato, R.L. Smith, Jr., High-Pressure densities of 1-alkyl-3-methylimidazolium hexafluorophosphates and 1-alkyl-3-methylimidazolium tetrafluoroborates at temperatures from (313 to 473) K and at pressures up to 200 MPa, J. Chem. Eng. Data 54 (2009) 22–27.

[B5] R.H. Perry, D.W. Green, Perry's chemical enginners' handbook seventh edition, McGraw-Hill, New York, 1997.

# Appendix C

**Table C.1** Description of chemicals used in this study

| Chemical Name | CAS Number | Source | Mass Fraction Purity[a] | Purification method |
|---|---|---|---|---|
| Choline chloride | 67-48-1 | Sigma-Aldrich, China | ≥ 0.98 | No |
| Urea | 57-13-6 | Sigma-Aldrich, Germany | ≥ 0.995 | No |
| Methyl isobutyl ketone | 108-10-1 | Thermo Fisher Scientific, France | ≥ 0.99 | No |
| 2-Pentanol | 6032-29-7 | Thermo Fisher Scientific, Germany | 0.99 | No |
| 5-hydroxymethylfurfural | 67-47-0 | AVA Biochem, Switzerland | ≥ 0.99 | No |
| Sodium chloride | 7647-14-5 | Sigma-Aldrich, USA | ≥ 0.99 | No |
| Methanol | 67-56-1 | Honeywell, France | ≥ 0.999 | No |
| Methanesulfonic acid | 75-75-2 | Sigma-Aldrich, France | ≥ 0.99 | No |
| Nitric acid | 7697-37-2 | Thermo Fisher Scientific, USA | 0.70[b] | No |
| Water | 7732-18-5 | Available in our Lab. | Deionized ultrapure water | No |

[a] Purity provided by supplier

[b] Mass fraction of its aqueous solution provided by supplier

**Table C.2** Experimental and literature values of densities ($\rho$) of chemicals used in this study at temperature $T$= 293.15 K and $P$= 0.1 MPa[a].

| Chemical Name | Chemical Formula | Molecular weight (g/mol) | $\rho$ (g/cm$^3$) | |
|---|---|---|---|---|
| | | | Expt. | Lit. |
| 5-hydroxymethylfurfural | $C_6H_6O_3$ | 126.11 | - | 1.2[b] |
| Methyl isobutyl ketone | $C_6H_{12}O$ | 100.16 | 0.8010 | 0.8010[c] |
| 2-Pentanol | $C_5H_{12}O$ | 88.15 | 0.8103 | 0.8090[d] |
| Methanol | $CH_4O$ | 32.04 | 0.7919 | 0.7914[e] |
| Sodium chloride | NaCl | 58.44 | - | 2.17[f] |
| Choline chloride urea | $C_5H_{14}ClNO$-$(CH_4N_2O)_2$ | 259.74 | 1.1999 | 1.2001[g] |
| Methanesulfonic acid | $CH_4O_3S$ | 96.11 | 1.4820 | 1.48[f] |
| Nitric acid (70 wt%) | $HNO_3$ | 63.01 | 1.4128 | 1.4134[h] |
| Water | $H_2O$ | 18.02 | 0.9986 | 0.9982[h] |

[a] Standard uncertainties are $u(T)$ = 0.01 K, $u(P)$ = 0.001 MPa, and $u(\rho)$ = 0.0008 g/cm$^3$; [b] Provided by AVA Biochem; [c] Ref. [C1]; [d] Ref. [C2]; [e] Ref. [C3]; [f] Provided by Sigma-Aldrich; [g] Ref. [C4]; [h] Ref. [C5].

**Table C.3** Experimental LLE tie-line data for MIBK (1)-HMF (2)-water (3)-DES (ChCl-urea) (4) systems in mass fraction ($w_i$) at temperature $T$= 313.15 K and $P$= 0.1 MPa[a]

| DES | Organic Phase[b] | | | | Aqueous Phase[b] | | | |
|---|---|---|---|---|---|---|---|---|
| | $w_1^I$ | $w_2^I$ | $w_3^I$ | $w_4^I$ | $w_1^{II}$ | $w_2^{II}$ | $w_3^{II}$ | $w_4^{II}$ |
| 10% | 0.9305 | 0.0417 | 0.0277 | 0.0000 | 0.0062 | 0.0288 | 0.8778 | 0.0872 |
| | 0.8830 | 0.0840 | 0.0330 | 0.0000 | 0.0059 | 0.0609 | 0.8273 | 0.1058 |
| | 0.8645 | 0.1004 | 0.0351 | 0.0000 | 0.0067 | 0.0802 | 0.7993 | 0.1138 |
| | 0.8285 | 0.1296 | 0.0419 | 0.0000 | 0.0072 | 0.1060 | 0.7696 | 0.1172 |
| | 0.8015 | 0.1549 | 0.0436 | 0.0000 | 0.0050 | 0.1363 | 0.7346 | 0.1241 |
| | 0.7616 | 0.1913 | 0.0470 | 0.0001 | 0.0055 | 0.1761 | 0.6925 | 0.1260 |
| | 0.7340 | 0.2144 | 0.0515 | 0.0001 | 0.0059 | 0.2062 | 0.6577 | 0.1302 |
| | 0.6843 | 0.2516 | 0.0640 | 0.0001 | 0.0050 | 0.2458 | 0.6087 | 0.1405 |
| 20% | 0.9432 | 0.0335 | 0.0233 | 0.0000 | 0.0081 | 0.0304 | 0.8187 | 0.1429 |
| | 0.9142 | 0.0613 | 0.0245 | 0.0000 | 0.0093 | 0.0567 | 0.7705 | 0.1635 |
| | 0.8797 | 0.0897 | 0.0305 | 0.0000 | 0.0076 | 0.0854 | 0.7130 | 0.1941 |
| | 0.8594 | 0.1102 | 0.0304 | 0.0001 | 0.0087 | 0.1065 | 0.6814 | 0.2034 |
| | 0.8273 | 0.1350 | 0.0377 | 0.0001 | 0.0072 | 0.1331 | 0.6468 | 0.2128 |

| DES | Organic Phase[b] | | | | Aqueous Phase[b] | | | |
|---|---|---|---|---|---|---|---|---|
| | $w_1^{\mathrm{I}}$ | $w_2^{\mathrm{I}}$ | $w_3^{\mathrm{I}}$ | $w_4^{\mathrm{I}}$ | $w_1^{\mathrm{II}}$ | $w_2^{\mathrm{II}}$ | $w_3^{\mathrm{II}}$ | $w_4^{\mathrm{II}}$ |
| | 0.7983 | 0.1577 | 0.0439 | 0.0001 | 0.0074 | 0.1656 | 0.6115 | 0.2154 |
| | 0.7666 | 0.1936 | 0.0396 | 0.0002 | 0.0076 | 0.2171 | 0.5530 | 0.2223 |
| | 0.7460 | 0.2132 | 0.0405 | 0.0003 | 0.0087 | 0.2503 | 0.5085 | 0.2325 |
| 30% | 0.9370 | 0.0342 | 0.0288 | 0.0000 | 0.0053 | 0.0326 | 0.7169 | 0.2453 |
| | 0.9103 | 0.0612 | 0.0285 | 0.0000 | 0.0085 | 0.0598 | 0.6527 | 0.2790 |
| | 0.8828 | 0.0889 | 0.0283 | 0.0000 | 0.0084 | 0.0876 | 0.5972 | 0.3068 |
| | 0.8400 | 0.1256 | 0.0343 | 0.0001 | 0.0063 | 0.1284 | 0.5322 | 0.3331 |
| | 0.8125 | 0.1504 | 0.0370 | 0.0001 | 0.0082 | 0.1616 | 0.5016 | 0.3286 |
| | 0.7952 | 0.1692 | 0.0354 | 0.0003 | 0.0085 | 0.1917 | 0.4697 | 0.3301 |
| | 0.7788 | 0.1867 | 0.0341 | 0.0004 | 0.0067 | 0.2171 | 0.4569 | 0.3192 |
| | 0.7634 | 0.2028 | 0.0331 | 0.0007 | 0.0067 | 0.2447 | 0.4416 | 0.3070 |

[a] Standard uncertainties are $u(T) = 0.02$ K and $u(P) = 0.001$ MPa

[b] Standard uncertainties are $u(w_i) = 0.0010$ (MIBK), 0.0009 (HMF), 0.0012 (water), 0.0007 (DES)

**Table C.4** Experimental LLE tie-line data for 2-pentanol (1)-HMF (2)-water (3)- DES (ChCl-urea) (4) systems in mass fraction ($w_{\mathrm{i}}$) at temperature $T$= 313.15 K and $P$= 0.1 MPa[a]

| DES | Organic Phase[b] | | | | Aqueous Phase[b] | | | |
|---|---|---|---|---|---|---|---|---|
| | $w_1^{\mathrm{I}}$ | $w_2^{\mathrm{I}}$ | $w_3^{\mathrm{I}}$ | $w_4^{\mathrm{I}}$ | $w_1^{\mathrm{II}}$ | $w_2^{\mathrm{II}}$ | $w_3^{\mathrm{II}}$ | $w_4^{\mathrm{II}}$ |
| 10% | 0.8436 | 0.0363 | 0.1198 | 0.0004 | 0.0312 | 0.0206 | 0.8570 | 0.0911 |
| | 0.8115 | 0.0671 | 0.1208 | 0.0006 | 0.0313 | 0.0391 | 0.8148 | 0.1148 |
| | 0.7771 | 0.0965 | 0.1254 | 0.0010 | 0.0364 | 0.0609 | 0.7878 | 0.1149 |
| | 0.7472 | 0.1227 | 0.1288 | 0.0014 | 0.0382 | 0.0851 | 0.7663 | 0.1105 |
| | 0.7136 | 0.1503 | 0.1339 | 0.0022 | 0.0401 | 0.1057 | 0.7406 | 0.1136 |
| | 0.6806 | 0.1747 | 0.1417 | 0.0030 | 0.0438 | 0.1230 | 0.7124 | 0.1207 |
| | 0.6506 | 0.2007 | 0.1442 | 0.0045 | 0.0443 | 0.1497 | 0.6794 | 0.1265 |
| | 0.6240 | 0.2226 | 0.1470 | 0.0064 | 0.0524 | 0.1756 | 0.6521 | 0.1199 |
| 20% | 0.8663 | 0.0331 | 0.0995 | 0.0011 | 0.0281 | 0.0228 | 0.7831 | 0.1660 |
| | 0.8312 | 0.0641 | 0.1035 | 0.0012 | 0.0317 | 0.0448 | 0.7187 | 0.2049 |
| | 0.8050 | 0.0914 | 0.1020 | 0.0016 | 0.0336 | 0.0686 | 0.6875 | 0.2103 |
| | 0.7860 | 0.1082 | 0.1034 | 0.0025 | 0.0344 | 0.0850 | 0.6544 | 0.2262 |
| | 0.7659 | 0.1299 | 0.1007 | 0.0035 | 0.0354 | 0.1080 | 0.6211 | 0.2355 |
| | 0.7498 | 0.1483 | 0.0972 | 0.0048 | 0.0349 | 0.1353 | 0.6083 | 0.2215 |
| | 0.7062 | 0.1823 | 0.1049 | 0.0065 | 0.0448 | 0.1699 | 0.5490 | 0.2363 |

| DES | Organic Phase[b] | | | | Aqueous Phase[b] | | | |
|---|---|---|---|---|---|---|---|---|
| | $w_1^{I}$ | $w_2^{I}$ | $w_3^{I}$ | $w_4^{I}$ | $w_1^{II}$ | $w_2^{II}$ | $w_3^{II}$ | $w_4^{II}$ |
| | 0.6733 | 0.2005 | 0.1158 | 0.0103 | 0.0414 | 0.1883 | 0.5351 | 0.2351 |
| 30% | 0.8770 | 0.0325 | 0.0892 | 0.0013 | 0.0279 | 0.0230 | 0.6733 | 0.2758 |
| | 0.8465 | 0.0594 | 0.0927 | 0.0014 | 0.0290 | 0.0426 | 0.6510 | 0.2774 |
| | 0.8054 | 0.0995 | 0.0929 | 0.0023 | 0.0285 | 0.0790 | 0.5789 | 0.3136 |
| | 0.7810 | 0.1222 | 0.0931 | 0.0036 | 0.0322 | 0.1043 | 0.5533 | 0.3102 |
| | 0.7669 | 0.1393 | 0.0892 | 0.0046 | 0.0338 | 0.1321 | 0.5237 | 0.3104 |
| | 0.7319 | 0.1627 | 0.0989 | 0.0066 | 0.0333 | 0.1586 | 0.4903 | 0.3179 |
| | 0.7196 | 0.1765 | 0.0963 | 0.0076 | 0.0363 | 0.1826 | 0.4731 | 0.3080 |
| | 0.6884 | 0.1936 | 0.1069 | 0.0111 | 0.0370 | 0.2053 | 0.4448 | 0.3130 |

[a] Standard uncertainties are $u(T) = 0.02$ K and $u(P) = 0.001$ MPa

[b] Standard uncertainties are $u(w_i) = 0.0006$ (2-pentanol), 0.0009 (HMF), 0.0012 (water), 0.0007 (DES)

**Table C.5** Separation factor (S) and distribution coefficients ($D_i$) for organic solvent (1)-HMF (2)-water (3)- DES (ChCl-urea) (4) systems at temperature $T$= 313.15 K and $P$= 0.1 MPa[a]

| MIBK-HMF-water-DES | | | | | MIBK-HMF-water-DES | | | | |
|---|---|---|---|---|---|---|---|---|---|
| | $w_2^{I}$ | $D_2$ | $D_3$ | S | | $w_2^{I}$ | $D_2$ | $D_3$ | S |
| 10% | 0.0417 | 1.45 | 0.032 | 45.3 | 20% | 0.0335 | 1.10 | 0.028 | 39.3 |
| | 0.0840 | 1.38 | 0.040 | 34.5 | | 0.0613 | 1.08 | 0.032 | 33.8 |
| | 0.1004 | 1.25 | 0.044 | 28.4 | | 0.0897 | 1.05 | 0.043 | 24.4 |
| | 0.1296 | 1.22 | 0.054 | 22.6 | | 0.1102 | 1.03 | 0.045 | 22.9 |
| | 0.1549 | 1.14 | 0.059 | 19.3 | | 0.1350 | 1.01 | 0.058 | 17.4 |
| | 0.1913 | 1.09 | 0.068 | 16.0 | | 0.1577 | 0.95 | 0.072 | 13.2 |
| | 0.2144 | 1.04 | 0.078 | 13.3 | | 0.1936 | 0.89 | 0.072 | 12.4 |
| | 0.2516 | 1.02 | 0.105 | 9.7 | | 0.2132 | 0.85 | 0.080 | 10.6 |
| MIBK-HMF-water-DES | | | | | 2-pentanol-HMF-water-DES | | | | |
| | $w_2^{I}$ | $D_2$ | $D_3$ | S | | $w_2^{I}$ | $D_2$ | $D_3$ | S |
| 30% | 0.0342 | 1.05 | 0.040 | 26.3 | 10% | 0.0363 | 1.76 | 0.140 | 12.6 |
| | 0.0612 | 1.02 | 0.044 | 23.2 | | 0.0671 | 1.72 | 0.148 | 11.6 |
| | 0.0889 | 1.01 | 0.047 | 21.5 | | 0.0965 | 1.59 | 0.159 | 10.0 |
| | 0.1256 | 0.98 | 0.064 | 15.3 | | 0.1227 | 1.44 | 0.168 | 8.6 |
| | 0.1504 | 0.93 | 0.074 | 12.6 | | 0.1503 | 1.42 | 0.181 | 7.8 |
| | 0.1692 | 0.88 | 0.075 | 11.7 | | 0.1747 | 1.42 | 0.199 | 7.1 |

| | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|
| | 0.1867 | 0.86 | 0.075 | 11.5 | | 0.2007 | 1.34 | 0.212 | 6.3 |
| | 0.2028 | 0.83 | 0.075 | 11.1 | | 0.2226 | 1.27 | 0.225 | 5.6 |
| | 2-pentanol-HMF-water-DES | | | | | 2-pentanol-HMF-water-DES | | | |
| | $w_2^I$ | $D_2$ | $D_3$ | S | | $w_2^I$ | $D_2$ | $D_3$ | S |
| 20% | 0.0331 | 1.46 | 0.127 | 11.5 | 30% | 0.0325 | 1.41 | 0.132 | 10.7 |
| | 0.0641 | 1.43 | 0.144 | 9.9 | | 0.0594 | 1.39 | 0.142 | 9.8 |
| | 0.0914 | 1.33 | 0.148 | 9.0 | | 0.0995 | 1.26 | 0.160 | 7.9 |
| | 0.1082 | 1.27 | 0.158 | 8.0 | | 0.1222 | 1.17 | 0.168 | 7.0 |
| | 0.1299 | 1.20 | 0.162 | 7.4 | | 0.1393 | 1.05 | 0.170 | 6.2 |
| | 0.1483 | 1.10 | 0.160 | 6.9 | | 0.1627 | 1.03 | 0.202 | 5.1 |
| | 0.1823 | 1.07 | 0.191 | 5.6 | | 0.1765 | 0.97 | 0.203 | 4.8 |
| | 0.2005 | 1.06 | 0.216 | 4.9 | | 0.1936 | 0.94 | 0.240 | 3.9 |

[a] Standard uncertainties are $u(T) = 0.02$ K and $u(P) = 0.001$ MPa

**Table C.6** Experimental LLE tie-line data for organic solvent (1)-HMF (2)-water (3)- DES (ChCl-urea) (4)-NaCl (5) systems in mass fraction ($w_i$) at temperature $T$= 313.15 K and $P$= 0.1 MPa[a]

| MIBK (1)-HMF (2)-water (3)- DES (ChCl-urea) (4)-NaCl (5) | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|
| Organic Phase[b] | | | | | Aqueous Phase[b] | | | | |
| $w_1^{I}$ | $w_2^{I}$ | $w_3^{I}$ | $w_4^{I}$ | $w_5^{I}$ | $w_1^{II}$ | $w_2^{II}$ | $w_3^{II}$ | $w_4^{II}$ | $w_5^{II}$ |
| 0.9376 | 0.0411 | 0.0213 | 0.0000 | 0.0000 | 0.0042 | 0.0179 | 0.8367 | 0.0759 | 0.0654 |
| 0.9157 | 0.0613 | 0.0229 | 0.0000 | 0.0000 | 0.0057 | 0.0274 | 0.8116 | 0.0861 | 0.0692 |
| 0.8878 | 0.0877 | 0.0244 | 0.0000 | 0.0001 | 0.0053 | 0.0455 | 0.7873 | 0.0971 | 0.0649 |
| 0.8603 | 0.1131 | 0.0264 | 0.0001 | 0.0001 | 0.0055 | 0.0599 | 0.7644 | 0.1000 | 0.0702 |
| 0.8325 | 0.1397 | 0.0276 | 0.0001 | 0.0000 | 0.0049 | 0.0747 | 0.7324 | 0.1118 | 0.0763 |
| 0.8180 | 0.1537 | 0.0280 | 0.0002 | 0.0000 | 0.0042 | 0.0836 | 0.7159 | 0.1154 | 0.0809 |
| 0.7961 | 0.1752 | 0.0284 | 0.0003 | 0.0000 | 0.0060 | 0.0961 | 0.6952 | 0.1165 | 0.0862 |
| 0.7547 | 0.2169 | 0.0279 | 0.0005 | 0.0000 | 0.0062 | 0.1192 | 0.6639 | 0.1178 | 0.0929 |
| 2-pentanol (1)-HMF (2)-water (3)- DES (ChCl-urea) (4)-NaCl (5) | | | | | | | | | |
| Organic Phase[b] | | | | | Aqueous Phase[b] | | | | |
| $w_1^{I}$ | $w_2^{I}$ | $w_3^{I}$ | $w_4^{I}$ | $w_5^{I}$ | $w_1^{II}$ | $w_2^{II}$ | $w_3^{II}$ | $w_4^{II}$ | $w_5^{II}$ |
| 0.8832 | 0.0430 | 0.0730 | 0.0006 | 0.0002 | 0.0125 | 0.0162 | 0.8039 | 0.1089 | 0.0585 |
| 0.8330 | 0.0805 | 0.0855 | 0.0008 | 0.0002 | 0.0119 | 0.0311 | 0.7760 | 0.1124 | 0.0687 |
| 0.8159 | 0.1000 | 0.0827 | 0.0011 | 0.0002 | 0.0113 | 0.0412 | 0.7641 | 0.1087 | 0.0748 |
| 0.7845 | 0.1328 | 0.0807 | 0.0017 | 0.0003 | 0.0108 | 0.0560 | 0.7409 | 0.1158 | 0.0765 |
| 0.7573 | 0.1590 | 0.0777 | 0.0023 | 0.0037 | 0.0101 | 0.0698 | 0.7261 | 0.1120 | 0.0820 |
| 0.7228 | 0.1932 | 0.0770 | 0.0033 | 0.0037 | 0.0105 | 0.0855 | 0.7122 | 0.1098 | 0.0820 |
| 0.6957 | 0.2202 | 0.0766 | 0.0047 | 0.0029 | 0.0098 | 0.0965 | 0.6973 | 0.1124 | 0.0840 |
| 0.6835 | 0.2383 | 0.0702 | 0.0054 | 0.0025 | 0.0085 | 0.1071 | 0.6769 | 0.1067 | 0.1008 |

[a] Standard uncertainties are $u(T) = 0.02$ K and $u(P) = 0.001$ MPa

[b] Standard uncertainties are $u(w_i) = 0.0010$ (MIBK), 0.0006 (2-pentanol), 0.0009 (HMF), 0.0012 (water), 0.0007 (DES), 0.0004 (NaCl)

**Table C.7** Validation results of the experimental LLE data of the studied systems for MIBK (1)-HMF (2)-water (3)-DES (ChCl-urea) (4)-NaCl (5) in mass fraction ($w_i$) at temperature $T$= 313.15 K and $P$= 0.1 MPa[a]

| Phase | Experimental LLE data of the studied systems (taken from Tables C.3 & C.6) | | | | | Validation Experimental LLE data | | | | |
|---|---|---|---|---|---|---|---|---|---|---|
| | $w_1$ | $w_2$ | $w_3$ | $w_4$ | $w_5$ | $w_1$[b] | $w_2$[b] | $w_3$[c] | $w_4$[d] | $w_5$[e] |
| Organic | 0.8830 | 0.0840 | 0.0330 | 0.0000 | 0.0000 | 0.8884 | 0.0848 | 0.0267 | 0.0000 | 0.0000 |
| Aqueous | 0.0059 | 0.0609 | 0.8273 | 0.1058 | 0.0000 | 0.0060 | 0.0609 | 0.8294 | 0.1036 | 0.0000 |
| Organic | 0.7616 | 0.1913 | 0.0470 | 0.0001 | 0.0000 | 0.7598 | 0.1917 | 0.0484 | 0.0001 | 0.0000 |
| Aqueous | 0.0055 | 0.1761 | 0.6925 | 0.1260 | 0.0000 | 0.0056 | 0.1763 | 0.6920 | 0.1261 | 0.0000 |
| Organic | 0.9103 | 0.0612 | 0.0285 | 0.0000 | 0.0000 | 0.9135 | 0.0613 | 0.0251 | 0.0001 | 0.0000 |
| Aqueous | 0.0085 | 0.0598 | 0.6527 | 0.2790 | 0.0000 | 0.0085 | 0.0598 | 0.6553 | 0.2765 | 0.0000 |
| Organic | 0.7952 | 0.1692 | 0.0354 | 0.0003 | 0.0000 | 0.7963 | 0.1688 | 0.0348 | 0.0001 | 0.0000 |
| Aqueous | 0.0085 | 0.1917 | 0.4697 | 0.3301 | 0.0000 | 0.0086 | 0.1913 | 0.4724 | 0.3278 | 0.0000 |
| Organic | 0.8180 | 0.1537 | 0.0280 | 0.0002 | 0.0000 | 0.8151 | 0.1552 | 0.0296 | 0.0000 | 0.0000 |
| Aqueous | 0.0042 | 0.0836 | 0.7159 | 0.1154 | 0.0809 | 0.0042 | 0.0839 | 0.6851 | 0.1191 | 0.1077 |

[a] Standard uncertainties are $u(T) = 0.02$ K and $u(P) = 0.001$ MPa
[b] HPLC instrument
[c] Karl Fischer instrument
[d] High Resolution Mass Spectrometer (ChCl) and UV-Vis Spectrofotometer (Urea) instruments
[e] ICP-OES instrument

## Analytical measurements for validation results of experimental LLE data (Table C.7)

The samples for validation in Table C.7 were analysed using several analytical instruments. HPLC equipped with a reversed phase column Phenomenex Gemini-NX 5µ C18 110A was applied to determine MIBK and HMF concentrations in both phases at 42°C. The UV/VIS (ultraviolet–visible) detector was used at a UV-wavelength of 278 nm. A mixture of water and methanol with volume ratio of 25:75 was prepared as eluent with flowrate of 1 mL/min for MIBK determination. The peak area of MIBK was detected with peak maxima at 3.6 mins. While for HMF determination, a mixture of water and methanol with a volume ratio of 95:5 was prepared with a flowrate of 1 mL/min. The peak area of HMF was detected with peak maxima at 6.7 min. The amount of water in the organic phase was measured by Karl Fischer titration using a Metrohm 737 KF. Whereas, the water content in the aqueous phase was determined by subtracting the sum of the other mass fractions from a value of 1. High Resolution Mass Spectrometer equipped with Electrospray + and Electrospray – was used to determine ChCl concentrations in both phases. Capillary Voltage was 3.5 and 2.2 kv for electrospray + and electrospray –, respectively. Each electrospray operating condition such as Extractor, Source Temperature, Desolvation Temperature, Desolvation Gas Flow, Cone Gas Flow, Mass Scan range, and Scan Rate were 60 v, 120°C, 400°C, 600 L/hr, 20 L/hr, 50-1200 Da, and 0.5 Da/s, respectively. While, UV-Vis Spectrofotometer was applied to determine Urea concentrations in both phases at a UV-wavelength of 553 nm using Urease as a reagent. In addition, ICP-OES (Inductively Coupled Plasma Optical Emission Spectroscopy) was used to analyse the concentrations of NaCl in both phases using 5% of $HNO_3$ as diluent. The mass fractions of each component in each phase were averaged from three replicated samples.

**Table C.8** Separation factor (S) and distribution coefficients ($D_i$) for organic solvent (1)-HMF (2)-water (3)- DES (ChCl-urea) (4)-NaCl (5) systems at temperature $T$= 313.15 K and $P$= 0.1 MPa[a]

| MIBK-HMF-water-DES-NaCl | | | | 2-pentanol-HMF-water-DES-NaCl | | | |
|---|---|---|---|---|---|---|---|
| $w_2^I$ | $D_2$ | $D_3$ | S | $w_2^I$ | $D_2$ | $D_3$ | S |
| 0.0411 | 2.30 | 0.025 | 92.0 | 0.0430 | 2.65 | 0.091 | 29.1 |
| 0.0613 | 2.24 | 0.028 | 80.0 | 0.0805 | 2.59 | 0.110 | 23.5 |
| 0.0877 | 1.93 | 0.031 | 62.3 | 0.1000 | 2.43 | 0.108 | 22.5 |
| 0.1131 | 1.89 | 0.035 | 54.0 | 0.1328 | 2.37 | 0.109 | 21.7 |
| 0.1397 | 1.87 | 0.038 | 49.2 | 0.1590 | 2.28 | 0.107 | 21.3 |
| 0.1537 | 1.84 | 0.039 | 47.2 | 0.1932 | 2.26 | 0.108 | 20.9 |
| 0.1752 | 1.82 | 0.041 | 44.4 | 0.2202 | 2.28 | 0.110 | 20.7 |
| 0.2169 | 1.82 | 0.042 | 43.3 | 0.2383 | 2.22 | 0.104 | 21.3 |

[a] Standard uncertainties are $u(T)$ = 0.02 K and $u(P)$ = 0.001 MPa

**Table C.9** Parameters of NRTL model for organic solvent (1)-HMF (2)-water (3)-DES (ChCl-urea) (4) systems at temperature $T$= 313.15 K and $P$= 0.1 MPa

| System | $i$-$j$ | $b_{ij}$ [a]($K$) | $b_{ji}$ [a]($K$) | $\alpha_{ij}$ | RMSD (%) |
|---|---|---|---|---|---|
| MIBK-HMF-water-DES | 1-2 | 483.26[b] | -738.00[b] | 0.20 | 0.8800 |
| | 1-3 | 199.41[b] | 1722.53[b] | 0.20 | |
| | 1-4 | 2744.37 | 1297.66 | 0.20 | |
| | 2-3 | -379.83[b] | 310.86[b] | 0.20 | |
| | 2-4 | 5890.33 | -1928.88 | 0.20 | |
| | 3-4 | 1878.56 | -1116.24 | 0.20 | |
| | 1-2 | 911.98[b] | -754.74[b] | 0.20 | |
| | 1-3 | -205.68[b] | 1777.28[b] | 0.20 | |

| System | *i-j* | $b_{ij}$ [a]($K$) | $b_{ji}$ [a]($K$) | $\alpha_{ij}$ | RMSD (%) |
|---|---|---|---|---|---|
| 2-pentanol-HMF-water-DES | 1-4 | 3984.04 | 206.43 | 0.20 | 1.9837 |
| | 2-3 | -379.83[b] | 310.86[b] | 0.20 | |
| | 2-4 | 5890.33 | -1928.88 | 0.20 | |
| | 3-4 | 1878.56 | -1116.24 | 0.20 | |

[a] $\tau_{ij} = \frac{b_{ij}}{T}$

[b] Fixed from the ternary LLE correlations of organic solvent-HMF-water [Chapter 2].

**Table C.10** Parameters of NRTL model for organic solvent (1)-HMF (2)-water (3)- DES **(**ChCl-urea**)** (4)-NaCl (5) systems at temperature $T$= 313.15 K and $P$= 0.1 MPa

| System | *i-j* | $b_{ij}$ [a]($K$) | $b_{ji}$ [a]($K$) | $\alpha_{ij}$ | RMSD (%) |
|---|---|---|---|---|---|
| MIBK-HMF-water-DES-NaCl | 1-5 | -9044.68[b] | 4925.37[b] | -0.0532[b] | 0.5532 |
| | 2-5 | -1776.15[b] | 1987.56[b] | -0.3133[b] | |
| | 3-5 | -13345.69[b] | 5478.59[b] | -0.0456[b] | |
| | 4-5 | -4442.97 | -4915.83 | 0.1245 | |
| 2-pentanol-HMF-water-DES-NaCl | 1-5 | 366.82[b] | 4479.63[b] | 0.5220[b] | 1.4353 |
| | 2-5 | -1776.15[b] | 1987.56[b] | -0.3133[b] | |
| | 3-5 | -13345.69[b] | 5478.59[b] | -0.0456[b] | |
| | 4-5 | -4442.97 | -4915.83 | 0.1245 | |

[a] $\tau_{ij} = \frac{b_{ij}}{T}$

[b] Fixed from the quaternary LLE correlations of organic solvent-HMF-water-NaCl [Chapter 2].

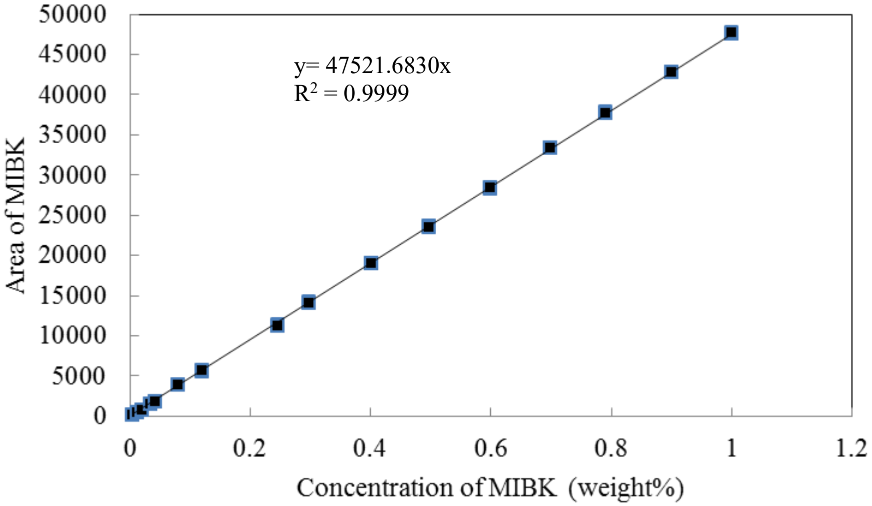


**Figure C.1** Calibration curve of MIBK (in LLE of MIBK-HMF-water-ChCl-urea-NaCl) by HPLC method.

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## Appendix D

**Table D.1** Description of chemicals used in this study

| Chemical Name | Source | Mass Fraction Purity | Purification method |
|---|---|---|---|
| 5-hydroxymethylfurfural | AVA Biochem, Switzerland | ≥ 0.99 | No |
| Methyl isobutyl ketone | Thermo Fisher Scientific, France | ≥ 0.99 | No |
| 1-ethyl-3-methylimidazolium tetrafluoroborate | Sigma-Aldrich, USA | ≥ 0.98 | No |
| Choline chloride | Sigma-Aldrich, China | ≥ 0.98 | No |
| Urea | Sigma-Aldrich, Germany | ≥ 0.995 | No |
| Sodium chloride | Sigma-Aldrich, USA | ≥ 0.99 | No |
| Fructose | Sigma-Aldrich, USA | ≥ 0.99 | No |
| Methanol | Honeywell, France | ≥ 0.999 | No |
| Methanesulfonic acid | Sigma-Aldrich (France) | ≥ 0.99 | No |
| Nitric acid | Thermo Fisher Scientific, USA | 0.70 | No |
| Water | Available in our Lab. | Deionized ultrapure water | No |

**Table D.2** Experimental LLE tie-line data of MIBK (1)-HMF (2)-water (3)-[EMIM][$BF_4$] (4)-NaCl (5)-fructose (6) system in mass fraction ($w_i$) at temperature $T$= 313.15 K and $P$= 0.1 MPa[a]

| Organic Phase | | | | | | Aqueous Phase | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|
| $w_1^{I}$ | $w_2^{I}$ | $w_3^{I}$ | $w_4^{I}$ | $w_5^{I}$ | $w_6^{I}$ | $w_1^{II}$ | $w_2^{II}$ | $w_3^{II}$ | $w_4^{II}$ | $w_5^{I}$ | $w_6^{I}$ |
| 0.9435 | 0.0352 | 0.0175 | 0.0031 | 0.0001 | 0.0005 | 0.0026 | 0.0220 | 0.6440 | 0.1145 | 0.1091 | 0.1078 |
| 0.9067 | 0.0676 | 0.0204 | 0.0046 | 0.0001 | 0.0006 | 0.0043 | 0.0461 | 0.5956 | 0.1173 | 0.1210 | 0.1156 |
| 0.8719 | 0.0975 | 0.0227 | 0.0069 | 0.0002 | 0.0008 | 0.0053 | 0.0681 | 0.5698 | 0.1219 | 0.1172 | 0.1178 |
| 0.8449 | 0.1200 | 0.0247 | 0.0094 | 0.0006 | 0.0006 | 0.0053 | 0.0911 | 0.5379 | 0.1202 | 0.1229 | 0.1225 |
| 0.8047 | 0.1551 | 0.0260 | 0.0124 | 0.0011 | 0.0007 | 0.0058 | 0.1052 | 0.5072 | 0.1203 | 0.1292 | 0.1324 |
| 0.7622 | 0.1912 | 0.0275 | 0.0173 | 0.0012 | 0.0006 | 0.0063 | 0.1331 | 0.4646 | 0.1169 | 0.1350 | 0.1442 |
| 0.7345 | 0.2150 | 0.0280 | 0.0209 | 0.0013 | 0.0003 | 0.0048 | 0.1439 | 0.4411 | 0.1170 | 0.1466 | 0.1466 |

[a] Standard uncertainties are $u(T)$ = 0.02 K, $u(P)$ = 0.001 MPa, and $u(w_i)$ = 0.0004 (MIBK), 0.0005 (HMF), 0.0009 (water), 0.0006 ([EMIM][$BF_4$]), 0.0007 (NaCl), 0.0004 (fructose).

**Table D.3** Experimental LLE tie-line data of MIBK (1)-HMF (2)-water (3)-ChCl-urea (4)-NaCl (5)-fructose (6) system in mass fraction ($w_i$) at temperature $T$= 313.15 K and $P$= 0.1 MPa[a]

| Organic Phase | | | | | | Aqueous Phase | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|
| $w_1^{I}$ | $w_2^{I}$ | $w_3^{I}$ | $w_4^{I}$ | $w_5^{I}$ | $w_6^{I}$ | $w_1^{II}$ | $w_2^{II}$ | $w_3^{II}$ | $w_4^{II}$ | $w_5^{I}$ | $w_6^{I}$ |
| 0.9397 | 0.0394 | 0.0200 | 0.0000 | 0.0006 | 0.0003 | 0.0010 | 0.0196 | 0.6955 | 0.0686 | 0.1146 | 0.1008 |
| 0.9108 | 0.0693 | 0.0192 | 0.0000 | 0.0004 | 0.0003 | 0.0032 | 0.0380 | 0.6469 | 0.0768 | 0.1265 | 0.1086 |
| 0.8680 | 0.1086 | 0.0228 | 0.0000 | 0.0002 | 0.0004 | 0.0032 | 0.0577 | 0.6069 | 0.0821 | 0.1353 | 0.1149 |
| 0.8311 | 0.1442 | 0.0239 | 0.0000 | 0.0003 | 0.0004 | 0.0039 | 0.0818 | 0.5749 | 0.0877 | 0.1361 | 0.1155 |
| 0.8113 | 0.1634 | 0.0248 | 0.0001 | 0.0002 | 0.0002 | 0.0033 | 0.0944 | 0.5559 | 0.0915 | 0.1312 | 0.1237 |
| 0.7738 | 0.2005 | 0.0251 | 0.0001 | 0.0002 | 0.0002 | 0.0032 | 0.1175 | 0.5229 | 0.0987 | 0.1354 | 0.1223 |
| 0.7548 | 0.2202 | 0.0243 | 0.0002 | 0.0003 | 0.0002 | 0.0034 | 0.1319 | 0.4774 | 0.1051 | 0.1494 | 0.1328 |

[a] Standard uncertainties are $u(T)$ = 0.02 K, $u(P)$ = 0.001 MPa, and $u(w_i)$ = 0.0004 (MIBK), 0.0005 (HMF), 0.0009 (water), 0.0002 (ChCl-urea), 0.0007 (NaCl), 0.0004 (fructose).

**Table D.4** Separation factor (S) and distribution coefficients ($D_i$) for MIBK (1)-HMF (2)-water (3)-[EMIM][$BF_4$] or ChCl-urea (4)-NaCl (5)-fructose (6) systems at temperature $T$= 313.15 K and $P$= 0.1 MPa

| MIBK-HMF-water-[EMIM][$BF_4$]-NaCl- fructose | | | | MIBK-HMF-water-ChCl-urea-NaCl- fructose | | | |
|---|---|---|---|---|---|---|---|
| $w_2^I$ | $D_2$ | $D_3$ | S | $w_2^I$ | $D_2$ | $D_3$ | S |
| 0.0352 | 1.60 | 0.027 | 59.3 | 0.0394 | 2.02 | 0.029 | 69.7 |
| 0.0676 | 1.46 | 0.034 | 42.9 | 0.0693 | 1.83 | 0.030 | 61.0 |
| 0.0975 | 1.43 | 0.040 | 35.8 | 0.1086 | 1.88 | 0.038 | 49.5 |
| 0.1200 | 1.32 | 0.046 | 28.7 | 0.1442 | 1.76 | 0.042 | 41.9 |
| 0.1551 | 1.47 | 0.051 | 28.8 | 0.1634 | 1.73 | 0.045 | 38.4 |
| 0.1912 | 1.44 | 0.059 | 24.4 | 0.2005 | 1.71 | 0.048 | 35.6 |
| 0.2150 | 1.49 | 0.064 | 23.3 | 0.2202 | 1.67 | 0.051 | 32.7 |

**Table D.5** Parameters of NRTL model for MIBK (1)-HMF (2)-water (3)-[EMIM][$BF_4$] or ChCl-urea (4)-NaCl (5)-fructose (6) systems at temperature $T$= 313.15 K and $P$= 0.1 MPa

| System | $i$-$j$ | $b_{ij}$ $^{a}$($K$) | $b_{ji}$ $^{a}$($K$) | $\alpha_{ij}$ | RMSD (%) |
|---|---|---|---|---|---|
| MIBK-HMF-water-[EMIM][$BF_4$]-NaCl-fructose | 1-2 | 483.26$^{b}$ | -738.00$^{b}$ | 0.2000 | 0.3684 |
| | 1-3 | 199.41$^{b}$ | 1722.53$^{b}$ | 0.2000 | |
| | 1-4 | 290.07$^{c}$ | 8545.18$^{c}$ | 0.2000 | |
| | 1-5 | -9044.68$^{b}$ | 4925.37$^{b}$ | -0.0532$^{b}$ | |
| | 1-6 | 3304.23 | 948.37 | 0.2000 | |
| | 2-3 | -379.83$^{b}$ | 310.86$^{b}$ | 0.2000 | |
| | 2-4 | -270.18$^{c}$ | -1282.76$^{c}$ | 0.2000 | |
| | 2-5 | -1776.15$^{b}$ | 1987.56$^{b}$ | -0.3133$^{b}$ | |
| | 2-6 | -9014.87 | 4610.43 | 0.2000 | |
| | 3-4 | 3177.31$^{c}$ | -1492.19$^{c}$ | 0.2000 | |
| | 3-5 | -13345.69$^{b}$ | 5478.59$^{b}$ | -0.0456$^{b}$ | |
| | 3-6 | -6718.90 | -1049.84 | 0.2000 | |
| | 4-5 | 6449.31$^{c}$ | 1149.44$^{c}$ | 0.0640$^{c}$ | |
| | 4-6 | -6798.23 | 1405.41 | 0.2000 | |
| | 5-6 | 5154.65 | -8697.13 | 0.0222 | |
| | 1-2 | 483.26$^{b}$ | -738.00$^{b}$ | 0.2000 | |
| | 1-3 | 199.41$^{b}$ | 1722.53$^{b}$ | 0.2000 | |
| | 1-4 | 2744.37 | 1297.66 | 0.2000 | |
| | 1-5 | -9044.68$^{b}$ | 4925.37$^{b}$ | -0.0532b | |

| System | $i$-$j$ | $b_{ij}$ [a]($K$) | $b_{ji}$ [a]($K$) | $\alpha_{ij}$ | RMSD (%) |
|---|---|---|---|---|---|
| MIBK-HMF-water-ChCl-urea-NaCl-fructose | 1-6 | 3304.23 | 948.37 | 0.2000 | 0.7132 |
| | 2-3 | -379.83[b] | 310.86[b] | 0.2000 | |
| | 2-4 | 5890.33[d] | -1928.88[d] | 0.2000 | |
| | 2-5 | -1776.15[b] | 1987.56[b] | -0.3133[b] | |
| | 2-6 | -9014.87 | 4610.43 | 0.2000 | |
| | 3-4 | 1878.56[d] | -1116.24[d] | 0.2000 | |
| | 3-5 | -13345.69[b] | 5478.5[b] | -0.045[b] | |
| | 3-6 | -6718.90 | -1049.84 | 0.2000 | |
| | 4-5 | -4442.97[d] | -4915.83[d] | 0.1245[d] | |
| | 4-6 | -7499.40 | -966.40 | 0.2000 | |
| | 5-6 | 5154.65 | -8697.13 | 0.0222 | |

[a] $\tau_{ij} = \frac{b_{ij}}{T}$

[b] Fixed from the LLE correlations of MIBK-HMF-water and MIBK-HMF-water-NaCl [Chapter 2].

[c] Fixed from the LLE correlations of MIBK-HMF-water-[EMIM][$BF_4$] and MIBK-HMF-water-[EMIM][$BF_4$]-NaCl [Chapter 3].

[d] Fixed from the LLE correlations of MIBK-HMF-water-ChCl-urea and MIBK-HMF-water-ChCl-urea-NaCl [Chapter 4].

**Table D.6** Correlated results of the Hand and Othmer-Tobias equations for MIBK (1)-HMF (2)-water (3)-[EMIM][$BF_4$] or ChCl-urea (4)-NaCl (5)-fructose (6) systems at temperature $T$= 313.15 K and $P$= 0.1 MPa

| System | Hand Correlation | | | Othmer-Tobias Correlation | | |
|---|---|---|---|---|---|---|
| | $a^*$ | $b^*$ | $R^2$ | $a$ | $b$ | $R^2$ |
| MIBK-HMF-water-[EMIM][$BF_4$]-NaCl-fructose | -0.2509 | 0.9094 | 0.9962 | -1.4316 | 2.1443 | 0.9808 |
| MIBK-HMF-water-ChCl-urea-NaCl-fructose | -0.0728 | 0.8684 | 0.9981 | -1.1219 | 1.8829 | 0.9703 |

## Appendix E

**Table E.1** Description of chemicals used in this study

| Chemical Name | Source | Mass Fraction Purity | Purification method |
|---|---|---|---|
| 5-hydroxymethylfurfural | AVA Biochem, Switzerland | ≥ 0.99 | No |
| Tributyl phosphate | Sigma-Aldrich, Germany | ≥ 0.99 | No |
| Choline chloride | Sigma-Aldrich, China | ≥ 0.98 | No |
| Urea | Sigma-Aldrich, Germany | ≥ 0.995 | No |
| Sodium chloride | Sigma-Aldrich, USA | ≥ 0.99 | No |
| Fructose | Sigma-Aldrich, USA | ≥ 0.99 | No |
| Methyl isobutyl ketone | Thermo Fisher Scientific, France | ≥ 0.99 | No |
| 1-ethyl-3-methylimidazolium tetrafluoroborate | Sigma-Aldrich, USA | ≥ 0.98 | No |
| Methanol | Honeywell, France | ≥ 0.999 | No |
| Methanesulfonic acid | Sigma-Aldrich, France | ≥ 0.99 | No |
| Nitric acid | Thermo Fisher Scientific, USA | 0.70 | No |
| Water | Available in our Lab. | Deionized ultrapure water | No |

**Table E.2** Experimental LLE tie-line data of the TBP (1)-HMF (2)-water (3) system in mass fraction ($w_i$) at temperature $T$= 298.15 and 313.15 K and $P$= 0.1 MPa[a]

| Temperature (K) | Organic Phase | | | Aqueous Phase | | |
|---|---|---|---|---|---|---|
| | $w_1^{I}$ | $w_2^{I}$ | $w_3^{I}$ | $w_1^{II}$ | $w_2^{II}$ | $w_3^{II}$ |
| 298.15 | 0.8941 | 0.0459 | 0.0601 | 0.0006 | 0.0129 | 0.9865 |
| | 0.8501 | 0.0915 | 0.0585 | 0.0007 | 0.0283 | 0.9710 |
| | 0.8122 | 0.1245 | 0.0633 | 0.0010 | 0.0463 | 0.9527 |
| | 0.7815 | 0.1580 | 0.0605 | 0.0010 | 0.0624 | 0.9366 |
| | 0.7578 | 0.1810 | 0.0611 | 0.0011 | 0.0826 | 0.9163 |
| | 0.7268 | 0.2099 | 0.0633 | 0.0013 | 0.1083 | 0.8904 |
| | 0.6925 | 0.2460 | 0.0615 | 0.0020 | 0.1681 | 0.8299 |
| | 0.6422 | 0.2874 | 0.0705 | 0.0063 | 0.2886 | 0.7051 |
| 313.15 | 0.8893 | 0.0508 | 0.0599 | 0.0008 | 0.0137 | 0.9855 |
| | 0.8369 | 0.1058 | 0.0573 | 0.0005 | 0.0326 | 0.9670 |
| | 0.8242 | 0.1225 | 0.0533 | 0.0002 | 0.0488 | 0.9509 |
| | 0.7647 | 0.1741 | 0.0613 | 0.0002 | 0.0708 | 0.9289 |
| | 0.7348 | 0.2079 | 0.0573 | 0.0004 | 0.1004 | 0.8992 |
| | 0.7232 | 0.2167 | 0.0601 | 0.0005 | 0.1274 | 0.8721 |
| | 0.6190 | 0.3188 | 0.0622 | 0.0015 | 0.1909 | 0.8076 |
| | 0.5964 | 0.3419 | 0.0616 | 0.0041 | 0.2822 | 0.7137 |

[a] Standard uncertainties are $u(T)$ = 0.02 K, $u(P)$ = 0.001 MPa, and $u(w_i)$ = 0.0012 (TBP), 0.0010 (HMF), and 0.0009 (water).

**Table E.3** Experimental LLE tie-line data of TBP (1)-HMF (2)-water (3)-ChCl-urea (4) systems in mass fraction ($w_i$) at temperature $T$= 313.15 K and $P$= 0.1 MPa[a]

| Organic Phase | | | | Aqueous Phase | | | |
|---|---|---|---|---|---|---|---|
| $w_1^{I}$ | $w_2^{I}$ | $w_3^{I}$ | $w_4^{I}$ | $w_1^{II}$ | $w_2^{II}$ | $w_3^{II}$ | $w_4^{II}$ |
| 0.8995 | 0.0406 | 0.0599 | 0.0001 | 0.0009 | 0.0137 | 0.9069 | 0.0786 |
| 0.8758 | 0.0728 | 0.0513 | 0.0001 | 0.0011 | 0.0288 | 0.8876 | 0.0825 |
| 0.8285 | 0.1160 | 0.0554 | 0.0000 | 0.0007 | 0.0575 | 0.8516 | 0.0902 |
| 0.7915 | 0.1555 | 0.0529 | 0.0001 | 0.0036 | 0.0907 | 0.8155 | 0.0902 |
| 0.7704 | 0.1740 | 0.0555 | 0.0001 | 0.0030 | 0.1021 | 0.7951 | 0.0998 |
| 0.7469 | 0.2004 | 0.0526 | 0.0001 | 0.0028 | 0.1364 | 0.7550 | 0.1058 |
| 0.7271 | 0.2205 | 0.0523 | 0.0002 | 0.0025 | 0.1717 | 0.7098 | 0.1160 |
| 0.7045 | 0.2434 | 0.0520 | 0.0000 | 0.0039 | 0.2126 | 0.6650 | 0.1185 |

[a] Standard uncertainties are $u(T)$ = 0.02 K, $u(P)$ = 0.001 MPa, and $u(w_i)$ = 0.0012 (TBP), 0.0010 (HMF), 0.0009 (water), 0.0004 (ChCl-urea).

**Table E.4** Separation factor (S) and distribution coefficients ($D_i$) for the TBP (1)-HMF (2)-water (3) and TBP (1)-HMF (2)-water (3)-ChCl-urea (4) systems at temperature *T*= 298.15 and 313.15 K and *P*= 0.1 MPa

| Temperature (K) | TBP (1)-HMF (2)-water (3) | | | | Temperature (K) | TBP (1)-HMF (2)-water (3) | | | |
|---|---|---|---|---|---|---|---|---|---|
| | $w_2^I$ | $D_2$ | $D_3$ | S | | $w_2^I$ | $D_2$ | $D_3$ | S |
| 298.15 | 0.0459 | 3.54 | 0.061 | 58.0 | 313.15 | 0.0508 | 3.70 | 0.061 | 60.7 |
| | 0.0915 | 3.23 | 0.060 | 53.8 | | 0.1058 | 3.25 | 0.059 | 55.1 |
| | 0.1245 | 2.69 | 0.066 | 40.8 | | 0.1225 | 2.51 | 0.056 | 44.8 |
| | 0.1580 | 2.53 | 0.065 | 38.9 | | 0.1741 | 2.46 | 0.066 | 37.3 |
| | 0.1810 | 2.19 | 0.067 | 32.7 | | 0.2079 | 2.07 | 0.064 | 32.3 |
| | 0.2099 | 1.94 | 0.071 | 27.3 | | 0.2167 | 1.70 | 0.069 | 24.6 |
| | 0.2460 | 1.46 | 0.074 | 19.7 | | 0.3188 | 1.67 | 0.077 | 21.7 |
| | 0.2874 | 1.00 | 0.100 | 10.0 | | 0.3419 | 1.21 | 0.086 | 14.1 |

| Temperature (K) | TBP (1)-HMF (2)-water (3)-ChCl-urea (4) | | | |
|---|---|---|---|---|
| | $w_2^I$ | $D_2$ | $D_3$ | S |
| 313.15 | 0.0406 | 2.97 | 0.066 | 45.0 |
| | 0.0728 | 2.53 | 0.058 | 43.6 |
| | 0.1160 | 2.02 | 0.065 | 31.1 |
| | 0.1555 | 1.71 | 0.065 | 26.3 |
| | 0.1740 | 1.70 | 0.070 | 24.3 |
| | 0.2004 | 1.47 | 0.070 | 21.0 |
| | 0.2205 | 1.28 | 0.074 | 17.3 |
| | 0.2434 | 1.15 | 0.078 | 14.7 |

**Table E.5** Experimental LLE tie-line data of TBP (1)-HMF (2)-water (3)-ChCl-urea (4)-NaCl (5) systems in mass fraction ($w_i$) at temperature $T$= 313.15 K and $P$= 0.1 MPa[a]

| Organic Phase | | | | | Aqueous Phase | | | | |
|---|---|---|---|---|---|---|---|---|---|
| $w_1^{I}$ | $w_2^{I}$ | $w_3^{I}$ | $w_4^{I}$ | $w_5^{I}$ | $w_1^{II}$ | $w_2^{II}$ | $w_3^{II}$ | $w_4^{II}$ | $w_5^{II}$ |
| 0.9001 | 0.0492 | 0.0506 | 0.0000 | 0.0001 | 0.0002 | 0.0111 | 0.8141 | 0.0768 | 0.0977 |
| 0.8687 | 0.0857 | 0.0455 | 0.0000 | 0.0001 | 0.0003 | 0.0224 | 0.7846 | 0.0832 | 0.1094 |
| 0.8410 | 0.1186 | 0.0404 | 0.0000 | 0.0001 | 0.0002 | 0.0348 | 0.7533 | 0.0894 | 0.1223 |
| 0.8191 | 0.1400 | 0.0408 | 0.0000 | 0.0001 | 0.0001 | 0.0445 | 0.7345 | 0.0946 | 0.1264 |
| 0.8091 | 0.1503 | 0.0405 | 0.0000 | 0.0001 | 0.0008 | 0.0500 | 0.7133 | 0.1006 | 0.1353 |
| 0.7706 | 0.1874 | 0.0419 | 0.0000 | 0.0001 | 0.0004 | 0.0642 | 0.6825 | 0.1074 | 0.1455 |
| 0.7442 | 0.2142 | 0.0413 | 0.0000 | 0.0002 | 0.0003 | 0.0902 | 0.6445 | 0.1114 | 0.1536 |
| 0.7319 | 0.2291 | 0.0387 | 0.0000 | 0.0003 | 0.0002 | 0.1110 | 0.6026 | 0.1186 | 0.1675 |

[a] Standard uncertainties are $u(T)$ = 0.02 K, $u(P)$ = 0.001 MPa, and $u(w_i)$ = 0.0012 (TBP), 0.0010 (HMF), 0.0009 (water), 0.0004 (ChCl-urea), and 0.0009 (NaCl).

**Table E.6** Experimental LLE tie-line data of TBP (1)-HMF (2)-water (3)-ChCl-urea (4)-NaCl (5)-fructose (6) system in mass fraction ($w_\mathrm{i}$) at temperature $T$= 313.15 K and $P$= 0.1 MPa[a]

| Organic Phase | | | | | | Aqueous Phase | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|
| $w_1^\mathrm{I}$ | $w_2^\mathrm{I}$ | $w_3^\mathrm{I}$ | $w_4^\mathrm{I}$ | $w_5^\mathrm{I}$ | $w_6^\mathrm{I}$ | $w_1^\mathrm{II}$ | $w_2^\mathrm{II}$ | $w_3^\mathrm{II}$ | $w_4^\mathrm{II}$ | $w_5^\mathrm{I}$ | $w_6^\mathrm{I}$ |
| 0.9156 | 0.0430 | 0.0409 | 0.0000 | 0.0004 | 0.0001 | 0.0005 | 0.0097 | 0.6970 | 0.0778 | 0.1110 | 0.1041 |
| 0.8649 | 0.0918 | 0.0428 | 0.0000 | 0.0004 | 0.0000 | 0.0008 | 0.0216 | 0.6698 | 0.0827 | 0.1201 | 0.1050 |
| 0.8386 | 0.1238 | 0.0371 | 0.0000 | 0.0003 | 0.0001 | 0.0005 | 0.0338 | 0.6280 | 0.0873 | 0.1206 | 0.1297 |
| 0.7846 | 0.1776 | 0.0377 | 0.0000 | 0.0000 | 0.0001 | 0.0005 | 0.0493 | 0.6096 | 0.0922 | 0.1269 | 0.1215 |
| 0.7819 | 0.1835 | 0.0343 | 0.0000 | 0.0001 | 0.0002 | 0.0003 | 0.0634 | 0.5837 | 0.0986 | 0.1393 | 0.1146 |
| 0.7748 | 0.1907 | 0.0343 | 0.0000 | 0.0001 | 0.0001 | 0.0003 | 0.0670 | 0.5722 | 0.1045 | 0.1420 | 0.1140 |
| 0.7245 | 0.2448 | 0.0304 | 0.0000 | 0.0002 | 0.0001 | 0.0003 | 0.0895 | 0.5215 | 0.1090 | 0.1536 | 0.1260 |

[a] Standard uncertainties are $u(T)$ = 0.02 K, $u(P)$ = 0.001 MPa, and $u(w_i)$ = 0.0012 (TBP), 0.0010 (HMF), 0.0009 (water), 0.0004 (ChCl-urea), 0.0009 (NaCl), 0.0007 (fructose).

**Table E.7** Separation factor (S) and distribution coefficients ($D_i$) for TBP (1)-HMF (2)-water (3)-ChCl-urea (4)-NaCl (5) in the absence and presence of fructose (6) at temperature $T$= 313.15 K and $P$= 0.1 MPa

| TBP-HMF-water-ChCl-urea-NaCl | | | | TBP-HMF-water-ChCl-urea-NaCl-fructose | | | |
|---|---|---|---|---|---|---|---|
| $w_2^I$ | $D_2$ | $D_3$ | S | $w_2^I$ | $D_2$ | $D_3$ | S |
| 0.0492 | 4.43 | 0.062 | 71.5 | 0.0430 | 4.45 | 0.059 | 75.4 |
| 0.0857 | 3.82 | 0.058 | 65.9 | 0.0918 | 4.25 | 0.064 | 66.4 |
| 0.1186 | 3.41 | 0.054 | 63.1 | 0.1238 | 3.66 | 0.059 | 62.0 |
| 0.1400 | 3.14 | 0.056 | 56.1 | 0.1776 | 3.60 | 0.062 | 58.1 |
| 0.1503 | 3.01 | 0.057 | 52.8 | 0.1835 | 2.89 | 0.059 | 49.0 |
| 0.1874 | 2.92 | 0.061 | 47.9 | 0.1907 | 2.85 | 0.060 | 47.5 |
| 0.2142 | 2.37 | 0.064 | 37.0 | 0.2448 | 2.73 | 0.058 | 47.1 |
| 0.2291 | 2.06 | 0.064 | 32.2 | | | | |

**Table E.8** NRTL and UNIQUAC parameters for organic solvent (1)-HMF (2)-water (3) systems at temperature $T$= 298.15 and 313.15 K and $P$= 0.1 MPa

| System | Model | $i$-$j$ | $b_{ij}$ [a] ($K$) | $b_{ji}$ [a] ($K$) | $\alpha_{ij}$ | RMSD (%) |
|---|---|---|---|---|---|---|
| MIBK-HMF-water[b] | NRTL | 1-2 | -515.80 | 1208.19 | 0.20 | 0.9459 |
| | | 1-3 | 213.97 | 1580.95 | 0.20 | |
| | | 2-3 | -732.33 | 1650.09 | 0.20 | |
| MIBK-HMF-water[b] | UNIQUAC | 1-2 | -87.14 | 136.04 | - | 0.5087 |
| | | 1-3 | -430.69 | -105.31 | - | |
| | | 2-3 | -112.85 | 249.85 | - | |
| TBP-HMF-water | NRTL | 1-2 | -1027.56 | 2190.13 | 0.20 | 1.4165 |
| | | 1-3 | -140.24 | 3038.91 | 0.20 | |
| | | 2-3 | -732.33 | 1650.09 | 0.20 | |
| TBP-HMF-water | UNIQUAC | 1-2 | 214.52 | 25.271 | - | 1.1618 |
| | | 1-3 | -80.955 | -96.338 | - | |
| | | 2-3 | -112.85 | 249.85 | - | |

[a] $\tau_{ij} = \frac{b_{ij}}{T}$ for NRTL; $\tau_{ij} = exp\left(\frac{b_{ij}}{T}\right)$ for UNIQUAC

[b] The experimental LLE data at 298.15 K from Mohammad *et al.* [29] and at 313.15 K from Altway *et al.* [14]

**Table E.9** Van der Waals volume and surface area parameters for the UNIQUAC model

| Parameter | HMF | MIBK | TBP | Water |
|---|---|---|---|---|
| $r_i$ | 4.2235 | 4.5959 | 10.4746 | 0.9200 |
| $q_i$ | 3.3280 | 3.9520 | 7.4040 | 1.4000 |

**Table E.10** Parameters of NRTL model for organic solvent (1)-HMF (2)-water (3)-ChCl-urea (4) systems at temperature $T$= 313.15 K and $P$= 0.1 MPa

| System | $i$-$j$ | $b_{ij}$ [a]($K$) | $b_{ji}$ [a]($K$) | $\alpha_{ij}$ | RMSD (%) |
|---|---|---|---|---|---|
| MIBK-HMF-water-ChCl-urea[b] | 1-4 | 1920.74 | 4159.51 | 0.20 | 0.8095 |
| | 2-4 | 212.35 | -500.33 | 0.20 | |
| | 3-4 | 1506.23 | -1144.56 | 0.20 | |
| TBP-HMF-water-ChCl-urea | 1-4 | 1469.28 | 1530.43 | 0.20 | 0.7058 |
| | 2-4 | 212.35 | -500.33 | 0.20 | |
| | 3-4 | 1506.23 | -1144.56 | 0.20 | |

[a] $\tau_{ij} = \frac{b_{ij}}{T}$

[b] The experimental LLE data from Altway *et al.* [16]

**Table E.11** Parameters of NRTL model for organic solvent (1)-HMF (2)-water (3)-ChCl-urea (4)-NaCl (5) systems at temperature $T$= 313.15 K and $P$= 0.1 MPa

| System | $i$-$j$ | $b_{ij}{}^{a}(K)$ | $b_{ji}{}^{a}(K)$ | $\alpha_{ij}$ | RMSD (%) |
|---|---|---|---|---|---|
| MIBK-HMF-water-ChCl-urea-NaCl[b] | 1-5 | 3111.52 | 6687.87 | 0.1422 | 0.2701 |
| | 2-5 | 9672.85 | 2859.19 | 0.0879 | |
| | 3-5 | -9486.80 | 2982.75 | -0.0942 | |
| | 4-5 | -2443.70 | -6178.20 | -0.0262 | |
| TBP-HMF-water-ChCl-urea-NaCl | 1-5 | 3323.22 | 4432.85 | 0.1723 | 0.5280 |
| | 2-5 | 9672.85 | 2859.19 | 0.0879 | |
| | 3-5 | -9486.80 | 2982.75 | -0.0942 | |
| | 4-5 | -2443.70 | -6178.20 | -0.0262 | |

[a] $\tau_{ij} = \frac{b_{ij}}{T}$

[b] The experimental LLE data from Altway *et al.* [16]

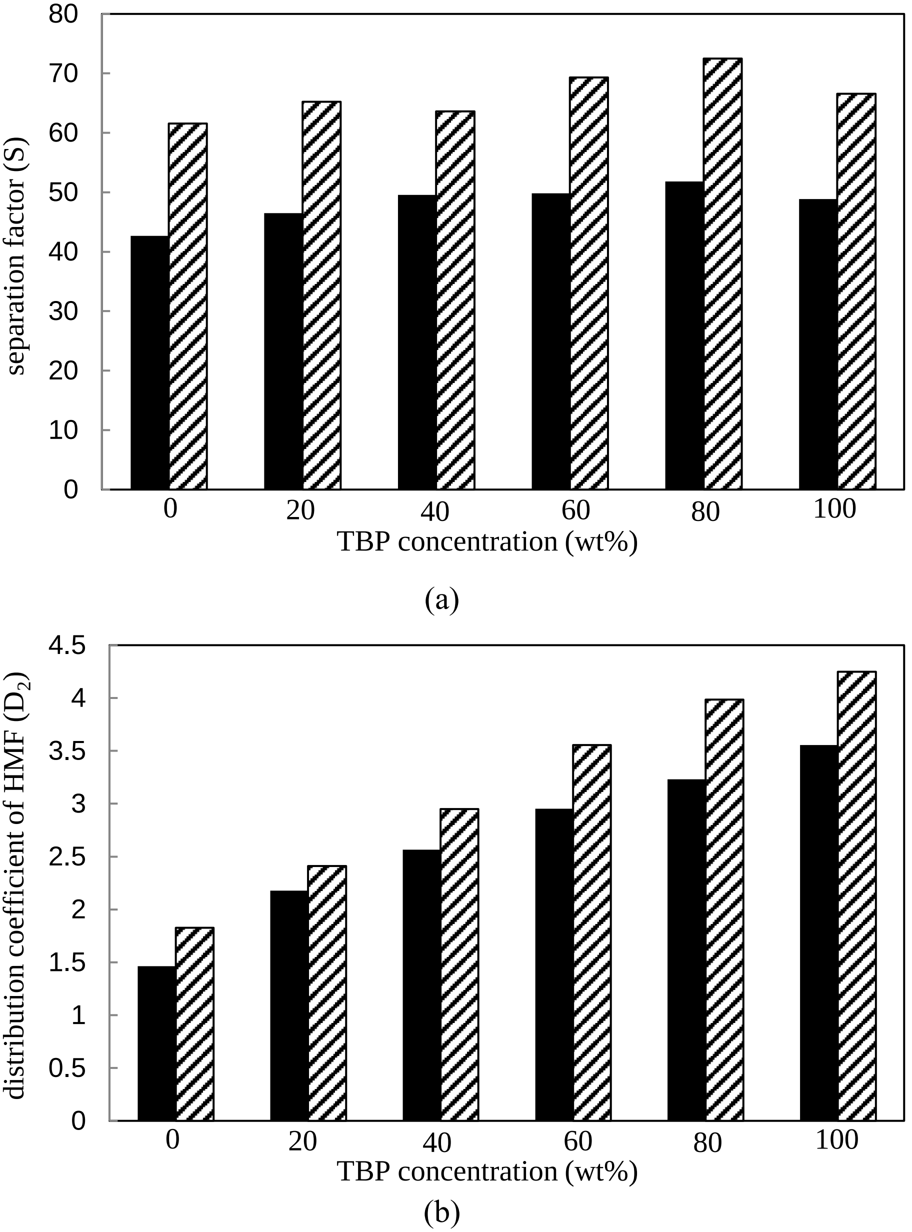
**Table E.12**

Parameters of NRTL model for organic solvent (1)-HMF (2)-water (3)-ChCl-urea (4)-NaCl (5)-fructose (6) systems at temperature *T*= 313.15 K and *P*= 0.1 MPa

| System | *i-j* | $b_{ij}$ [a]($K$) | $b_{ji}$ [a]($K$) | $\alpha_{ij}$ | RMSD (%) |
|---|---|---|---|---|---|
| MIBK-HMF-water-ChCl-urea-NaCl-fructose[b] | 1-6 | -1228.74 | 3872.17 | 0.2 | 0.4559 |
| | 2-6 | 13609.69 | -338.19 | 0.2 | |
| | 3-6 | -655.19 | -804.59 | 0.2 | |
| | 4-6 | 324.91 | 1846.84 | 0.2 | |
| | 5-6 | -2796.17 | 15166.95 | 0.1813 | |
| TBP-HMF-water-ChCl-urea-NaCl-fructose | 1-6 | 9484.30 | 256.34 | 0.2 | 0.7850 |
| | 2-6 | 13609.69 | -338.19 | 0.2 | |
| | 3-6 | -655.19 | -804.59 | 0.2 | |
| | 4-6 | 324.91 | 1846.84 | 0.2 | |
| | 5-6 | -2796.17 | 15166.95 | 0.1813 | |

[a] $\tau_{ij} = \frac{b_{ij}}{T}$

[b] The experimental LLE data from Altway *et al.* [17]



(a)

(b)

**Figure E.1** Relationship of (a) separation factor (S) and (b) HMF distribution coefficient ($D_2$) with TBP concentration (wt%) for MIBK-HMF-water-[EMIM][$BF_4$] or ChCl-urea-NaCl-fructose with the addition of TBP 0-100 wt% and constant HMF concentration (10 wt%) at $T$= 313.15 K and atmospheric pressure (0.1 MPa); ■ : [EMIM][$BF_4$] (10 wt%) ; ▨ : ChCl-urea (10 wt%).

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# List of Publications

## Journal Publications

1. S. Altway, S.C. Pujar, A.B. de Haan, Liquid-liquid equilibria of ternary and quaternary systems involving 5-hydroxymethylfurfural, water, organic solvents, and salts at 313.15 K and atmospheric pressure, Fluid Phase Equilib. 475 (2018) 100–110.

2. S. Altway, S.C. Pujar, A.B. de Haan, Effect of 1–ethyl–3–methylimidazolium tetrafluoroborate on the phase equilibria for systems containing 5-hydroxymethylfurfural, water, organic solvent in the absence and presence of sodium chloride, J. Chem. Thermodynamics 132 (2019) 257–267.

3. S. Altway, M. Yuan, S.C. Pujar, B. Azhar, A.H. Tiwikrama, A.B. de Haan, Choline chloride urea effect on liquid–liquid equilibria of 5-hydroxymethylfurfural–water–organic solvent systems in the absence and presence of sodium chloride, J. Chem. Eng. Data 66 (2021) 4684–4696.

4. S. Altway, S.C. Pujar, A.B. de Haan, Fructose Effect on the Extraction Performance of 5-Hydroxymethylfurfural in Aqueous 1–Ethyl–3–methylimidazolium Tetrafluoroborate or Choline Chloride Urea Solution with the Aid of Sodium Chloride Using the Methyl Isobutyl Ketone Solvent, Ind. Eng. Chem. Res. 61 (2022) 7163–7171.

5. S. Altway, S.C. Pujar, A.B. de Haan, Liquid - liquid equilibrium data

for 5-hydroxymethylfurfural separation from aqueous solution using tributyl phosphate as extraction solvent, *to be submitted in Ind. Eng. Chem. Res.*

**Oral Conference Presentation**

1. S. Altway, S.C. Pujar, A.B. de Haan, Effect of 1–Ethyl–3–methylimidazolium tetrafluoroborate and Sodium Chloride on the Liquid-Liquid Equilibria of 5-Hydroxymethylfurfural, Methyl Isobutyl Ketone, Water, THERMAM 2018, Rostock, Germany, July 2018.
2. S. Altway, S.C. Pujar, A.B. de Haan, The influence of HMF reaction mixture constituents on extraction solvent performance, CHISA 2018, Prague, Czech Republic, August 2018.

**Poster Conference Publication**

1. S. Altway, S.C. Pujar, A.B. de Haan, Liquid-liquid equilibria of 5-hydroxymethylfurfural, organic solvent, water, inorganic salt systems, The Netherlands Process Technology Symposium - NPS 2018, Enschede, Netherlands, May 2018.

# Curriculum Vitae

Saidah Altway was born on 18 August 1988 in Pasuruan, Indonesia. She had graduated from bachelor degree in Chemical Engineering Department of Institut Teknologi Sepuluh Nopember Surabaya (ITS), Indonesia at 2010. Then, she took master degree in Chemical Engineering Department ITS and National Taiwan University of Science and Technology (NTUST) at 2010-2012. Since December 2012, she became junior lecturer in Industrial Chemical Engineering Department ITS. In October 2015 she started a PhD study at Delft University of Technology (TU Delft), Netherlands in Transport Phenomena Research Group under the supervision of Prof. Andre de Haan, on the research topic of “Effect of biphasic system constituents on liquid-liquid extraction of 5-hydroxymethylfurfural”. The results of her research are presented in this dissertation.

**Saidah Altway**