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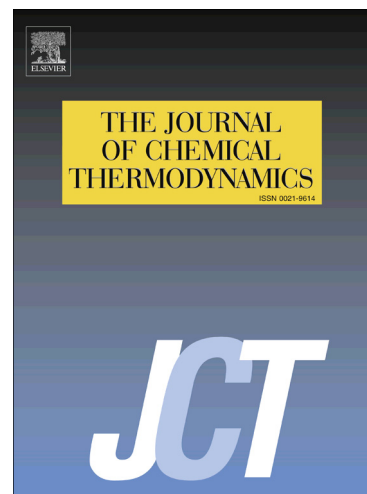Saidah Altway*, Snehal C. Pujar, André B. de Haan

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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 0.97% and 0.63% 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 0.28% for MIBK-HMF-water-[EMIM][BF$_4$]-NaCl and 0.90% for 2-pentanol-HMF-water-[EMIM][BF$_4$]-NaCl.

Keywords: Extraction performance; [EMIM][BF$_4$]; 5-Hydroxymethylfurfural; NaCl; Phase equilibria

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1. Introduction

HMF (5-hydroxymethylfurfural) is a bio renewable material which can be used to produce biofuel and chemical products [1]. The main application of HMF in the chemical industry is a platform chemical for making PET (polyethylene terephthalate) [2]. Carbohydrates are the renewable feedstocks to produce HMF which are abundantly available in nature [1]. In HMF productions, liquid-liquid extraction can be beneficially applied to recover HMF from reaction medium into the organic solvent phase, hence it improves the yield and selectivity of HMF. Alcohols and ketones have been widely used in HMF production as extraction solvents [1, 3-6]. These polar compounds can interact with HMF through strong hydrogen bonding interactions. In the present study, methyl isobutyl ketone (MIBK) or 2-pentanol was used for the extraction of HMF. Besides, the partitioning of HMF into the organic phase can be enhanced with the presence of inorganic salt [7-10]. Our previous study indicated that sodium chloride (NaCl) has a good salting-out ability for HMF extraction, hence the extraction performance can be improved both with MIBK and 2-pentanol as extraction solvents by introducing NaCl into the HMF aqueous solution [10].

In the recent years, the dehydration process of carbohydrates into HMF have been investigated using ionic liquid (IL) to achieve yields up to 96% over a wide range of ionic liquid concentration 3-100 wt% [11-20]. 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 [21]. The imidazole group based ionic liquid as cation with chloride and tetrafluoroborate as anion are the most common ionic liquids used in HMF synthesis [11-19]. However, the separation of HMF from pure ionic liquid is challenging [22] 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 [19]. 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.

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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 [22-25]. 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. 313.15 K was selected in this study as a moderate operating temperature for the HMF extraction which was explained in our previous study [10]. 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.

2. Experimental Section

2.1. Chemicals

The description of chemicals used in this study are presented in Table 1. The experimental and literature values of densities (ρ) of all chemicals are also described in Table S1. 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.

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2.2. Tie-line measurements

The LLE tie-lines were measured using jacketed equilibrium cell at 313.15 K and atmospheric pressure (0.1 MPa). Water from heating circulator bath (Tamson-instruments TC 6B, Holland) was circulated to keep equilibrium cell at constant temperature with the standard uncertainty u(T) of 0.02 K. Feed containing aqueous solutions of HMF-water-[EMIM][BF$_4$] in the absence and presence of NaCl were prepared and weighed on analytical balance Mettler Toledo (MS 304S/01, Switzerland) with a precision of ± 0.0001 g. Then, the organic solvent (MIBK or 2-pentanol) was added into the aqueous solution with the mass ratio of aqueous solution and organic solvent is 1:1. 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.* [8] as comparison. The results are presented in Figures S1 and S2 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.

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 were 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

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maxima at 6.7 min. Calibration curves for these components were made prior to the analysis as presented in Figure S3. 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. Results and discussion

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 2 and 3. 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]) [10]. Figures 1 and 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 1 and 2, the tie-lines slope are positive for the LLE systems in the absence of [EMIM][BF_4], then with increasing [EMIM][BF_4]

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concentration the slope of tie-lines become more pronounced negative, especially at 30 wt% of [EMIM][BF₄] 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 1 (c and d) with Figures 2 (b and c), and also Table 2 with Table 3, it becomes evident that at the same [EMIM][BF₄] 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][BF₄] system in the organic-rich phase is also much lower than that of 2-pentanol-HMF-water-[EMIM][BF₄] 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 1 (c) with 2 (b) and Figure 1 (d) with Figure 2 (c) that the tie-line slopes in the MIBK-HMF-water-[EMIM][BF₄] system are more negative than that in the 2-pentanol-HMF-water-[EMIM][BF₄] system, especially at higher HMF concentrations for 10 wt% of [EMIM][BF₄]. 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][BF₄], the [EMIM][BF₄] content in the organic-rich phase is higher than in the MIBK-HMF-water-[EMIM][BF₄] system at the same ionic liquid concentrations indicating the lower solubility of [EMIM][BF₄] in MIBK solvent, as listed in Tables 2 and 3. 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.

Liquid-liquid extraction is a separation method to separate one or more components in a homogeneous mixture by the addition of a solvent which makes them separate into two phases. The separation depends on physical and chemical properties of the components [26-27]. In liquid-liquid extraction, the separation factor is used to determine the capability of an extraction solvent to extract solute (HMF) from the solution. The separation factor (S) is defined as the ratio of the solute (D_2) to water (D_3) distribution coefficient, as given in Eq. (1) :

$$S = \frac{D_2}{D_3} = \frac{w_2^I / w_2^{II}}{w_3^I / w_3^{II}} \tag{1}$$

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The superscript I and II in Eq. (1) represent the organic-rich and the aqueous-rich phase, respectively. w_2 and w_3 are the mass fraction of solute (HMF) and water, respectively. The values of the separation factors and the distribution coefficients for MIBK-HMF-water-[EMIM][BF$_4$] and 2-pentanol-HMF-water-[EMIM][BF$_4$] systems are listed in Table 4 and shown in Figure 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][BF$_4$] concentrations, demonstrating a favorable HMF extraction. Additionally, as seen in Table 4 and Figure 3, the biphasic systems using aqueous ionic liquid show much better HMF distribution coefficients compared to the systems using pure ionic liquid reported by Wang *et al.* [22] 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 ionic liquid. They confirmed that [BF$_4^-$] has the weakest hydrogen bond acceptor ability. Therefore, [BF$_4^-$] is a better anion of ionic liquid applied in the HMF extraction process. The interactions between ionic liquid and HMF are mainly controlled by the strong hydrogen bonding interactions of anion of ionic liquid with −OH group of HMF [22]. In this case, extraction solvent and anion of ionic liquid 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 ionic liquid. As a result the interaction between anion of ionic liquid and HMF is decreased and HMF can be more easily extracted with organic solvent.

From Figure 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 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 4 and Figure 3. These confirm that

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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 4. 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 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 4. 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 4 and 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.

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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 [28] 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 [29-31]. 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 (α_{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 [10]. 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 5. The calculated LLE tie-lines from the NRTL model and experimental LLE tie-lines are compared in Figures 1 and 2. The closed and open symbols represent the experimental and calculated LLE tie-line data, respectively. It shows that the NRTL model provides good agreement with the LLE experimental tie-line data. The RMSD (root mean square deviation) between experimental and calculated LLE tie-line data is determined in Eq. (2).

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

in which *M* and *N* are the number of tie-line data and the number of components, respectively. While, w_{ijk}^{expt} and w_{ijk}^{calc} denote the experimental and calculated mass fractions of component *i* in phase *j* on tie-line *k*, respectively. The RMSD are 0.97% for MIBK-HMF-water-[EMIM][BF$_4$] and 0.63% for 2-pentanol-HMF-water-[EMIM][BF$_4$] systems. Besides, it can be seen in Figure 3 that the NRTL model also gives good description of S and D$_2$, except for higher concentration of HMF, the D$_2$ shows larger deviation. However, overall the NRTL model correlates well the experimental data with the RMSD below 1% for all investigated systems.

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

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(0.1 MPa), as given in Table 6 and Figures 6-7 (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 [10].

Figures 6 and 7 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 1 c and 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 6 and 7, 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 [10]. This salting out effect improves the separation factor and the distribution coefficient of HMF, as seen in Table 7 and Figure 8. From Figure 8, 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 4 and 7. 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 [10], as shown in Figures 8 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

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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 7. 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 7 and Figure 8 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 7) compared to those for the LLE system with salt using MIBK (Figure 6). 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 2) to below 1 wt% (Table 6) with the addition of NaCl for MIBK and from 4-12 wt% (Table 3) to around 1 wt% (Table 6) for 2-pentanol over the whole range of initial HMF concentrations. It can be seen in Tables 3 and 6 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 6-7 and Table 6 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][BF$_4$]-NaCl also exhibit sufficiently high, above 1.4 over the whole range of

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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][BF$_4$]) with inorganic salt (NaCl) can improve the extraction performance, making the extraction of HMF more favorable over the whole range of initial HMF concentrations.

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 6 and 7. NaCl was assumed as one molecular species, additionally the nonrandomness parameter (α_{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 8. Whereas, the α_{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 [10]. 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 [10] and quaternary LLE of organic solvent-HMF-water-[EMIM][BF$_4$] systems, as given in Table 5. The results in Figures 6 and 7 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 0.28% and 0.90%, respectively, as listed in Table 8. Besides, it represents in Figure 8 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 α_{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 α_{ij}. In this case, the determined α_{ij} values also give a crucial effect in generating a good correlation with the experimental LLE data involving salt [10, 32-33]. This NRTL model provides a simple and much easier calculation than the electrolyte NRTL [34] and electrolyte Perturbed Chain-SAFT [35] models. Hence, this NRTL model can be

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applied further for development of the HMF extraction process design in the presence of salt and ionic liquid.

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 0.97% for the MIBK-HMF-water-[EMIM][BF$_4$] and 0.63% 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 0.28% and 0.90% for MIBK and 2-pentanol as extraction solvents, respectively.

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Appendix A. Supplementary data

The supplementary data include the experimental and literature values of densities (ρ) of chemicals used in this study, the method validation, and calibration curves.

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Notes

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Table 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
2-Pentanol	Thermo Fisher Scientific, Germany	0.99	No
Methanol	Honeywell, France	≥ 0.999	No
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

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Table 2

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$_4$]).

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Table 3

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$_4$]).

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Table 4
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$_4$]					MIBK-HMF-water-[EMIM][BF$_4$]			
	w_2^I	D_2	D_3	S		w_2^I	D_2	D_3	S
5%	0.0284	1.14	0.023	49.6	10%	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$_4$]					2-pentanol-HMF-water-[EMIM][BF$_4$]			
	w_2^I	D_2	D_3	S		w_2^I	D_2	D_3	S
30%	0.0198	0.58	0.031	18.7	10%	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$_4$]			
	w_2^I	D_2	D_3	S
30%	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

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Table 5
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)	α_{ij}	RMSD (%)
MIBK-HMF-water-[EMIM][BF$_4$]	1-2	483.26[b]	-738.00[b]	0.20	
	1-3	199.41[b]	1722.53[b]	0.20	
	1-4	101.13	8545.18	0.20	0.9734
	2-3	-379.83[b]	310.86[b]	0.20	
	2-4	-197.36	-1456.00	0.20	
	3-4	2779.53	-1548.18	0.20	
2-pentanol-HMF-water-[EMIM][BF$_4$]	1-2	470.52[b]	-453.78[b]	0.20	
	1-3	-209.25[b]	1764.17[b]	0.20	
	1-4	207.39	3391.80	0.20	0.6257
	2-3	-987.02[b]	1871.24[b]	0.20	
	2-4	838.21	-937.94	0.20	
	3-4	3231.36	-1425.60	0.20	

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

[b] Regressed from the ternary LLE systems of organic solvent-HMF-water [10].

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Table 6
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).

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Table 7
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.

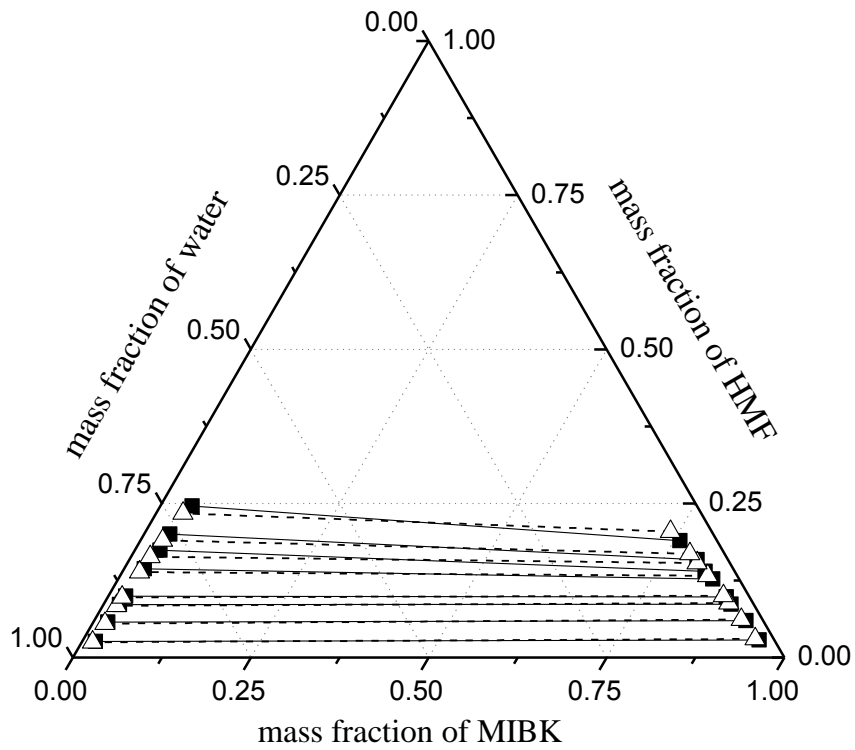| MIBK-HMF-water-[EMIM][BF$_4$]-NaCl				2-pentanol-HMF-water-[EMIM][BF$_4$]-NaCl			
w_2^{I}	D_2	D_3	S	w_2^{I}	D_2	D_3	S
0.0303	1.61	0.027	59.6	0.0343	2.02	0.106	19.1
0.0489	1.53	0.030	51.0	0.0679	1.94	0.103	18.8
0.0896	1.53	0.037	41.4	0.0968	1.94	0.107	18.1
0.1250	1.49	0.045	33.1	0.1200	1.96	0.116	16.9
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

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Table 8

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)	α_{ij}	RMSD (%)
MIBK-HMF-water-[EMIM][BF$_4$]-NaCl	1-5	-3208.68[b]	-2911.24[b]	0.0399[b]	0.2808
	2-5	8170.85[b]	4459.64[b]	0.1149[b]	
	3-5	-8696.65[b]	-5534.76[b]	-0.0562[b]	
	4-5	6787.99	1178.81	0.4056	
2-pentanol-HMF-water-[EMIM][BF$_4$]-NaCl	1-5	1240.07[b]	-7301.43[b]	-0.0010[b]	0.8958
	2-5	9853.62[b]	2938.78[b]	0.1462[b]	
	3-5	-8386.34[b]	-5084.01[b]	-0.0715[b]	
	4-5	-1022.79	-1686.40	0.4574	

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

[b] Regressed from the quaternary LLE systems of organic solvent-HMF-water-NaCl [10].

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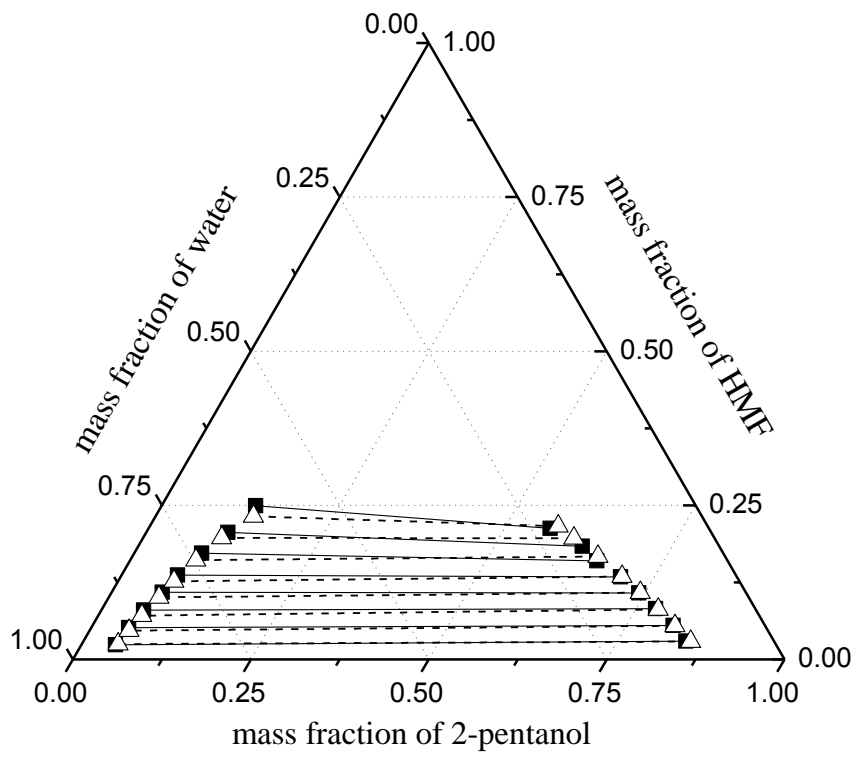E-mail: s.altway@tudelft.nl
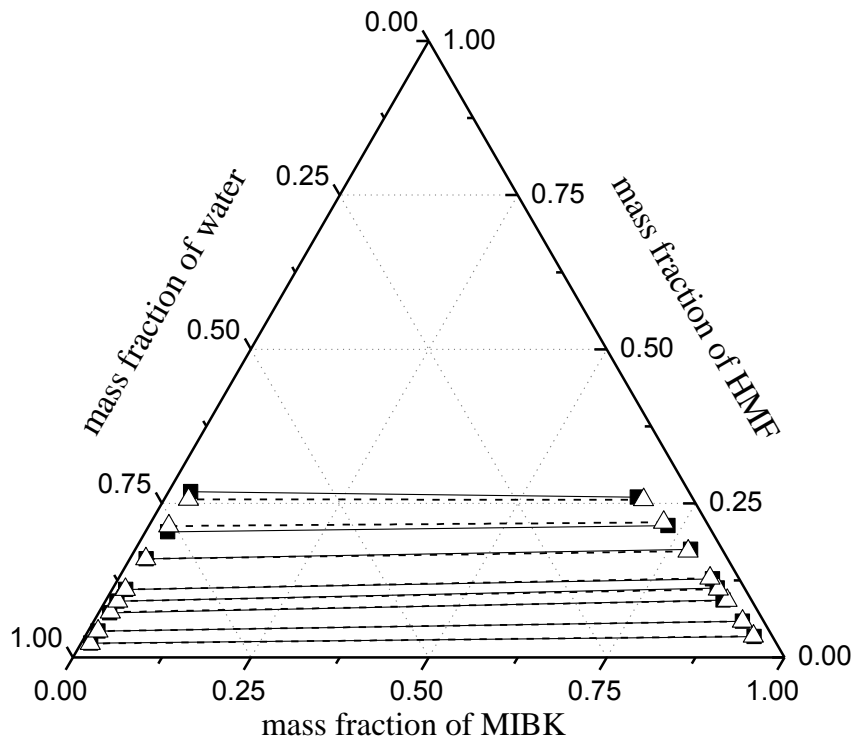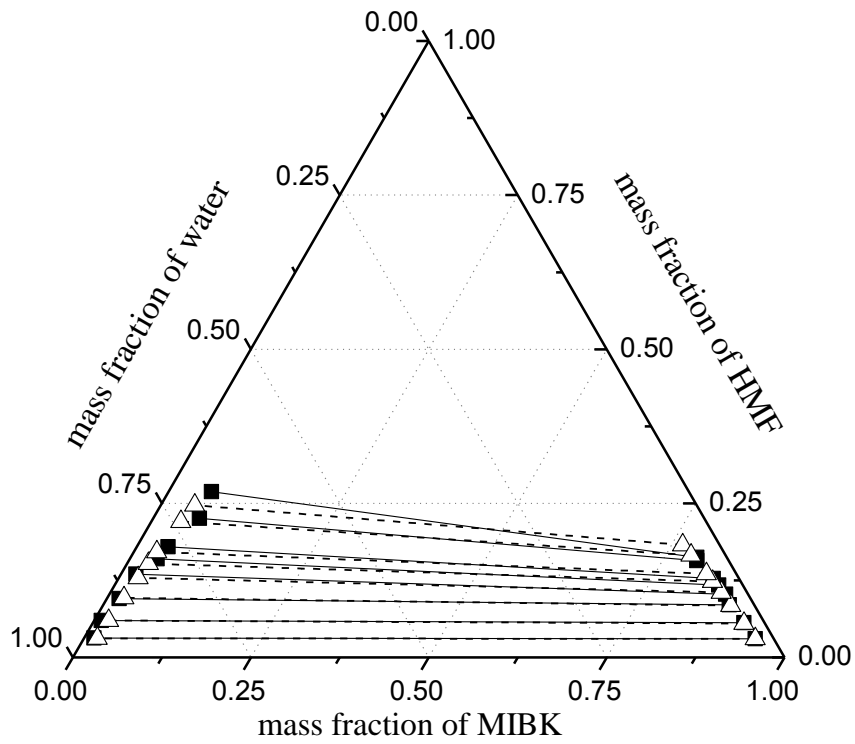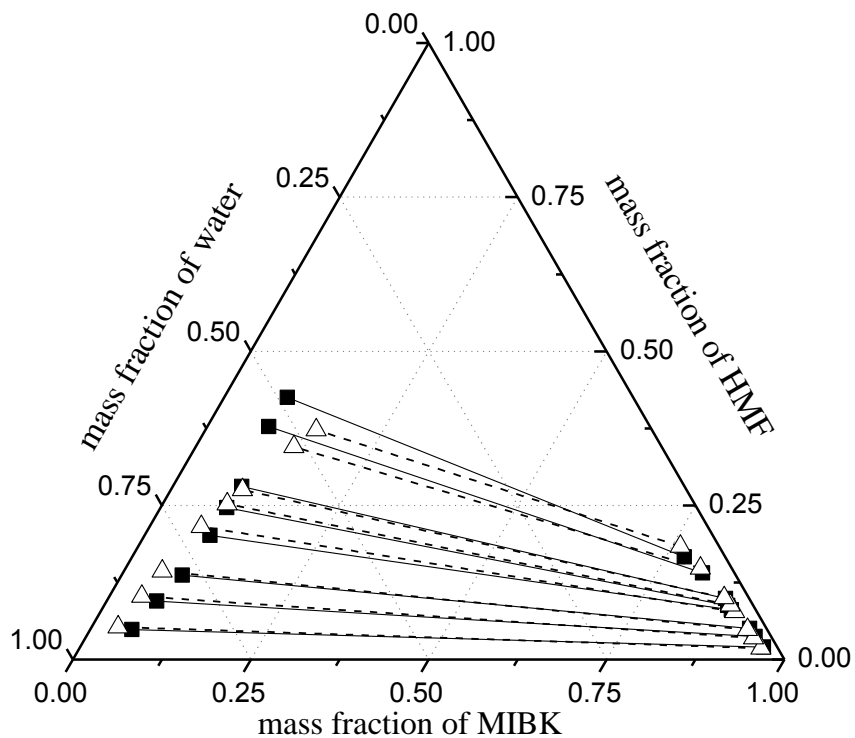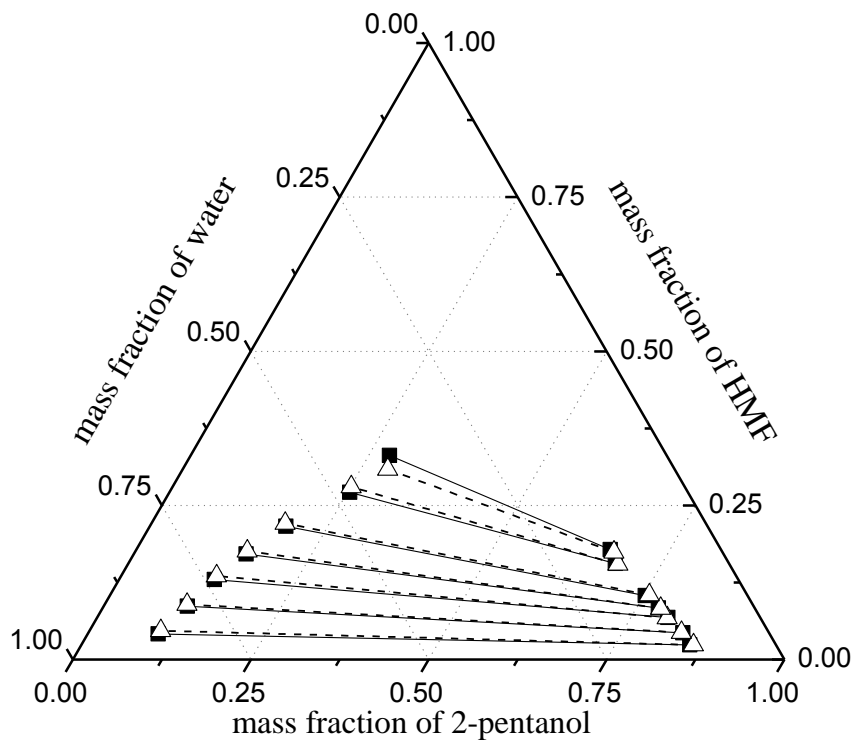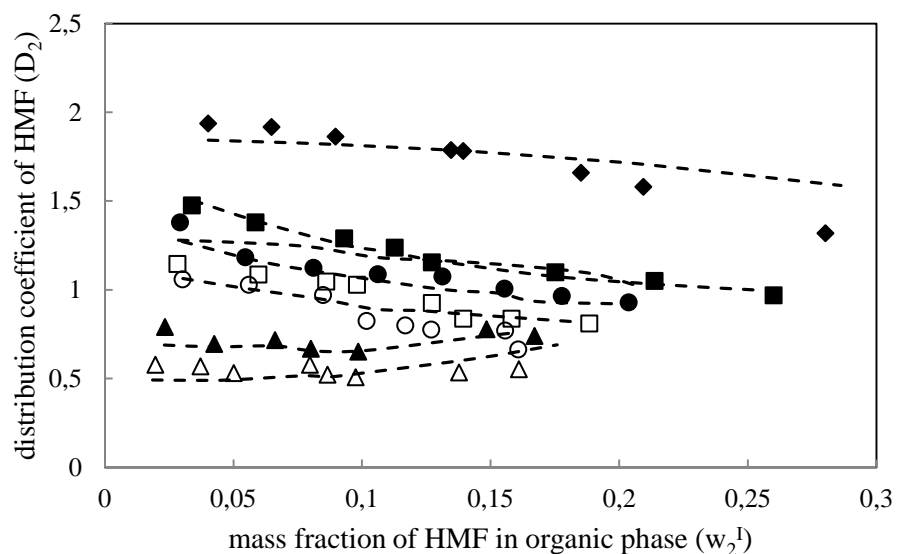
(d)

Figure 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$_4$] [10]; (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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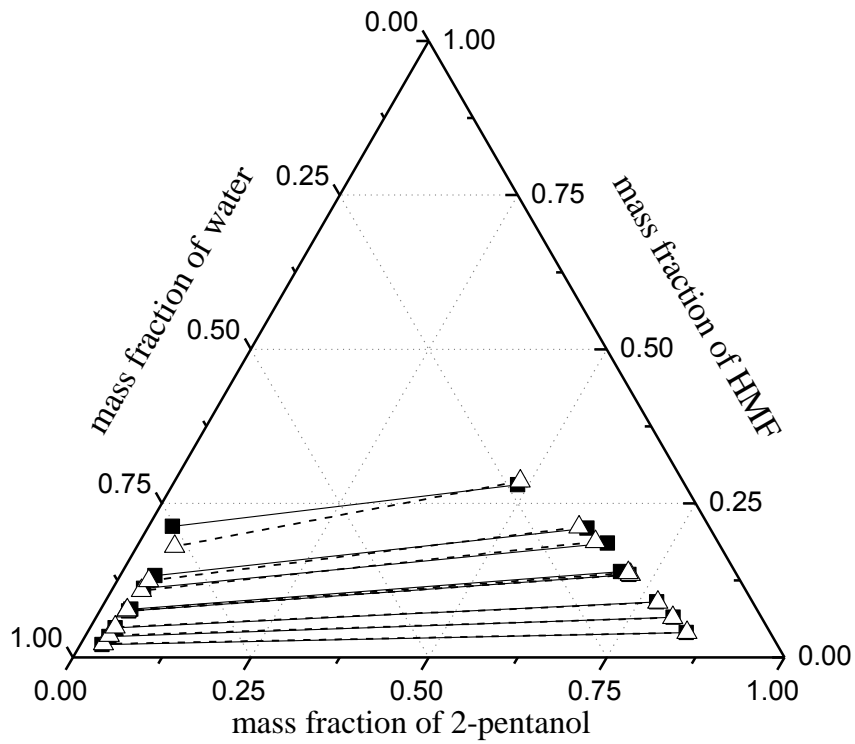
(c)

Figure 2. Phase diagram of the experimental and calculated LLE tie-line data for 2-pentanol-HMF-water and 2-pentanol-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$_4$] [10]; (b) 10 wt% [EMIM][BF$_4$]; (c) 30 wt% [EMIM][BF$_4$]; —■— : experimental data; --△-- : NRTL model.

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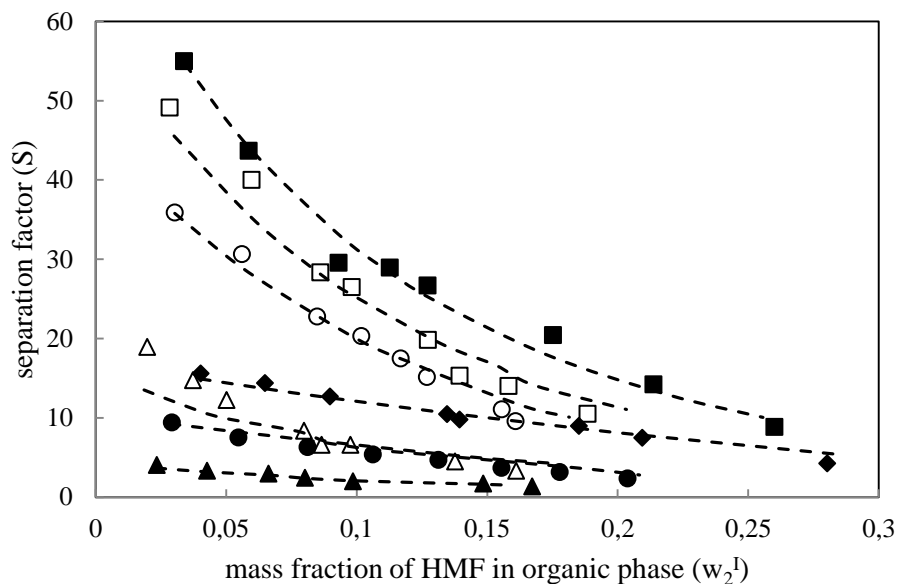
(a)

(b)

Figure 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$_4$]) [10]; □ : 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.

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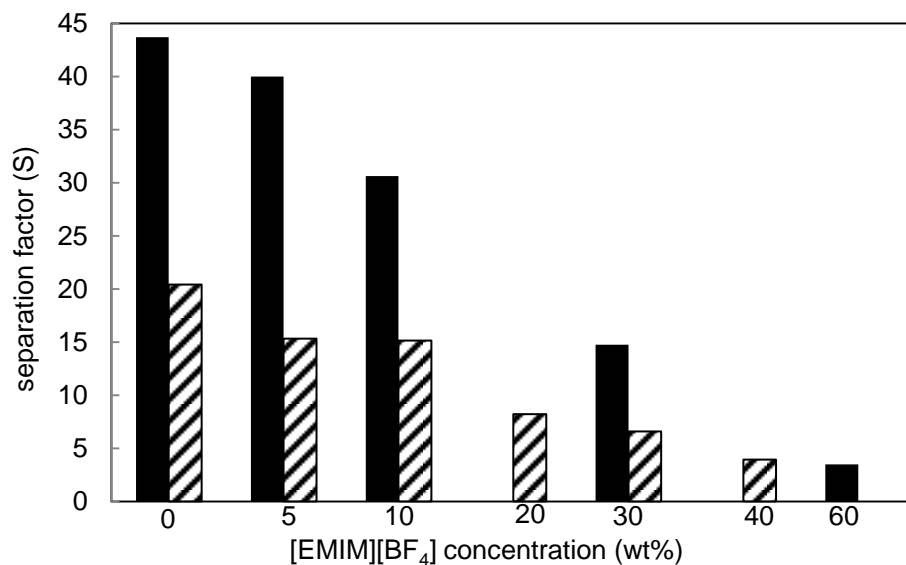
Figure 4. Relationship between separation factor (S) and [EMIM][BF$_4$] concentration (wt%) for MIBK-HMF-water-[EMIM][BF$_4$] systems at *T*= 313.15 K and atmospheric pressure (0.1 MPa); ■ : 10 wt% of initial HMF concentration; ▨ : 30 wt% of initial HMF concentration.
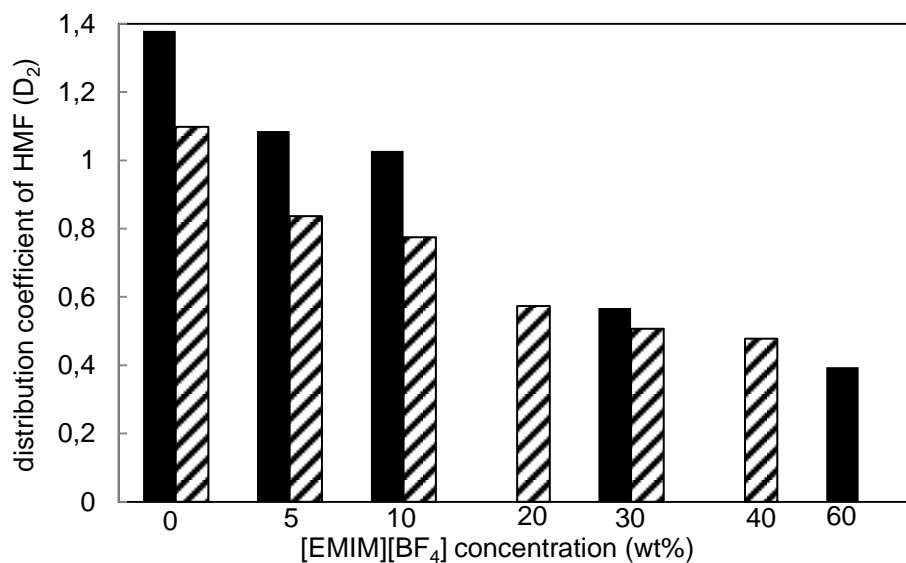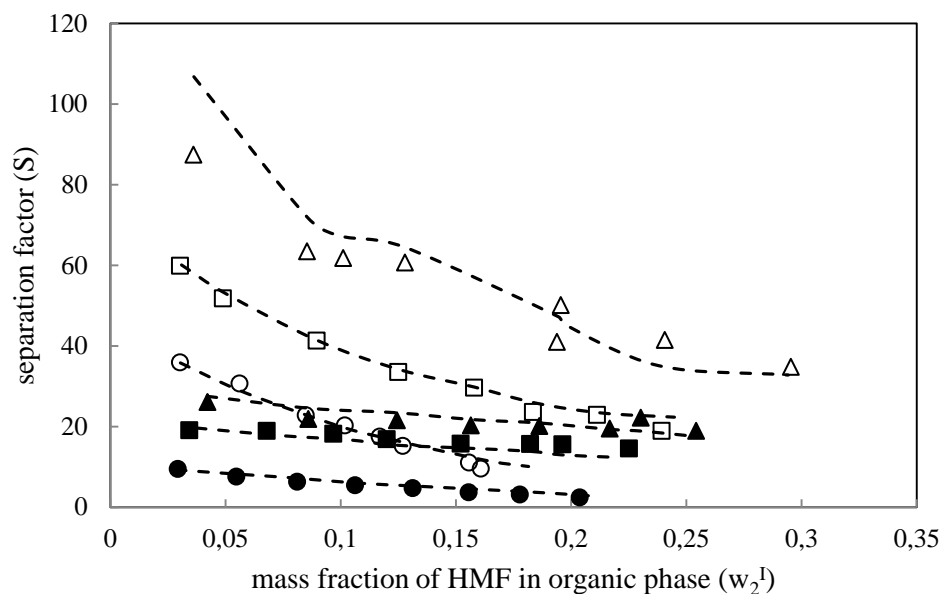

Figure 5. Relationship between distribution coefficient of HMF (D$_2$) and [EMIM][BF$_4$] concentration (wt%) for MIBK-HMF-water-[EMIM][BF$_4$] systems at *T*= 313.15 K and atmospheric pressure (0.1 MPa); ■ : 10 wt% of initial HMF concentration; ▨ : 30 wt% of initial HMF concentration.

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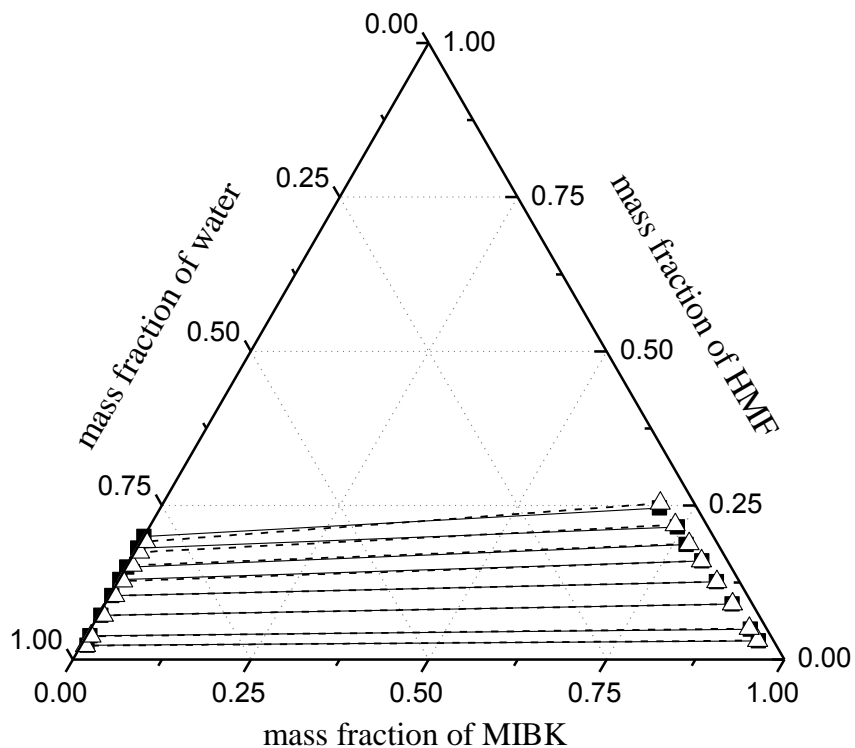
Figure 6. Phase diagram of the experimental and calculated LLE tie-line data for MIBK-HMF-water-[EMIM][BF$_4$]-NaCl system on IL and salt free basis at T= 313.15 K and atmospheric pressure (0.1 MPa) for 10 wt% [EMIM][BF$_4$] and 10 wt% NaCl using NRTL model ; —■— : experimental data; --△-- : NRTL model.

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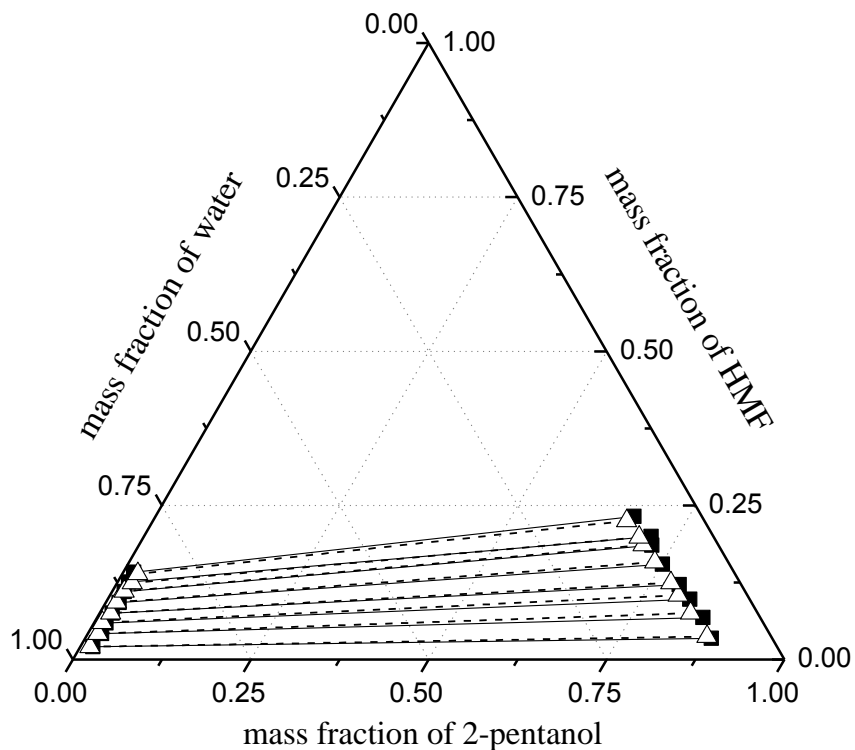
Figure 7. Phase diagram of the experimental and calculated LLE tie-line data for 2-pentanol-HMF-water-[EMIM][BF$_4$]-NaCl system on IL and salt free basis at T= 313.15 K and atmospheric pressure (0.1 MPa) for 10 wt% [EMIM][BF$_4$] and 10 wt% NaCl using NRTL model; ─■─: experimental data; ---△---: NRTL model.

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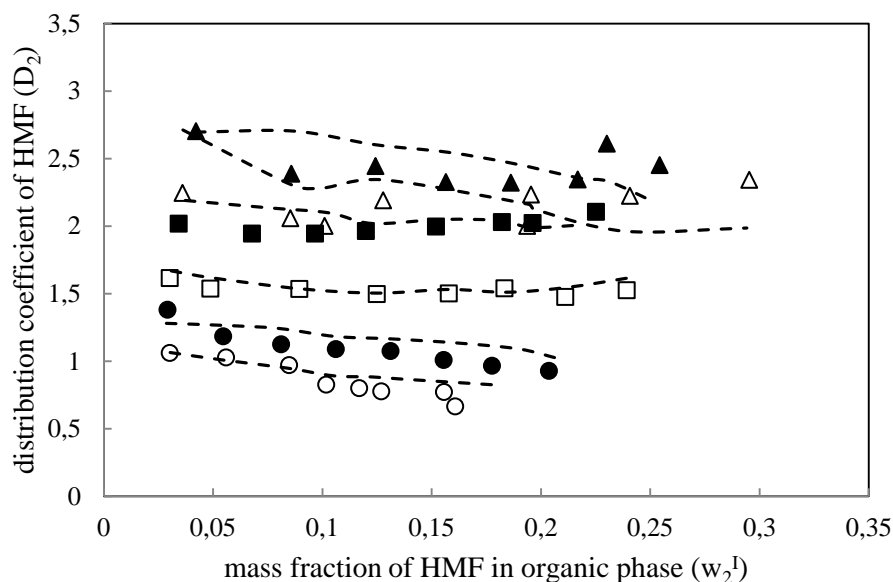
(b)

Figure 8. (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 [10];▲: 2-pentanol-HMF-water-NaCl [10]; − − − : NRTL model.

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Highlights

- LLE of MIBK or 2-pentanol-HMF-water-[EMIM][BF$_4$] were measured at 313.15 K.

- LLE of MIBK or 2-pentanol-HMF-water-[EMIM][BF$_4$] in the presence of NaCl were also measured.

- [EMIM][BF$_4$] caused a negative effect on the LLE.

- Combined effect of aqueous [EMIM][BF$_4$] with NaCl can enhance extraction performance making HMF extraction more favorable.

- LLE data were correlated using NRTL model & binary interaction parameters were obtained.

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