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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^{o}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 0.81% and 0.77% 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

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1. Introduction

The development of biomass conversion into building blocks for the production of fuels and chemicals has been considered in various studies [1-6] to reduce the dependence on fossil resources. 5-hydroxymethylfurfural (HMF) is one of the promising platform chemicals, that can be obtained through hexose dehydration, and can be used for producing biofuels and a wide range of industrially important chemicals [6]. The main potential industrial application of HMF is the production of FDCA (2,5-Furandicarboxylic acid), a renewable material to replace the use of PTA (para-terephthalic acid) in the synthesis of PET (polyethylene terephthalate) used for production of synthetic fibers and plastic bottles [7].

A large number of studies provide improvements in understanding the mechanism and kinetics of the dehydration process for HMF production [6, 8-16]. Researchers investigated the production of HMF in monophasic systems which resulted in low yields [6, 8-9] due to the degradation of HMF and the formation of by-products. The use of biphasic systems involving organic solvents proved advantageous through higher yields. However the low separation factor and difficult separation of HMF from organic solvents made the HMF production economically infeasible. In the biphasic system, selection of the organic solvent plays a crucial role in order to improve the separation of HMF.

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. In HMF production, the feed stream in the reactor unit contains fructose (carbohydrates), water, and catalyst as aqueous phase. In addition, the organic solvent is included in the reactor. The reaction takes place and HMF is extracted in the reactor into the organic phase which prevents the formation of side product. The aqueous phase from the bottom of the reactor which is still containing HMF enters the extraction unit. As we know that HMF can be more easily degraded at high temperature, as studied by Girisuta *et al.* [17]. They studied the decomposition of HMF in a temperature window of 98-181^{o}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^{o}C [4-6], the

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temperature in the extraction unit should be higher than room temperature. Hence 40^{o}C (313.15 K) was selected in this study as a moderate operating temperature for the HMF extraction.

High boiling point organic solvents, such as DMSO (Dimethylsulfoxide), can give high yield and selectivity of HMF, but involve high cost and high energy consumption for separating HMF by distillation [6]. Therefore, more volatile polar compounds like alcohol and ketone have been considered as promising alternative solvents for HMF extraction [18-20]. 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 [18, 19]. 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 [18, 19-23]. Xiong *et al*. [20] have used the COSMO-SAC model [24] to predict the LLE systems containing HMF using primary alcohol as extraction solvent at 30^{o}C. The ePC-SAFT [25-26] was used to especially correlate the experimental LLE systems involving HMF using MIBK solvent in the presence of salt at 25^{o}C [19]. Dalmolin *et al.* [23] reported the LLE in systems containing HMF using alcohol as solvent at 25^{o}C and used the NRTL (Non-Random Two-Liquid) [27] 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^{o}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 [27] and UNIQUAC [28] activity coefficient models are good correlation models which are widely applied for describing phase equilibrium data in various systems [29-33]. They are direct models available in ASPEN Plus and much easier to use in process simulation. However, the thermodynamics study using these two well-

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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 [23]. Besides, the NRTL model can also be used to correlate LLE systems containing salts [34-35]. The NRTL model using de Haan and Niemann approach [34-35] provides a more simple calculation compared to the e-NRTL [36-37] and ePC-SAFT [25-26] 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. Experimental Section

2.1. Chemicals

All chemicals used in this study are described in Table 1. Methyl isobutyl ketone (MIBK) and 2-Pentanol were used as extraction solvent. Butylated hydroxyanisole (BHA) was used as antioxidant for HMF stability validation. Dimethylformamide (DMF) was used in HMF and organic solvent analyses as internal standard. Nitric acid (HNO_3) was used as diluent in salt analysis. The water used for the experiments was deionized ultrapure water with resistance of 18.2 MΩ.cm.

2.2. HMF stability validation

The stability of HMF in the aqueous and organic phase was evaluated using BHA (Butylated hydroxyanisole) [38]. Sanborn *et al.* [38] 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.

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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.

2.4. Analytical method

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^{o}C for 4 min, then ramped to 250^{o}C at 10^{o}C/min, and finally held at 250^{o}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

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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.

3. Results and discussion

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 it'sdistribution between the aqueous solution and the organic solvent phase. As shown in Figure 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.

3.2. LLE of organic solvent-HMF-water systems

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 2-3. Figures 2 and 3 illustrate that the area of the two phase region for MIBK-HMF-water is larger than that for the 2-pentanol-

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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.

3.2.2. Correlation of ternary LLE data for organic solvent-HMF-water systems

The NRTL [27] and UNIQUAC [28] 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 [39]. The non-randomness parameter (α_{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 4. The van der Waals volume (r_i) and surface area (q_i) parameters for the UNIQUAC model were estimated by Bondi method [40], as seen in Table 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 S1-S12 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 and 3. 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 with all the RMSD (root mean square deviation) below 1%. The RMSD between experimental and calculated LLE tie-line data was defined as follows.

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

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where N is the number of components and M is the number of tie-line data. While, w_{ijk}^{expt} and w_{ijk}^{calc} represent the experimental and calculated mass fractions of component i in phase j on tie-line k, respectively. The RMSD of NRTL and UNIQUAC models are 0.42% and 0.48% for MIBK-HMF-water and 0.81% and 0.77% for 2-pentanol-HMF-water, as listed in Table 4. From Figure 3, 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. The NRTL and UNIQUAC models are more appropriate for correlating LLE containing ketone (MIBK) than alcohol (2-pentanol) in the LLE system of organic solvent-HMF-water.

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 [41-42]. The two main parameters for liquid-liquid extraction are the distribution coefficient (D_2) and the separation factor (S).

The separation factor is used to determine the ability of an extraction solvent to selectively extract the solute (material extracted) from the solution. The higher the separation factor, the greater the separation ability. In this study the separation factor (S) is defined as the ratio of the solute distribution coefficient (D_2) to the distribution coefficient of water (D_3). Additionally, the distribution coefficient of component i is the ratio of the mass fraction of component i in the organic phase (I) to the mass fraction of component i in the aqueous phase (II) :

$$S = \frac{D_2}{D_3} = \frac{w_2^I / w_2^{II}}{w_3^I / w_3^{II}} \qquad (2)$$

where w_2^I and w_3^I are the mass fractions of HMF and water in the organic phase and w_2^{II} and w_3^{II} the HMF and water mass fractions in the aqueous phase, respectively. The separation factor and distribution coefficient of HMF and water with MIBK and 2-pentanol as extraction solvent are shown in Figure 4 and Table 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

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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 4. 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 4 and Table 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 and 3 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 [42] 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.

3.3. LLE of organic solvent-HMF-water-salt systems

The salts investigated in this study were NaCl, KCl, Na_2SO_4, and K_2SO_4 which were selected based on the variety of cation and anion. The effect salt presence in the aqueous HMF solution on the phase equilibria, HMF distribution coefficient, and separation factor was investigated.

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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 7 and 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 5 and 6 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 with Figure 5 and Figure 3 with Figure 6 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 5 and 6 (a and c) with Figures 5 and 6 (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 and 3 with Figures 5 and 6, 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

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1-5 wt% in the absence of salt (Table 2 and 3) to values significantly below 1 wt% with the addition of salt (Table 7 and 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 3) to 9-11 wt% (Table 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.

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 5 and 6. 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 (α_{ij}) were regressed instead of setting it to the default value for the interactions of the salt with water, HMF and solvent [34-35]. The NRTL parameters (b_{ij}, b_{ji}, and α_{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 4. The resulting parameters for the interactions with the salts are presented in Table 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 0.75%, 0.74%, 0.67%, and 0.73% for NaCl, KCl, Na_2SO_4, and K_2SO_4, respectively. Moreover, the RMSD values of the 2-pentanol-HMF-water-salt systems are 0.71%, 0.57%, 0.77%, and 0.59% for NaCl, KCl, Na_2SO_4, and K_2SO_4, respectively, as seen in Table 9. Therefore, the NRTL model using de Haan and Niemann approach [34-35] can be used further to

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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 [36-37] and ePC-SAFT [25-26] models. Even though the negative values were obtained for α_{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 α_{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 [34-35].

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 7. 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 7 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 [43]. The Hofmeister series is the ranking of ions of salts with respect to their ability either to salt out or salt in solutes [44]. Lyklema [45] 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 [43, 45]. 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-},

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resulting in a reduced stabilization. Therefore, with the same cation, Cl^- anion gives greater salting-out ability than SO_4^{2-}.

Figure 7, 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 10 and 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 6 and 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 [46-47] 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

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cost for the following product purification and solvent recovery. Therefore, the use of salt is promising and competitive proposal for HMF extraction.

4. Conclusions

The liquid-liquid equilibria 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 activity coefficient 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.

Appendix A. Supplementary data

The supplementary data include the topological analysis of the Gibbs energy of mixing function (G^M) for liquid-liquid equilibrium correlations.

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Notes

The authors declare no competing financial interest.

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Table 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

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Table 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
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)

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Table 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)

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Table 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*	α_{ij}	b''_{ij} [a](*J/mol*)	b''_{ji} [a](*J/mol*)	RMSD (%)
MIBK-HMF-water	NRTL	1-2	0.20	4018.03	-6136.10	0.4188
		1-3	0.20	1658.00	14321.9	
		2-3	0.20	-3158.05	2584.65	
MIBK-HMF-water	UNIQUAC	1-2	-	-606.33	1372.94	0.4760
		1-3	-	-3464.11	-1061.84	
		2-3	-	-1133.96	2712.63	
2-pentanol-HMF-water	NRTL	1-2	0.20	3912.08	-3772.95	0.8140
		1-3	0.20	-1739.82	14668.1	
		2-3	0.20	-8206.50	15558.4	
2-pentanol-HMF-water	UNIQUAC	1-2	-	-1192.51	1191.70	0.7734
		1-3	-	-577.28	-1719.03	
		2-3	-	2546.43	-2956.02	

[a] $\tau_{ij} = \frac{b_{ij}}{T} = \left(\frac{b"_{ij}}{R}\right)\frac{1}{T}$ for NRTL; $\tau_{ij} = exp\left(\frac{b_{ij}}{T}\right) = exp\left\{\left(\frac{b"_{ij}}{R}\right)\frac{1}{T}\right\}$ for UNIQUAC

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Table 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

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Table 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

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Table 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
	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)

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Table 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)

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Table 9

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

System	*i-j*	b''_{ij} [a](*J/mol*)	b''_{ji} [a](*J/mol*)	α_{ij}	RMSD (%)
MIBK-HMF-water-NaCl	1-4	2964.24	-22564.6	-0.0619	0.7476
	2-4	18269.8	28207.0	0.2316	
	3-4	-25909.0	-9329.13	-0.2042	
MIBK-HMF-water-KCl	1-4	74772.6	-74471.3	0.0147	0.7395
	2-4	48669.7	-35251.2	0.0661	
	3-4	-76659.9	9314.69	-0.0618	
MIBK-HMF-water-Na_2SO_4	1-4	7299.51	-2348.24	0.3478	0.6682
	2-4	54404.2	17461.1	0.1764	
	3-4	-79981.5	-9403.81	-0.2521	
MIBK-HMF-water-K_2SO_4	1-4	37037.1	-15099.7	0.1898	0.7280
	2-4	63220.7	17038.5	0.1693	
	3-4	-77580.8	-10327.0	-0.2282	
2-pentanol-HMF-water-NaCl	1-4	10310.5	-60707.5	-0.0010	0.7105
	2-4	81927.6	24434.4	0.1462	
	3-4	-69727.9	-42270.8	-0.0715	
2-pentanol-HMF-water-KCl	1-4	22378.2	-20723.5	0.0534	0.5711
	2-4	43121.8	15981.1	0.2714	
	3-4	-34994.7	-7736.08	-0.1959	
2-pentanol-HMF-water- Na_2SO_4	1-4	24470.9	-3671.11	-0.5097	0.7742
	2-4	20466.1	-35281.5	-0.4260	
	3-4	20441.6	-7575.18	0.3132	
2-pentanol-HMF-water- K_2SO_4	1-4	21793.8	-2690.43	0.1720	0.5942
	2-4	55213.9	5349.62	0.4191	
	3-4	-32117.6	3858.47	-0.7153	

[a] $\tau_{ij} = \frac{b_{ij}}{T} = \left(\frac{b"_{ij}}{R}\right)\frac{1}{T}$

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Table 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

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Table 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

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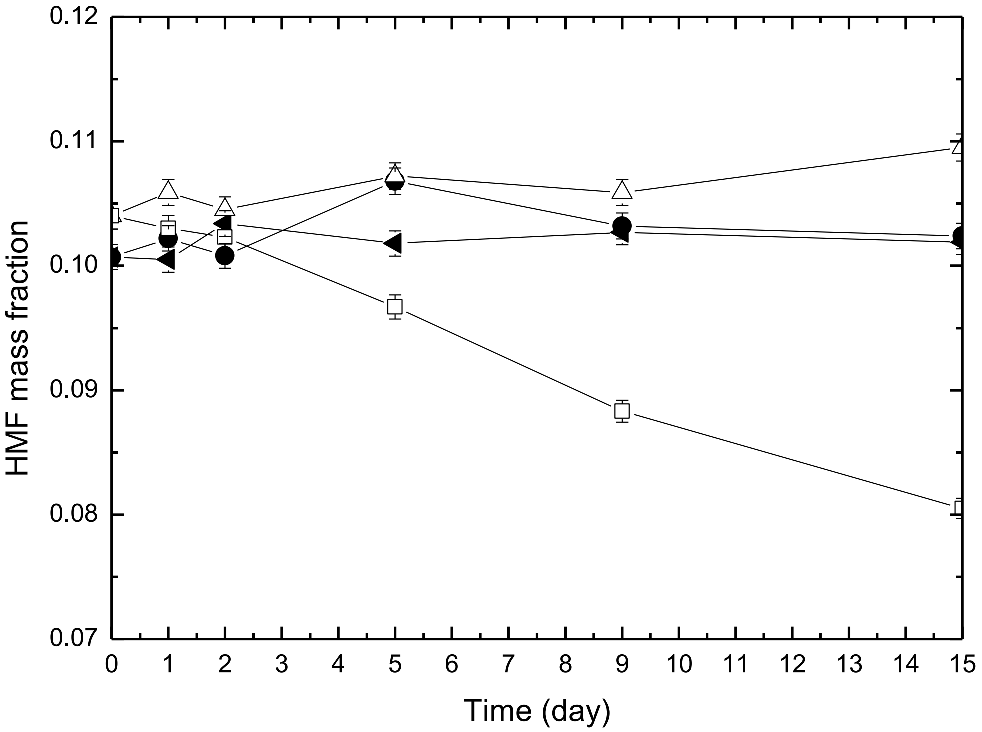

Fig. 1. HMF stability validation at T= 313.15 K and atmospheric pressure; (—◀—) HMF in water with BHA; (—●—) HMF in water without BHA; (—△—) HMF in MIBK with BHA; (—□—) HMF in MIBK without BHA.

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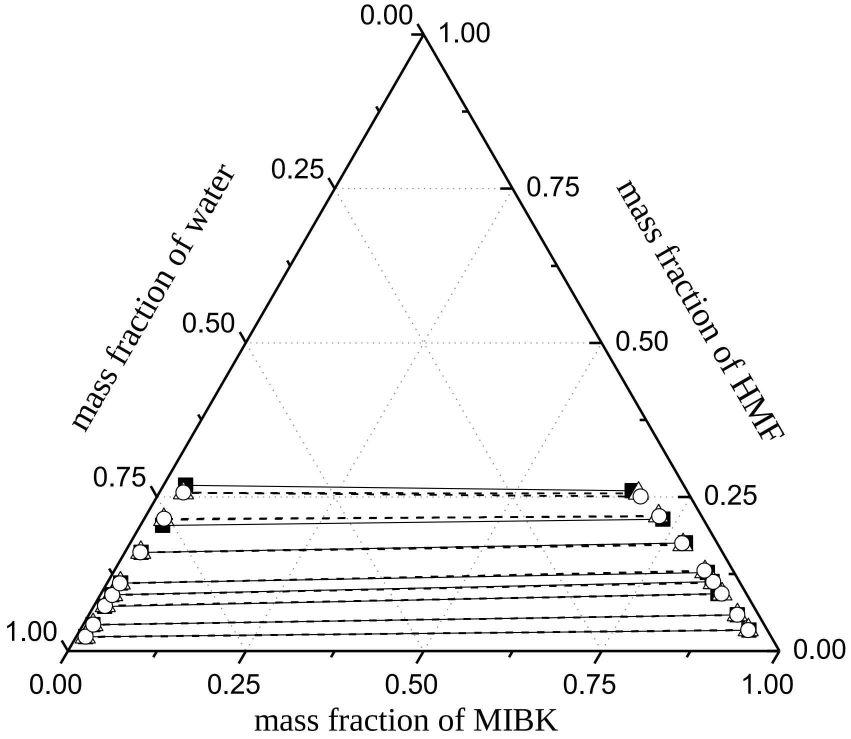

Fig. 2. Phase diagram of the experimental and calculated LLE tie-line data for the ternary system MIBK-HMF-water at *T*= 313.15 K and atmospheric pressure using NRTL and UNIQUAC models; (—■—) experimental data; (- -△- -) NRTL model; (- -○- -) UNIQUAC model.

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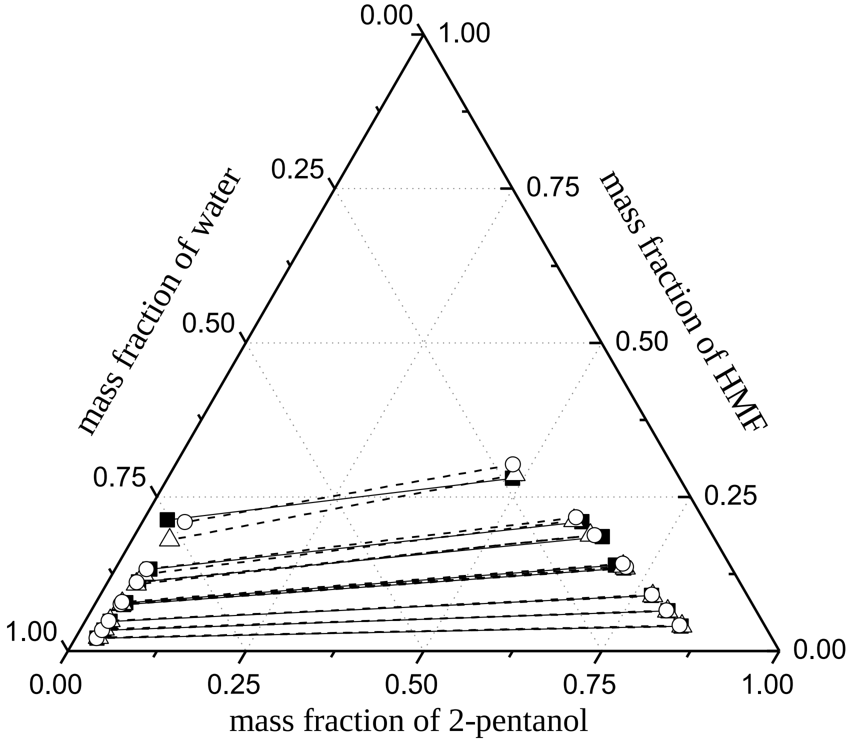

Fig. 3. Phase diagram of the experimental and calculated LLE tie-line data for the ternary system 2-pentanol-HMF-water at *T*= 313.15 K and atmospheric pressure using NRTL and UNIQUAC models; (—■—) experimental data; (--△--) NRTL model; (--○--) UNIQUAC model.

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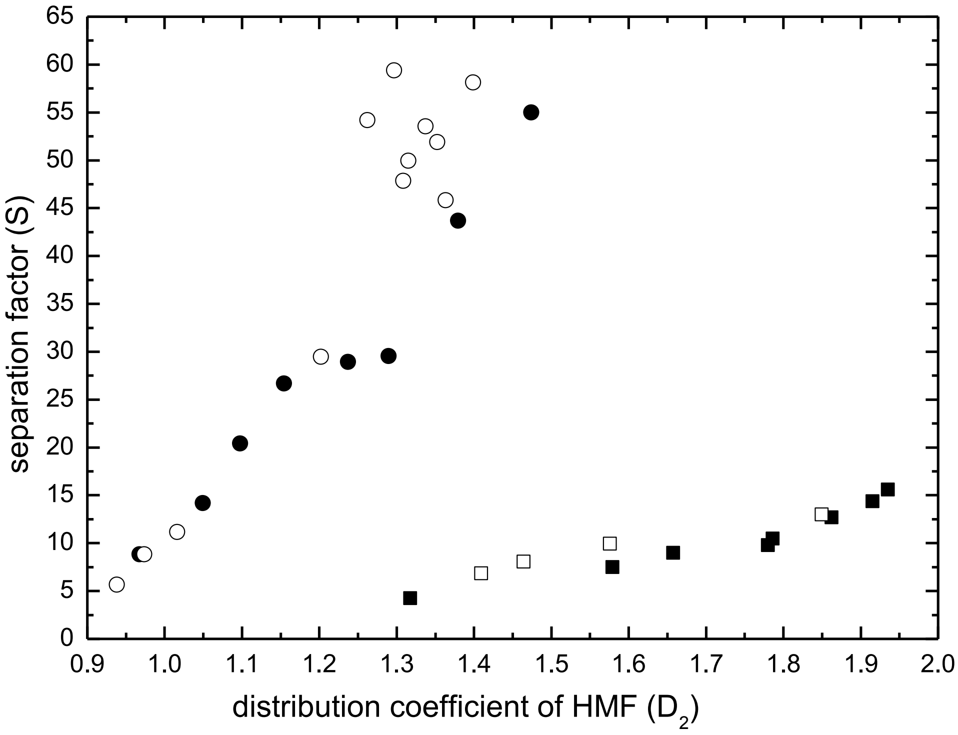

Fig. 4. Relationship between separation factor (S) and distribution coefficient of HMF (D_2) for the organic solvent-HMF-water systems at *T*= 313.15 K and 298.15 K, and atmospheric pressure; (●) MIBK-HMF-water at 313.15 K (this study) ; (○) MIBK-HMF-water at 298.15 K [19]; (■) 2-pentanol-HMF-water at 313.15 K (this study); (□) 2-pentanol-HMF-water at 298.15 K [23].

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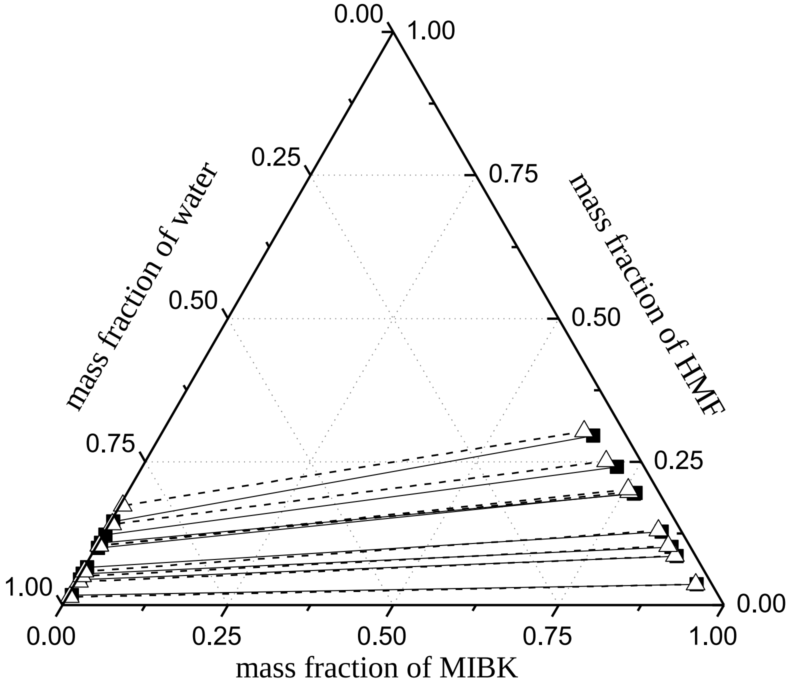

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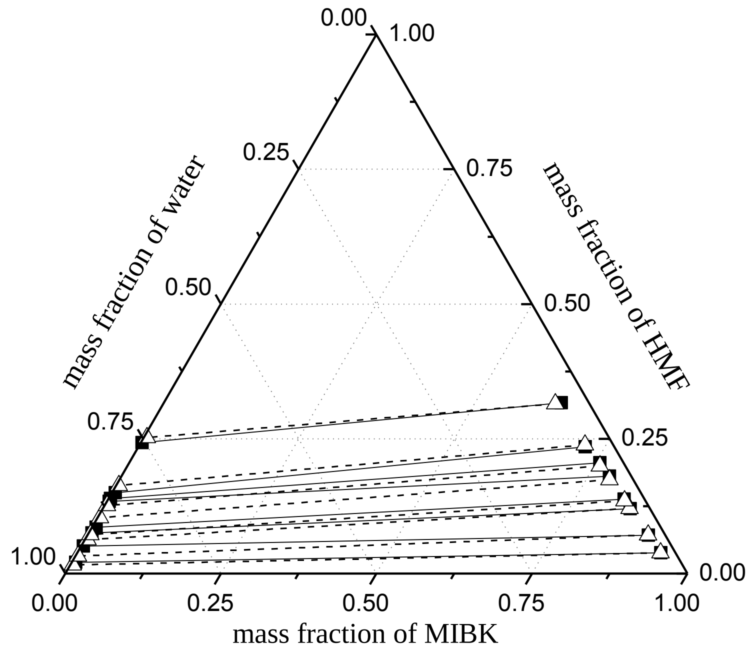

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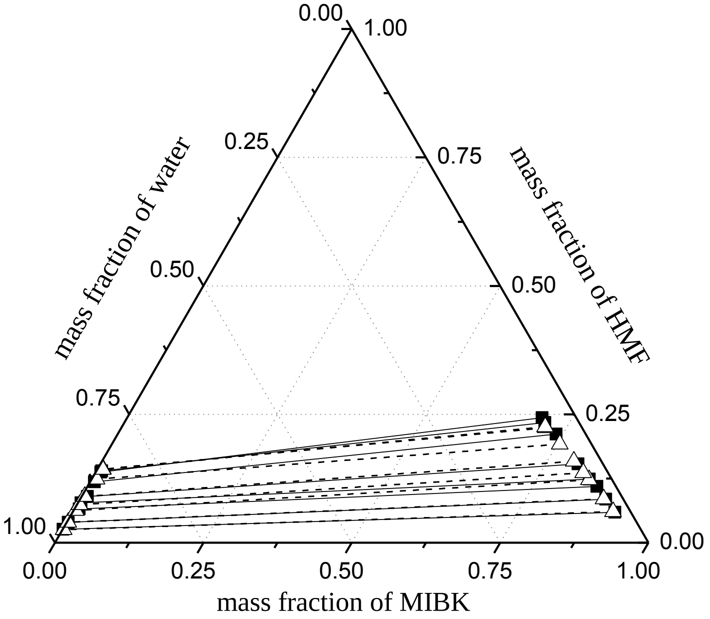

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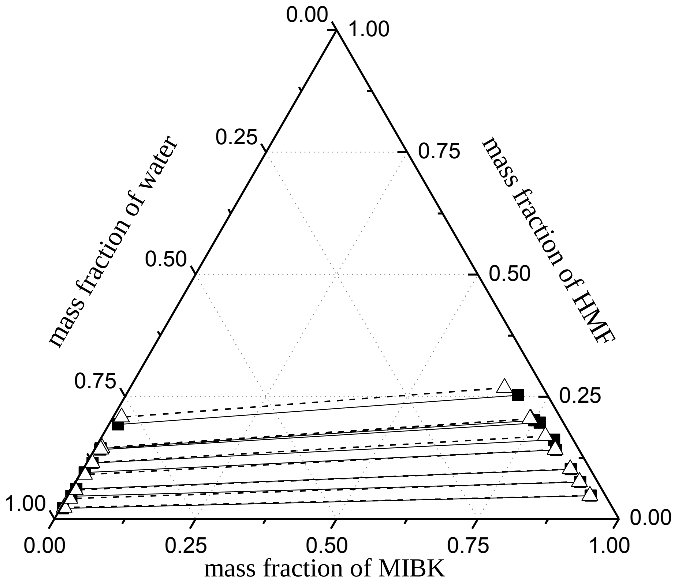

(d)

Fig. 5. 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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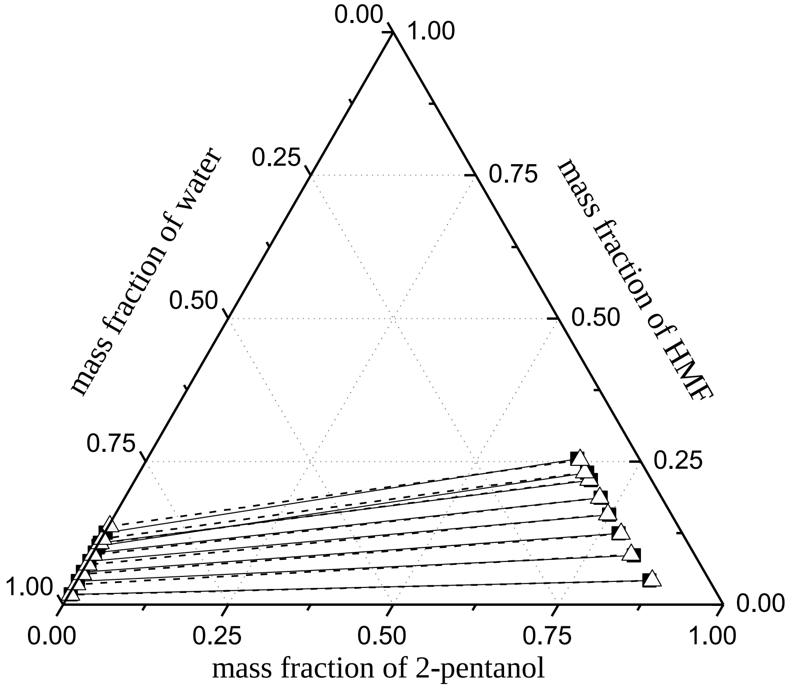

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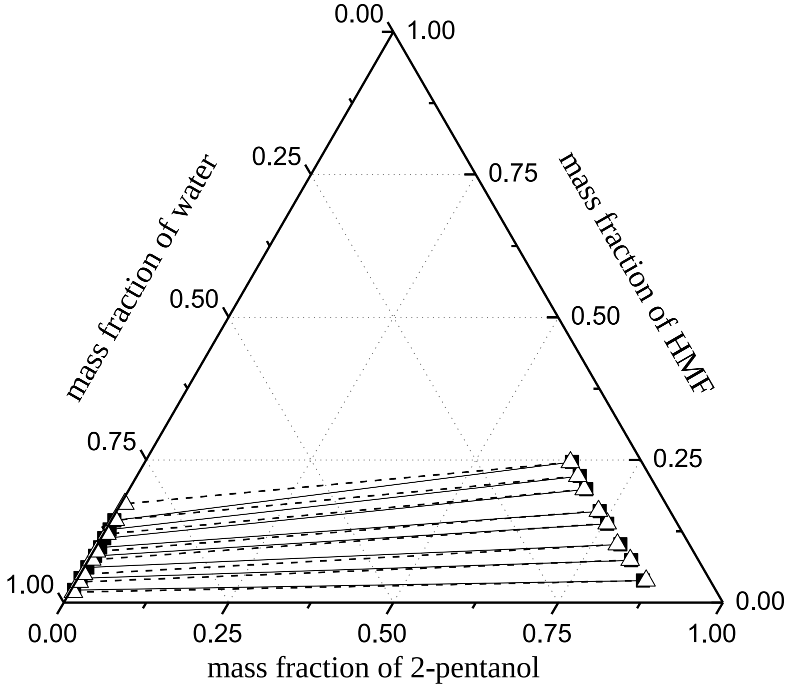

(b)

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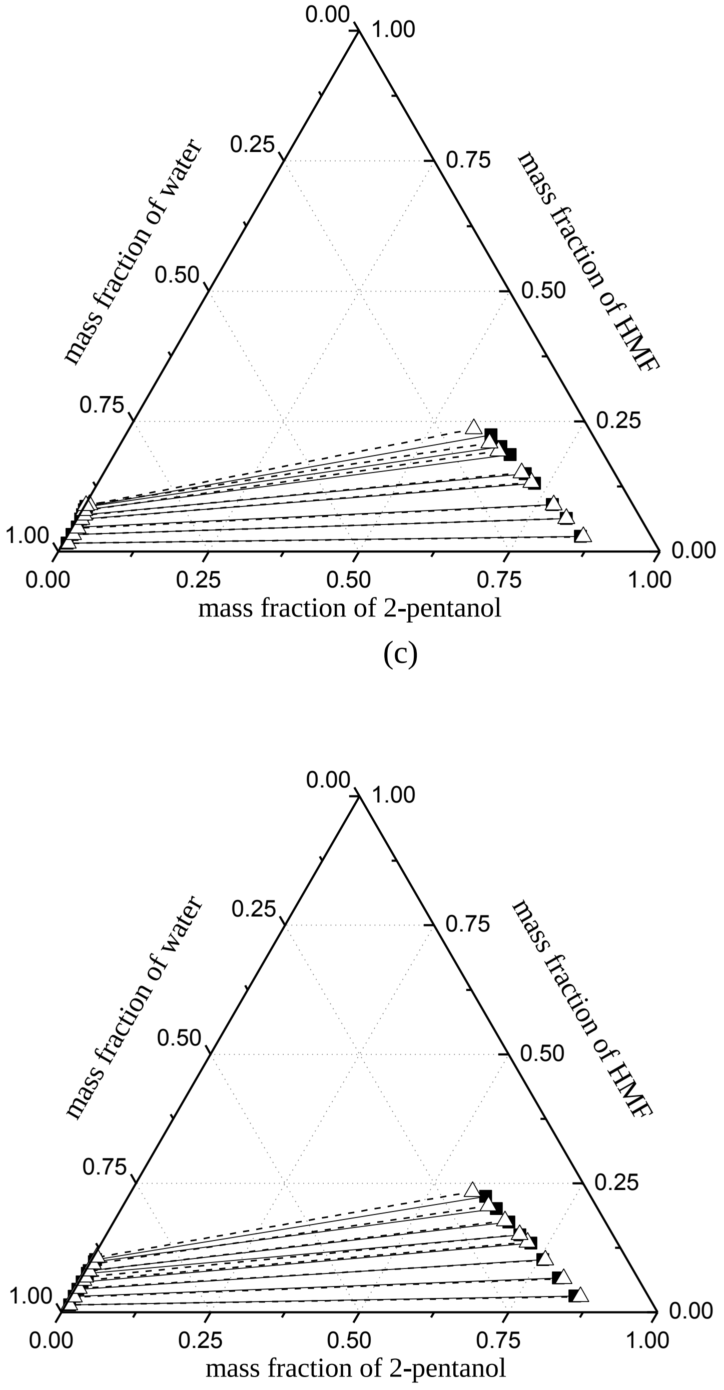

(c)

(d)

Fig. 6. 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_2SO_4; (d) 2.5 wt% K_2SO_4;(—■—) experimental data; (- - -△- - -) NRTL model.

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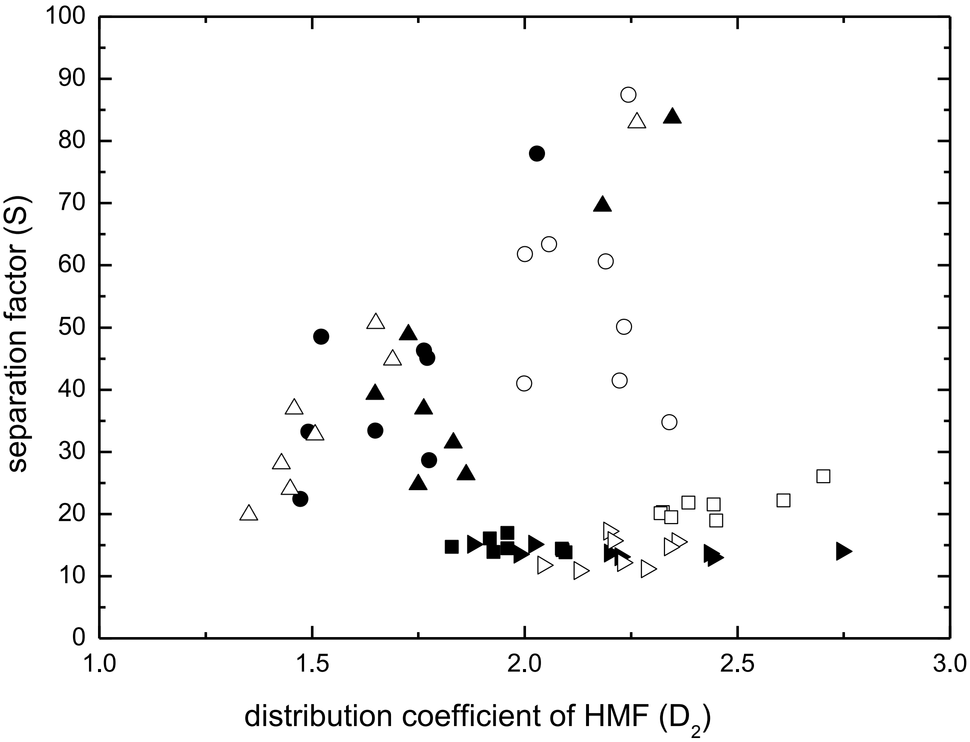

Fig. 7. Relationship between separation factor (S) and distribution coefficient of HMF (D_2) for the organic solvent-HMF-water-salt systems at *T*= 313.15 K and atmospheric pressure; (○) MIBK-HMF-water-NaCl; (●) MIBK-HMF-water-KCl; (▲) MIBK-HMF-water-Na_2SO_4; (△) MIBK-HMF-water-K_2SO_4; (□) 2-pentanol-HMF-water-NaCl; (■) 2-pentanol-HMF-water-KCl; (▶) 2-pentanol-HMF-water-Na_2SO_4; (▷) 2-pentanol-HMF-water-K_2SO_4.

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