Fructose Effect on the Extraction Performance of 5-Hydroxymethylfurfural in Aqueous 1-Ethyl-3-methylimidazolium Tetrafluoroborate or Choline Chloride Urea Solution with the Aid of Sodium Chloride Using the Methyl Isobutyl Ketone Solvent

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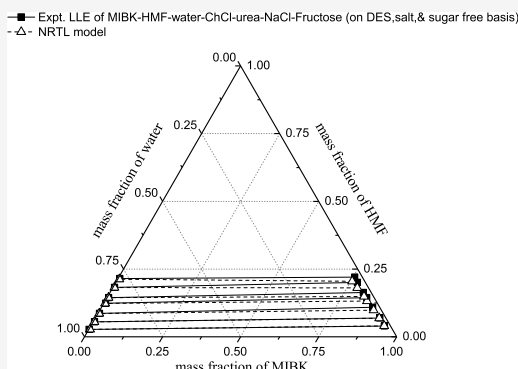
1. INTRODUCTION

The utilization of bio-renewable feedstocks to produce fuels and chemicals has increased immensely.[1−3] Expansion of the worldwide population will also increase the world energy consumption and petroleum demand. Hence, biomass needs to be used as a potential material that is sustainable and biodegradable.[3,4] 5-Hydroxymethylfurfural (HMF) is a versatile platform chemical that can be converted to biofuels and various chemical products. HMF can be synthesized by a triple dehydration of hexose feedstocks such as fructose or glucose.[3] The use of fructose as the starting reactant gives a high yield for HMF formation. Fructose was first used as the model C_6 sugar for the dehydration process due to its higher reactivity, which required a lower temperature and a shorter reaction time compared to glucose. The rate of fructose conversion and selectivity to HMF are higher than with glucose.[3] Therefore, the studies that examined the formation of HMF from fructose

showed significant improvement in the catalytic system and reaction engineering studies.[5−9] Besides, HMF can also be formed by integrating glucose isomerization with fructose dehydration in a "one-pot" reactor configuration in a biphasic system to achieve a high yield of HMF.[3] Liquid−liquid extraction can be applied in the HMF production process to enhance the yield and selectivity of HMF. HMF can be extracted from a reaction medium into the organic solvent phase, which prevents the degradation of HMF.

Table 1. Description of Chemicals Used in This Study

chemical name	source	mass fraction purity	purification method
HMF	AVA Biochem, Switzerland	≥0.99	no
MIBK	Thermo Fisher Scientific, France	≥0.99	no
1-ethyl-3-methylimidazolium	Sigma-Aldrich, USA	≥0.98	no
tetrafluoroborate			no
choline chloride	Sigma-Aldrich, China	≥0.98	no
urea	Sigma-Aldrich, Germany	≥0.995	no
sodium chloride	Sigma-Aldrich, USA	≥0.99	no
fructose	Sigma-Aldrich, USA	≥0.99	no
methanol	Honeywell, France	≥0.999	no
methanesulfonic acid	Sigma-Aldrich (France)	≥0.99	no
nitric acid	Thermo Fisher Scientific, USA	0.70	no
water	available in our lab.	deionized ultrapure water	no

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

Few researchers have systematically investigated the thermodynamics of HMF extraction.[23,24,28−31] There is still a great need for thermodynamic data, such as the partitioning of HMF into the organic solvent phase and the liquid−liquid equilibrium (LLE) of systems containing HMF with their correlations, which are required as the basis for the extraction process design. It is also essential to study the effect of the biphasic system constituents on the LLE. Our previous works have investigated the effect of salt and the presence of ILs and DESs on the LLE.[23,24,29] In the HMF production process, the conversion from sugar (fructose) to HMF is not always 100%. It is therefore crucial to investigate the extraction of HMF in the presence of unreacted fructose. In the present study, we systematically investigated the effect of a reactant (fructose) on the extraction performance of HMF in a water−IL or a DES−NaCl solution at 313.15 K and an atmospheric pressure of 0.1 MPa. Methyl isobutyl ketone (MIBK) was used as the selective extraction solvent for HMF extraction.[23,24] 1-ethyl-3-methyl-imidazolium tetrafluoroborate ([EMIM][BF$_4$]) and choline chloride urea (ChCl−urea), which are the hydrophilic IL and DES, were also applied in this work, respectively. The extraction performance was evaluated based on the values of the separation factor and the HMF distribution coefficient, which were obtained from the LLE data. Additionally, the reliability of the experimental LLE data was ascertained by the Hand and Othmer−Tobias correlations. The experimental LLE data were also correlated using the non-random two-liquid (NRTL) thermodynamic model, and the binary interaction parameters were generated in this study. The NRTL model is an appropriate correlation model to describe the LLE data in various systems including the LLE systems containing salts, which is also available in Aspen Plus and can be applied easily for process simulation. The present study also introduces new biphasic systems containing HMF and expands the scope for the thermodynamics studies of HMF extraction.

2. EXPERIMENTAL SECTION

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

2.2. Tie-Line Measurements. The experimental LLE tie-lines of MIBK, HMF, water, [EMIM][BF$_4$] or ChCl−urea, and NaCl in the presence of fructose were measured using a jacketed equilibrium cell at 313.15 K (40 °C) and an atmospheric pressure of 0.1 MPa. The thermostated water from a water bath (TamsonInstruments TC 6B, Holland) was circulated to control the equilibrium cell at a constant temperature with the standard uncertainty $u(T)$ of 0.02 K. ChCl−urea was prepared by heating choline chloride and urea with a molar ratio of 1:2 at 80 °C and stirring for 1 h until a homogeneous liquid was formed.[17] In general, feeds containing aqueous solutions of HMF−water−[EMIM][BF$_4$] or ChCl−urea−NaCl in the presence of fructose were prepared and weighed on an analytical balance Mettler Toledo (MS 304S/01, Switzerland) with a precision of ±0.0001 g. The initial HMF concentration was varied in the range of 5−35 wt % while keeping the [EMIM][BF$_4$] or ChCl−urea, NaCl, and fructose at constant concentrations. Subsequently, MIBK as the extraction solvent was added into the mixtures with a mass ratio of 1:1 between MIBK and the aqueous feed solution. The mixture was stirred in the equilibrium cell for 2.5 h and allowed to settle for 20 h for low HMF concentrations and at least 22 h for high HMF concentrations at 313.15 K until the two liquid phases were completely separated and reached equilibrium.

Table 2. Experimental LLE Tie-Line Data of MIBK (1) HMF (2) Water (3) [EMIM][BF$_4$] (4) NaCl (5) Fructose (6) System in Mass Fraction (w_i) at Temperature T = 313.15 K and P = 0.1 MPa[a]

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

[a]Standard uncertainties are $u(T)$ = 0.02 K, $u(P)$ = 0.001 MPa, and $u(w_i)$ = 0.0004 (MIBK), 0.0005 (HMF), 0.0009 (water), 0.0006 ([EMIM][BF$_4$]), 0.0007 (NaCl), and 0.0004 (fructose).

Table 3. Experimental LLE Tie-Line Data of MIBK (1) HMF (2) Water (3) ChCl−Urea (4) NaCl (5) Fructose (6) System in Mass Fraction (w_i) at Temperature T = 313.15 K and P = 0.1 MPa[a]

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

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

Then, approximately 5 mL of the sample was required for analytical measurements, which were taken from the organic and aqueous phases, respectively. The organic and aqueous samples were placed in an oven at 40 °C before further sample preparation for analytical measurements.

2.3. Analytical Measurements. The concentrations of HMF, MIBK, and fructose from organic and aqueous phases were analyzed using high-performance liquid chromatography (HPLC). A high-performance liquid chromatograph equipped with a reversed phase column C18 Zorbax ODS was applied to determine HMF and MIBK using an ultraviolet−visible (UV−vis) detector at a UV-wavelength of 278 nm and 42 °C. However, for fructose, the high-performance liquid chromatograph was equipped with a Rezex RPM-Monosaccharide column at 75 °C using a refractive index detector. The HPLC analysis method was according to our previous studies using water and methanol as eluents to detect the peak area of HMF and MIBK.[23,24] Furthermore, the peak area of fructose was detected with peak maxima at 6.3 min using water as the eluent with a flowrate of 1.5 mL/min. The Karl Fischer titration (Metrohm 756 KF) was used to analyze the water content in the organic phase. In addition, the amount of water in the aqueous phase was determined by subtracting the sum of the other mass fractions from a value of 1. The concentrations of salt in the organic and aqueous phases were analyzed using an inductively coupled plasma optical emission spectroscope(Spectro Arcos EOP) using 3% nitric acid (HNO_3) as the diluent. In addition, the IL and DES concentrations in both phases were also analyzed based on our previous studies' method using inductively coupled plasma optical emission spectroscopy and ion exchange chromatography performed with a Dionex DX-120 ion chromatograph using aqueous methane sulfonic acid as the eluent,

respectively.[23,24] The mass fractions of each component in both phases were averaged from three replicated samples. The standard uncertainties $u(w_i)$ of MIBK, HMF, water, [EMIM]-[BF$_4$], ChCl−urea, NaCl, and fructose were estimated to be 0.0004, 0.0005, 0.0009, 0.0006, 0.0002, 0.0007, and 0.0004 in the mass fraction, respectively.

3. RESULTS AND DISCUSSION

3.1. Effect of Fructose on the Extraction Performance of HMF. The experimental LLE tie-line data for the systems containing MIBK−HMF−water−[EMIM][BF$_4$]−NaCl−fructose and MIBK−HMF−water−ChCl−urea−NaCl−fructose are presented in Tables 2 and 3 and Figures 1 and 2 (on the IL/DES, salt, and sugar free basis). The initial HMF concentration ranged from 5 to 35 wt % with a constant amount of [EMIM][BF$_4$] or ChCl−urea, NaCl, and fructose. The concentrations of [EMIM][BF$_4$] and ChCl−urea were selected at 10 wt %. Taking the benefit of the IL and the DES as a stabilizing agent for HMF, the presence of 10 wt % of [EMIM][BF$_4$] or ChCl−urea in the solution is appropriate, which generated a better extraction performance compared to the ones with higher IL or DES concentrations.[23,24] The NaCl concentration was fixed at 10 wt %, which is near the maximum NaCl solubility in the highest HMF concentration used in our previous study (40 wt % of HMF).[29] Additionally, we provided the LLE data when fructose and HMF were both present in the mixture. Thus, the presence of fructose in the aqueous solution indicated the unreacted fructose. In this case, the fructose content should be less; therefore, 10 wt % of fructose was adequate and selected in this study. It will be more difficult to observe the fructose effect at a lower concentration.
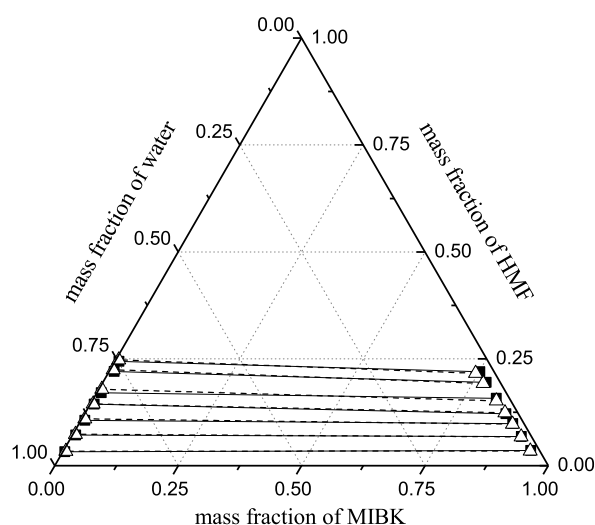
Figure 1. Phase diagram of the experimental and calculated LLE tie-line data for the MIBK−HMF−water−[EMIM][BF$_4$]−NaCl−fructose system on the IL, salt, and sugar free basis at T = 313.15 K and an atmospheric pressure of 0.1 MPa for 10 wt % [EMIM][BF$_4$], 10 wt % NaCl, and 10 wt % fructose using the NRTL model; hyphen box solid: experimental data; endash triangle up open: NRTL model.
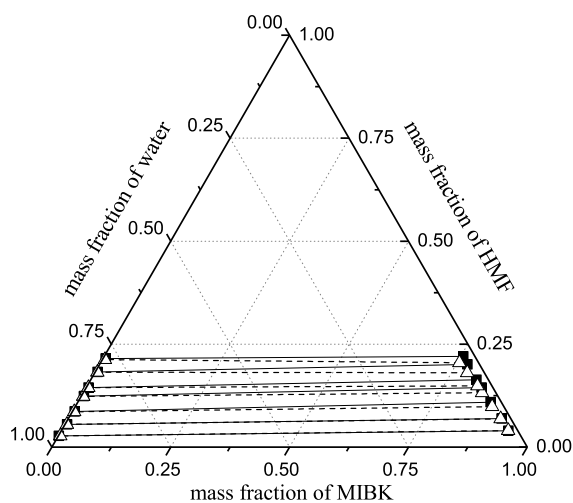

Figure 2. Phase diagram of the experimental and calculated LLE tie-line data for the MIBK−HMF−water−ChCl−urea−NaCl−fructose system on the DES, salt, and sugar free basis at T = 313.15 K and an atmospheric pressure of 0.1 MPa for 10 wt % ChCl−urea, 10 wt % NaCl, and 10 wt % fructose using the NRTL model; hyphen box solid: experimental data; endash triangle up open: NRTL model.

From Tables 2 and 3, it is evident that the ChCl−urea contents in the organic phase are much lower than the [EMIM][BF$_4$] contents, which are below 0.05 wt % for all initial HMF concentrations. It also indicates that ChCl−urea has limited solubility in the MIBK solvent, which is lower than that of [EMIM][BF$_4$] in MIBK. This has the advantages of cost-saving and energy-saving for the further product purification and solvent recycling processes. From Tables 2 and 3, it can also be seen that the concentrations of NaCl and fructose in the organic phase are very low. The NaCl concentrations range from 0.01 to 0.1 wt % and the fructose concentrations are below 0.1 wt % over the whole range of initial HMF concentrations for both LLE systems using [EMIM][BF$_4$] and ChCl−urea. The low NaCl and fructose

contents in the organic phase demonstrate good extraction and simplify the further product purification process.

In liquid−liquid extraction process, the separation factor and the distribution coefficient of HMF are the two key parameters to evaluate the extraction performance. The separation factor is used to determine the capability of an extraction solvent (MIBK) to extract the solute (HMF) from the aqueous solution. In general, the extraction depends on the physical and chemical properties of the components and the interaction of each component with the extraction solvent.[32,33] eqs 1 and 2 represent the formulas to calculate the separation factor (S) and the distribution coefficient (D_i), respectively.[32]

$$S = \frac{D_2}{D_3} \tag{1}$$

$$D_i = \frac{w_i^{\mathrm{I}}}{w_i^{\mathrm{II}}} \tag{2}$$

The separation factor (S) is defined as the ratio of the solute (HMF) distribution coefficient (D_2) to the distribution coefficient of water (D_3). w_i^{I} and w_i^{II} are the mass fractions of component i in the organic and aqueous phases, respectively. The separation factors and the distribution coefficients for the LLE of MIBK−HMF−water−[EMIM][BF$_4$]−NaCl−fructose and MIBK−HMF−water−ChCl−urea−NaCl−fructose are shown in Table 4 and Figure 3, respectively. It illustrates

Table 4. Separation Factor (S) and Distribution Coefficients (D_i) for MIBK (1) HMF (2) Water (3) [EMIM][BF$_4$] or ChCl−Urea (4) NaCl (5) Fructose (6) Systems at Temperature T = 313.15 K and P = 0.1 MPa

MIBK−HMF−water−[EMIM][BF4]−NaCl−fructose				MIBK−HMF−water−ChCl−urea−NaCl−fructose			
w_2^{I}	D_2	D_3	S	w_2^{I}	D_2	D_3	S
0.0352	1.60	0.027	59.3	0.0394	2.02	0.029	69.7
0.0676	1.46	0.034	42.9	0.0693	1.83	0.030	61.0
0.0975	1.43	0.040	35.8	0.1086	1.88	0.038	49.5
0.1200	1.32	0.046	28.7	0.1442	1.76	0.042	41.9
0.1551	1.47	0.051	28.8	0.1634	1.73	0.045	38.4
0.1912	1.44	0.059	24.4	0.2005	1.71	0.048	35.6
0.2150	1.49	0.064	23.3	0.2202	1.67	0.051	32.7

that with the increase of the HMF (solute) mass fraction in the solution at the same amount of extraction solvent, the solution becomes more concentrated, which causes the distribution coefficient of HMF (solute) and the separation factor to decrease. The reason is that with an increasing HMF (solute) mass fraction at the same amount of extraction solvent, the solvent molecules are unable to bind and take all the HMF (solute) molecules from the aqueous solution to the organic phase; there are some HMF (solute) molecules that are trapped in the aqueous solution, which also interact with the water molecules. The greater the HMF (solute) mass fraction in the solution, the more the HMF (solute) molecules interact with water molecules, causing a lower in HMF distribution coefficient; thus, the separation factor decreases as well. Furthermore, it can be seen in Table 4 and Figure 3 that the separation factors are much higher than 1 for all initial concentrations of HMF, reaching up to 59.3 for the LLE system with [EMIM][BF$_4$] and up to 69.7 for the LLE system with ChCl−urea. Besides, both systems also exhibit sufficiently
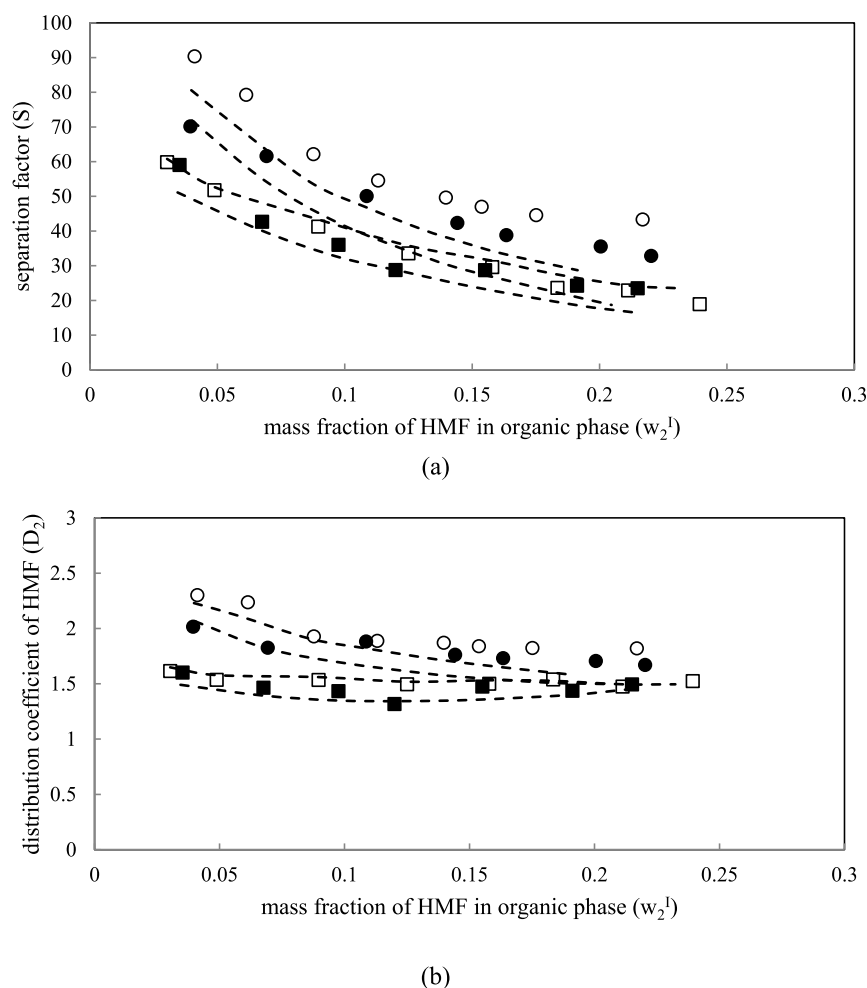
(a)

(b)

Figure 3. (a) Separation factor (S) and (b) distribution coefficient of HMF (D_2) for MIBK−HMF−water−[EMIM][BF$_4$] or ChCl−urea−NaCl systems in the absence and presence of fructose at T = 313.15 K and an atmospheric pressure of 0.1 MPa; box: MIBK−HMF−water−[EMIM][BF$_4$]−NaCl;[23] circle open: MIBK−HMF−water−ChCl−urea−NaCl;[24] box solid: MIBK−HMF−water−[EMIM][BF$_4$]−NaCl−fructose; circle solid: MIBK−HMF−water−ChCl−urea−NaCl−fructose; hyphen NRTL model.

high HMF distribution coefficients, which are above 1.3 over the whole range of initial HMF concentrations. These results confirm that the extraction of HMF from an aqueous solution containing water−[EMIM][BF$_4$] or ChCl−urea−NaCl in the presence of fructose using the MIBK extraction solvent is favorable over the whole range of initial HMF concentrations. A ketone is a polar compound in which oxygen is a relatively electronegative atom, and it can form a strong dipole when it is bound to hydrogen and carbon covalently. The dipole can allow this compound to take part in strong hydrogen bonding interactions with HMF as the hydrogen bond donor molecule. In addition, the MIBK solvent has limited solubility in water, as illustrated by the low MIBK concentrations in the aqueous phase for both systems using [EMIM][BF$_4$] and ChCl−urea, which are all below 1%, as seen in Tables 2 and 3 and Figures 1 and 2. This can minimize the solvent losses, which is good for the extraction process. The water contents in the organic phase are also sufficiently low, ranging from 2 to 3 wt % over the whole range of initial HMF concentrations for both systems. From the energy efficiency point of view, the low water content in the organic phase can also minimize the energy demand in the following product purification and solvent recycling processes.

Furthermore, from Table 4 and Figure 3, it can be inferred that the HMF extraction from an aqueous IL or DES also demonstrates a much a better distribution coefficient of HMF compared to that from a pure IL or DES, with the HMF distribution coefficient reaching up to 0.287 using a pure IL[21] and up to 0.45 using a pure DES.[15] The IL and DES can interact with the HMF molecule through hydrogen bonding interactions. Therefore, the IL or DES and the extraction solvent compete with each other to make the hydrogen bonding interaction with HMF, which causes the extraction of HMF with the extraction solvent more difficult. In this case, the presence of water as a hydrogen bond donor molecule in the solution is beneficial for the HMF extraction process. It can interact with the IL or DES, which reduces the interactions between the IL or DES and HMF. With the presence of water in the solution, the HMF molecule is more easily extracted and the HMF distribution coefficient considerably increases as well.

The effect of fructose on the extraction performance of HMF in the water−[EMIM][BF$_4$] or ChCl−urea−NaCl solution using the MIBK solvent can also be seen in Figure 3 by comparing with the LLE systems in the absence of fructose.[23,24] It indicates that fructose has a minimal effect on the separation factor and the HMF distribution coefficient. In the LLE system using [EMIM][BF$_4$], the separation factors

Table 5. Parameters of the NRTL Model for MIBK (1) HMF (2) Water (3) [EMIM][BF$_4$] or ChCl−Urea (4) NaCl (5) Fructose (6) Systems at Temperature T = 313.15 K and P = 0.1 MPa

system	i−j	$b_{ij}{}^a$ (K)	$b_{ji}{}^a$ (K)	α_{ij}	rmsd (%)
MIBK−HMF−water−[EMIM][BF4]−NaCl−fructose	1−2	483.26[b]	−738.00[b]	0.2000	0.3684
	1−3	199.41[b]	1722.53[b]	0.2000	
	1−4	290.07[c]	8545.18[c]	0.2000	
	1−5	−9044.68[b]	4925.37[b]	−0.0532[b]	
	1−6	3304.23	948.37	0.2000	
	2−3	−379.83[b]	310.86[b]	0.2000	
	2−4	−270.18[c]	−1282.76[c]	0.2000	
	2−5	−1776.15[b]	1987.56[b]	−0.3133[b]	
	2−6	−9014.87	4610.43	0.2000	
	3−4	3177.31[c]	−1492.19[c]	0.2000	
	3−5	−13345.69[b]	5478.59[b]	−0.0456[b]	
	3−6	−6718.90	−1049.84	0.2000	
	4−5	6449.31[c]	1149.44[c]	0.0640[c]	
	4−6	−6798.23	1405.41	0.2000	
	5−6	5154.65	−8697.13	0.0222	
MIBK−HMF−water−ChCl−urea−NaCl−fructose	1−2	483.26[b]	−738.00[b]	0.2000	0.7132
	1−3	199.41[b]	1722.53[b]	0.2000	
	1−4	2744.37	1297.66	0.2000	
	1−5	−9044.68[b]	4925.37[b]	−0.0532[b]	
	1−6	3304.23	948.37	0.2000	
	2−3	−379.83[b]	310.86[b]	0.2000	
	2−4	5890.33[d]	−1928.88[d]	0.2000	
	2−5	−1776.15[b]	1987.56[b]	−0.3133[b]	
	2−6	−9014.87	4610.43	0.2000	
	3−4	1878.56[d]	−1116.24[d]	0.2000	
	3−5	−13345.69[b]	5478.5[b]	−0.045[b]	
	3−6	−6718.90	−1049.84	0.2000	
	4−5	−4442.97[d]	−4915.83[d]	0.1245[d]	
	4−6	−7499.40	−966.40	0.2000	
	5−6	5154.65	−8697.13	0.0222	

[a]$\tau_{ij} = b_{ij}/T$. [b]Regressed from the experimental LLE systems of MIBK−HMF−water and MIBK−HMF−water−NaCl.[29] [c]Regressed from the experimental LLE systems of MIBK−HMF−water−[EMIM][BF$_4$] and MIBK−HMF−water−[EMIM][BF$_4$]−NaCl.[23] [d]Regressed from the experimental LLE systems of MIBK−HMF−water−ChCl−urea and MIBK−HMF−water−ChCl−urea−NaCl.[24]

decrease by around 1.1 times. The distribution coefficients of HMF are comparable with the LLE system in the absence of fructose. Furthermore, in the LLE system using ChCl−urea, fructose reduces the extraction performance by around 1.3 times for the separation factors and by 1.1 times for the HMF distribution coefficients. In the HMF production process, a small amount of fructose is usually present in the solution after the reaction, indicating unreacted fructose. Therefore, this study confirms that the presence of fructose in the solution does not significantly affect the extraction performance. A good separation factor and HMF distribution coefficient can be achieved in both biphasic systems in the presence and absence of fructose. Additionally, from comparing the IL and DES in Table 4 and Figure 3, it is confirmed that the extraction of HMF from an aqueous DES (ChCl−urea) exhibits better extraction performance with the HMF separation factor and distribution coefficient values 1.4 and 1.2 times higher than those of HMF extraction from an aqueous IL ([EMIM][BF$_4$]), respectively. Hence, a DES can be used as a potential stabilizing agent alternative to an IL in HMF production, which also shows sufficiently high extraction performance in the HMF extraction process with the presence of water.

3.2. LLE Correlation for MIBK−HMF−Water−IL or DES−Salt−Sugar Systems. The NRTL model[34] is used in the present study to correlate the experimental LLE data of the investigated systems using Aspen Plus V8.8, as listed in eq 3.

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

$$(3)$$

where γ_i represents the activity coefficient of component i, N is the number of components, $G_{ij} = \exp(-\alpha_{ij} \tau_{ij})$, $\tau_{ij} = b_{ij}/T$, $\tau_{ii} = \tau_{jj} = 0$, and $\alpha_{ij} = \alpha_{ji}$. This activity coefficient model is able to calculate the multicomponent LLE compositions only using the constituent binary parameters. The nonrandomness parameters (α_{ij}) among MIBK, HMF, water, [EMIM][BF$_4$], ChCl−urea, and fructose were set at 0.2. In the correlation, NaCl was considered as one molecular species. The α_{ij} parameters for the interactions of NaCl with MIBK, HMF, water, [EMIM][BF$_4$], and ChCl−urea were regressed, instead of setting it to the default value, from the experimental LLE data in the MIBK−HMF−water−NaCl and MIBK−HMF−water−[EMIM][BF$_4$] or ChCl−urea−NaCl systems.[23,24,29] The α_{ij} parameter of the NRTL model plays an important role in obtaining a good correlation in the experimental LLE systems containing salt.[35,36] The NRTL correlation model gives more flexibility to allow negative values for the α_{ij} parameter, leaving any supposed physical meaning. In addition,

Table 6. Correlated Results of the Hand and Othmer−Tobias equations for MIBK (1) HMF (2) Water (3) [EMIM][BF₄] or ChCl−Urea (4) NaCl (5) Fructose (6) Systems at Temperature T = 313.15 K and P = 0.1 MPa

	Hand correlation			Othmer−Tobias correlation		
system	$a*$	$b*$	R^2	a	b	R^2
MIBK−HMF−water−[EMIM][BF4]−NaCl−fructose	−0.2509	0.9094	0.9962	−1.4316	2.1443	0.9808
MIBK−HMF−water−ChCl−urea−NaCl−fructose	−0.0728	0.8684	0.9981	−1.1219	1.8829	0.9703

the binary interaction parameters (b_{ij} and b_{ji}) among MIBK, HMF, water, and NaCl were regressed from the experimental LLE of MIBK−HMF−water and MIBK−HMF−water−NaCl systems.[29] b_{ij} and b_{ji} for the interactions of [EMIM][BF₄] or ChCl−urea with MIBK, HMF, water, and NaCl were regressed from the experimental LLE of MIBK−HMF−water−[EMIM]-[BF₄] or ChCl−urea and MIBK−HMF−water−[EMIM][BF₄] or ChCl−urea−NaCl systems.[23,24] However, the b_{ij} and b_{ji} parameters for the interactions of fructose with other components investigated and α_{ij} of fructose with NaCl were regressed in this study, as listed in Table 5.

A comparison of the calculated LLE data from the NRTL model with the experimental LLE data is shown in Figures 1 and 2. The open and closed symbols denote the calculated and experimental LLE data, respectively. The NRTL model shows good agreement with the experimental LLE data with the root mean square deviations (rmsd) of 0.37% for MIBK−HMF−water−[EMIM][BF₄]−NaCl−fructose and 0.71% for MIBK−HMF−water−ChCl−urea−NaCl−fructose systems, as presented in Table 5. The rmsd between experimental and calculated LLE data is defined in eq 4.

$$\text{rmsd} = \sqrt{\frac{\sum_{k=1}^{M}\sum_{i=1}^{N}\sum_{j=I}^{II}(w_{ijk}^{\text{exp t}} - w_{ijk}^{\text{calc}})^2}{2NM}} \times 100\% \tag{4}$$

in which w_{ijk}^{expt} and w_{ijk}^{calc} are the experimental and calculated mass fractions of component i in phase j on tie-line k, respectively. M and N are the number of tie-line data and the number of components, respectively. Furthermore, it can be seen in Figure 3 that the NRTL model also provides a good description of the separation factor and HMF distribution coefficient, except that at some points, it shows a larger deviation. However, overall, the NRTL model correlates well the experimental LLE data with the rmsd below 1% for the investigated LLE systems.

3.3. Consistency of LLE Tie-Line Data. The Hand[37] and Othmer−Tobias[38] correlations were used to ascertain the consistency of the experimental LLE tie-line data. The equations of Hand and Othmer−Tobias are defined in eqs 5 and 6, respectively.

$$\ln\left(\frac{w_2^I}{w_1^I}\right) = a* + b*\ln\left(\frac{w_2^{II}}{w_3^{II}}\right) \tag{5}$$

$$\ln\left(\frac{1 - w_1^I}{w_1^I}\right) = a + b\ln\left(\frac{1 - w_3^I}{w_3^I}\right) \tag{6}$$

where w_1, w_2, and w_3 are the mass fraction of MIBK, HMF, and water, respectively. The superscripts I and II demonstrate the organic and aqueous phases, respectively. The optimal values of $a*$ and $b*$ for the Hand correlation and a and b for the Othmer−Tobias correlation are determined by fitting the LLE tie-line data to eqs 5 and 6, respectively, as listed in Table 6, in which the square of the correlation coefficient (R^2) is a

measure of the consistency of the LLE tie-line data. The correlated results of the Hand and Othmer−Tobias equations are compared to the experimental values in Figures 4 and 5,
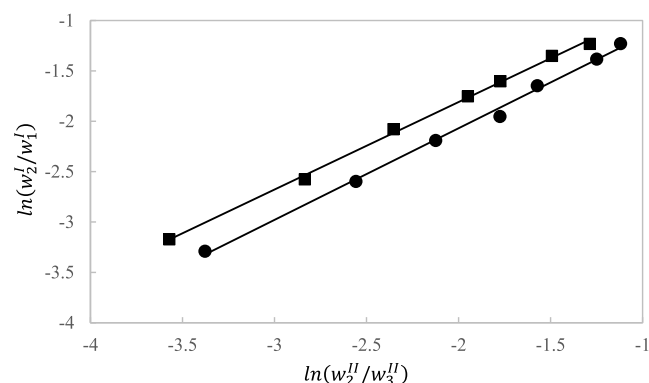
Figure 4. Hand plots for LLE data of MIBK−HMF−water−[EMIM][BF₄] or ChCl−urea−NaCl systems in the presence of fructose at T = 313.15 K and atmospheric pressure (0.1 MPa); circle solid: MIBK−HMF−water−[EMIM][BF₄]−NaCl−fructose; box solid: MIBK−HMF−water−ChCl−urea−NaCl−fructose; emdash: Hand correlation.
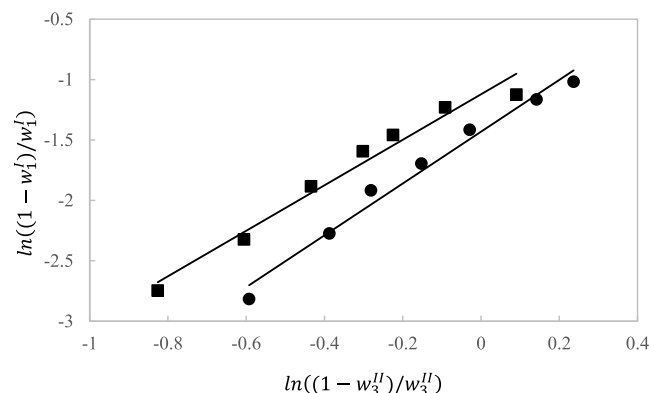
Figure 5. Othmer−Tobias plots for LLE data of MIBK−HMF−water−[EMIM][BF₄] or ChCl−urea−NaCl systems in the presence of fructose at T = 313.15 K and an atmospheric pressure of 0.1 MPa; circle solid: MIBK−HMF−water−[EMIM][BF₄]−NaCl−fructose; box solid: MIBK−HMF−water−ChCl−urea−NaCl−fructose; emdash: Othmer−Tobias correlation.

respectively. As seen from the graphs and the tabulated values of R^2, a high degree of consistency is obtained between the experimental data and both correlations, ascertaining the reliability of the experimental data.

4. CONCLUSIONS

The effects of fructose on the extraction performance of HMF in water−IL ([EMIM][BF₄]) or DES (ChCl−urea)−NaCl solution were studied at 313.15 K and an atmospheric pressure of 0.1 MPa using MIBK as a selective extraction solvent. The

separation factor and the distribution coefficient of HMF were determined from the LLE data investigated to evaluate the extraction performance. The results showed that fructose had a limited effect on the separation factor and the HMF distribution coefficient. The extraction performance for the LLE systems of MIBK−HMF−water−[EMIM][BF$_4$] or ChCl−urea−NaCl in the presence of fructose was compared to the one without. It demonstrated that for the LLE system using [EMIM][BF$_4$], the separation factors decreased by around 1.1 times. However, the distribution coefficients of HMF were comparable with the LLE system in the absence of fructose. For the LLE system using ChCl−urea, the extraction performance with the presence of fructose decreased by around 1.3 and 1.1 times for the separation factors and the HMF distribution coefficients, respectively. In addition, from comparing the IL ([EMIM][BF$_4$]) and the DES (ChCl−urea), it can be inferred that the extraction of HMF from aqueous DES (ChCl−urea) generated a better extraction performance with the values of the separation factor and the HMF distribution coefficient 1.4 and 1.2 times higher than those of HMF extraction from an aqueous IL ([EMIM][BF$_4$]), respectively. The NRTL activity coefficient model was also used to correlate the experimental LLE of the investigated systems. The correlation model provided good agreement with the experimental data with the rmsd for the LLE systems of MIBK−HMF−water−[EMIM][BF$_4$]−NaCl−fructose and MIBK−HMF−water−ChCl−urea−NaCl−fructose being 0.37 and 0.71%, respectively. The consistency of the LLE tie-line data measured in this study was also satisfactorily ascertained by the Hand and Othmer−Tobias correlations.

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Notes

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