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Liquid-liquid phase equilibrium and interaction exploration for separation of azeotrope (2,2,3,3-tetrafluoro-1-propanol + water) with two imidazolium-based ionic liquids

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Abstract

For separating azeotropic mixture 2,2,3,3-tetrafluoro-1-propanol (TFP) and water, two kinds of imidazolium-based ionic liquids 1-hexyl-3-methylimidazolium trifluoromethanesulfonate ([HMIM][OTf]) and 1-octyl-3-methylimidazolium trifluoromethanesulfonate ([OMIM][OTf]) were adopted to separate TFP and water. The liquid-liquid equilibrium behavior for the mixtures (water + TFP + [HMIM][OTf]) and (water + TFP + [OMIM][OTf]) were measured at temperature of 298.15 K and pressure of 101.3 kPa. The extraction ability of [HMIM][OTf] and [OMIM][OTf] was explored with partition ratio and selectivity. In the meantime, the hydrogen bond lengths, total electron density, interaction energies and deformation electron density were calculated to analyze the interactions between the [HMIM][OTf] / [OMIM][OTf] and (TFP / water). Also, the liquid-liquid equilibrium data was fitted by the NRTL model.

Keywords: Extraction; ionic liquids; azeotrope; 2,2,3,3-tetrafluoro-1-propanol; liquid-liquid equilibrium

1. Introduction

2,2,3,3-Tetrafluoro-1-propanol as a fluorine-containing solvent has the advantages of good solubility, fast gasification, low toxicity [1] and good lubricity, which has been widely applied for preparation of medicine, pesticides, dyes [2] and can be used as processing additive and cleaning agent [3, 4]. Usually, during the utilization of TFP, there are different concentrations of aqueous solutions of TFP appeared. Since TFP can form an azeotrope with water with the composition of (TFP / water, 72.5 / 27.5, mass fraction) at $T = 365.7$ K [5]. It is impossible to separate TFP from the azeotrope by conventional distillation.

Generally, it is essential to adopt some special distillation technologies to separate azeotropic mixtures, for instance, pressure-swing distillation [6, 7], extractive distillation [8-11] and reactive distillation [12, 13]. In order to separate the azeotrope of TFP and water, Shi et al. adopted azeotropic distillation with the entrainers chloroform and p-xylene [14] and explored the process design and control strategies [15]. Li et al. [16] applied extractive distillation to separate TFP and water with N-methyl pyrrolidone, N, N-dimethyl formamide and N-methyl formamide as the entrainers. In addition, Diao et al. [17] also applied extractive distillation but chose the different entrainers [EMIM][Ac] and [EMIM][Cl] to recover TFP from its aqueous solution.

Compared to those above special distillation technologies, for the separation of the azeotrope TFP and water, liquid-liquid extraction [18, 19] was adopted due to its advantage of energy-saving. Therefore, the liquid-liquid equilibrium (LLE) data are required to develop the separation process. Recently, Jia et al. [20] selected the solvents anisole and 1-octanol to separate TFP and water and measured the LLE data for two systems (water + TFP + Anisole) and (water + TFP + 1-octanol). Li et al. [21] adopted tert-butyl methyl ether and isopropyl ether as extractants and explored the liquid-liquid phase behavior for (water + TFP + isopropyl ether) and (water + TFP +

tert-butyl methyl ether). Xu et al. [22] achieved the LLE data for the mixtures (ethyl acetate + TFP + water) and (isopropyl acetate+ TFP + water). Until now, ionic liquid (ILs) have been adopted to separate alcohols from its aqueous mixtures due to the advantages of good thermal, chemical stability and recyclable [23-26]. However, there have been no literatures reported the LLE data about the separation of (TFP + water) with ILs as extractants.

For separating TFP from its azeotrope by liquid-liquid extraction, two ILs [HMIM][OTf] and [OMIM][OTf] were adopted as the extractants. The LLE data of the mixtures (water + TFP + [HMIM][OTf]) and (water + TFP + [OMIM][OTf]) were determined at the temperature of 298.15 K. The extraction capacity of the two ILs was explored with partition ratio and selectivity. In the meantime, the hydrogen bond lengths, total electron density, interaction energies and deformation electron density were calculated to analyze the interactions between ILs and (TFP / water). Furthermore, the NRTL [27-29] thermodynamic model was adopted to correlate the LLE experimental data.

2. Experimental section

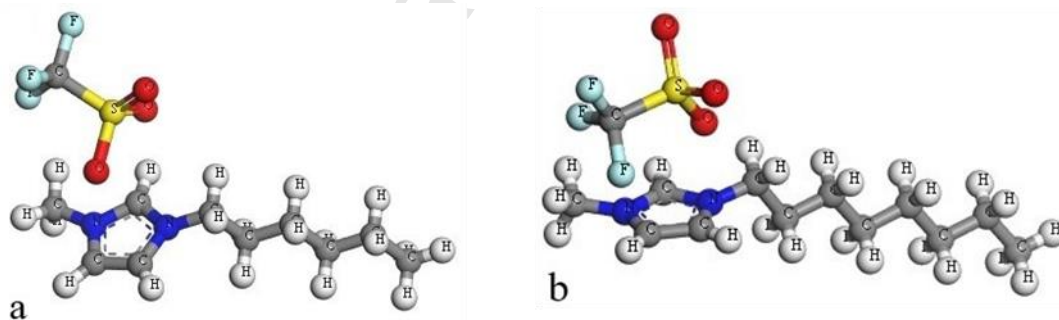
2.1 Chemicals

2,2,3,3-Tetrafluoro-1-propanol (TFP), 1-hexyl-3-methylimidazolium trifluoromethanesulfonate ([HMIM][OTf]) and 1-octyl-3-methylimidazolium trifluoromethanesulfonate ([OMIM][OTf]) were commercially purchased. TFP was used directly with its purity confirmed by GC. The water content of ILs was validated by Karl Fischer method. Before used, [HMIM][OTf] and [OMIM][OTf] were dried at 423.2 K in a vacuum rotary evaporator. The deionized water with conductivity of about 1.0 $\mu\text{s}/\text{cm}$ was prepared by the ultra-pure water machine in our lab. The details of reagents are detailed in Table 1 and the structures of [HMIM][OTf] and [OMIM][OTf] are plotted in Fig. 1.

Table 1

Information of chemicals used in this work.

Component	CAS number	Mass fraction purity	Water content/ 10^{-6}	Supplier	Analysis method
2,2,3,3-tetrafluoro-1-propanol	76-37-6	0.996	-	Shandong Fluoro Technology Co., Ltd.	GC ^a
1-hexyl-3-methylimidazolium trifluoromethanesulfonate	460345-16-8	≥ 0.98	252	Lanzhou Zhongke Ketko Industry & Trade Co. Ltd.	Karl Fischer titration ^b
1-octyl-3-methylimidazolium trifluoromethanesulfonate	403842-84-2	≥ 0.98	129	Lanzhou Zhongke Ketko Industry & Trade Co. Ltd.	Karl Fischer titration ^b
Deionized water	7732-18-5	-	-	Made in lab	-

^a Gas chromatograph.^b Determined by KLS701 Micro-moisture Meter.**Fig. 1.** ILs structures: a, [HMIM][OTf]; b, [OMIM][OTf]

2.2 Experimental apparatus and procedure

The LLE experiment was performed at the temperature of 298.15 K. To ensure the immiscible area of two phases as possible, the mass of [HMIM][OTf] / [OMIM][OTf] was fixed with the mass of TFP decreased and that of water increased. [30] Then, the prepared mixed solution was discharged into the specific LLE equilibrium cell [31] with a sample port near the bottom. To ensure the mixing completely, the mixed

solutions were agitated for 3 h using a magnetic stirrer at speed of 1000 rpm in a water bath. After settling for 13 h, the state of equilibrium was achieved. Then the samples were collected by syringes from the two phases for analysis.

2.3 Sample Analysis

GC (SP6890, Lunan) equipped with a TCD, a pre-column and a packed column was applied for sample analysis. The analysis conditions are detailed in Table 2. To get the compositions of TFP and water, the calibration normalization method [32] was used. The gravimetric method [33, 34] was adopted to determine the compositions of [HMIM][OTf] / [OMIM][OTf] and a vacuum drying oven (DZF-6020, Shanghai Jiecheng Experimental Instrument Co., Ltd.) was used to evaporate TFP and water. The weight of sample was accurately measured before and after evaporation of TFP and water by an electronic balance (AR124CN) and the IL mass in the mixture was obtained. The calculated standard uncertainty of the components (mass fraction) is less than 0.0061. In addition, the standard uncertainties of the temperature and the pressure are 0.05 K and 0.35 kPa, respectively.

Table 2

Detailed operation conditions for GC

Name	Characteristic	Description
Packed column	Specification	GDX-403(2m×0.53mm×1.00μm), Zibo Gannuo Instrument Co., Ltd.
Pre-column	Specification	GDX-403(10cm×0.53mm×1.00μm), Zibo Gannuo Instrument Co., Ltd.
Carrier gas	Type	Hydrogen
	Purity	0.9999
	Flow rate	50 mL/min
Injector	Temperature	443.15 K
Oven	Temperature	423.15 K
Detector	Type	Thermal conductivity detector (TCD)
	Temperature	443.15 K

3. Results and discussion

3.1 LLE Experimental data

The experimental data on LLE for the mixtures (water + TFP + [HMIM][OTf]) and (water + TFP + [OMIM][OTf]) were measured at 298.15 K and 101.3 kPa. These measured results for the two systems are shown by mass fraction in Table 3, where w represents the mass fraction, the subscript i stands for the chemical composition in the systems, the superscript I is the raffinate phase and the superscript II is the extraction phase. Meanwhile, the ternary phase diagrams of (water + TFP + [HMIM][OTf]) and (water + TFP + [OMIM][OTf]) are drawn in Figs. 2 and 3 to explore the extraction ability of ILs with same anions but different alkyl chain length in separating the azeotrope TFP and water. All the ternary phase diagrams belong to Treybal type I.

Table 3

LLE experimental data on mass fraction w , partition ratio (β) and selectivity (S) for the ternary system water (1) + TFP (2) + ILs (3) at $T = 298.15$ K and $P = 101.3$ kPa.^a

Upper phase		Lower phase		β	S
w_1^I	w_2^I	w_1^{II}	w_2^{II}		
water (1) + TFP (2) + [HMIM][OTf] (3)					
0.7094	0.2382	0.1696	0.5180	2.175	9.093
0.7426	0.2078	0.1519	0.4826	2.322	11.35
0.7736	0.1804	0.1333	0.4490	2.490	14.45
0.8001	0.1570	0.1280	0.4012	2.556	15.97
0.8276	0.1342	0.1102	0.3504	2.611	19.61
0.8533	0.1125	0.0979	0.3053	2.714	23.65
0.8766	0.0913	0.0888	0.2589	2.837	28.02
0.9029	0.0683	0.0773	0.2028	2.970	34.70
water (1) + TFP (2) + [OMIM][OTf] (3)					
0.7698	0.2001	0.1465	0.5340	2.669	14.02
0.7848	0.1865	0.1299	0.5031	2.698	16.30
0.8022	0.1719	0.1118	0.4697	2.733	19.62
0.8247	0.1513	0.1046	0.4219	2.788	21.97
0.8455	0.1323	0.0927	0.3730	2.820	25.72
0.8671	0.1127	0.0791	0.3307	2.933	32.16
0.8869	0.0941	0.0686	0.2853	3.032	39.23
0.9145	0.0668	0.0592	0.2114	3.165	48.90

^a Standard uncertainties u are $u(T) = 0.05$ K, $u(p) = 0.35$ kPa, $u(w) = 0.0061$

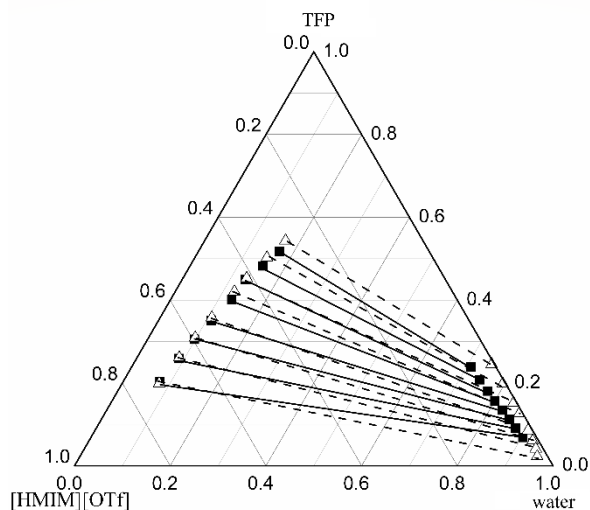


Fig. 2. Measured LLE data and correlated values by NRTL model for the ternary mixture water (1) + TFP (2) + [HMIM][OTf] (3) at 298.15 K: (—■—), experimental data; (--Δ--), correlated value by NRTL model.

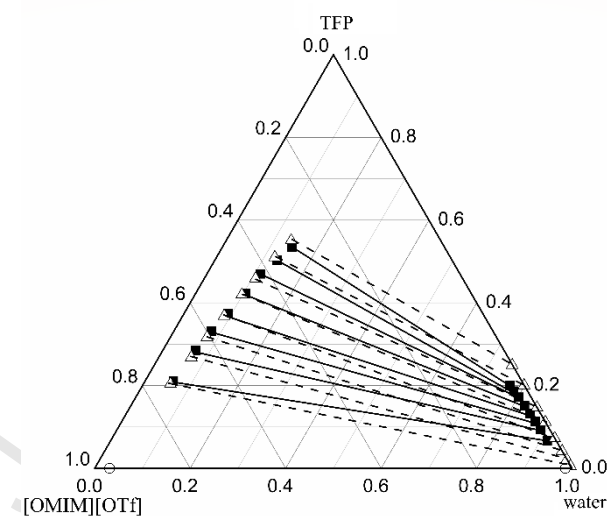


Fig. 3. Measured LLE data and correlated values by NRTL model for the ternary mixture water (1) + TFP (2) + [OMIM][OTf] (3) at 298.15 K: (—■—), experimental data; (--Δ--), correlated value by NRTL model; (○), Ref [35].

As shown in Fig. 3, the tendency of the experimental data for the system (water + TFP + [OMIM][OTf]) is consistent with the binary endpoint LLE data of the system water + [OMIM][OTf] from Santos's work [35]. In addition, the immiscible area increases with increasing the alkyl chain length of cations in ILs.

3.2 Partition ratio (β) and selectivity (S)

To investigate the extraction capability of [HMIM][OTf] / [OMIM][OTf], the partition ratio and selectivity were adopted and are presented by the following equations [36, 37]:

$$\beta = \frac{w_2^{\text{II}}}{w_2^{\text{I}}} \quad (1)$$

$$S = \frac{(w_2^{\text{II}}/w_2^{\text{I}})}{(w_1^{\text{II}}/w_1^{\text{I}})} \quad (2)$$

where w_2^{I} , w_2^{II} refer to mass fractions of TFP in water-rich phase and ionic liquid-rich phase; w_1^{I} and w_1^{II} denote mass fractions of water in water-rich phase and ionic liquid-rich phase. The calculated values of partition ratio and selectivity are presented in Table 3 and plotted in Figs. 4 and 5. As shown in Figs. 4 and 5, the calculated results of β and S decrease with increasing w_2^{I} .

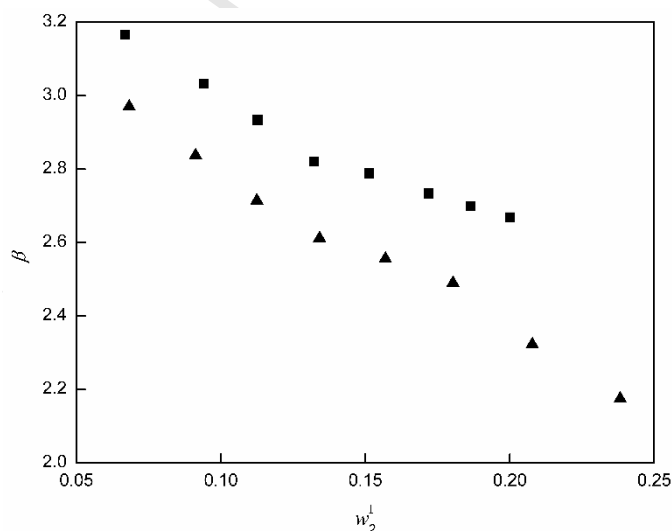


Fig. 4. The partition ratio (β) for the ternary system of water + TFP + ILs. (▲), water + TFP + [HMIM][OTf]; (■), water + TFP + [OMIM][OTf].

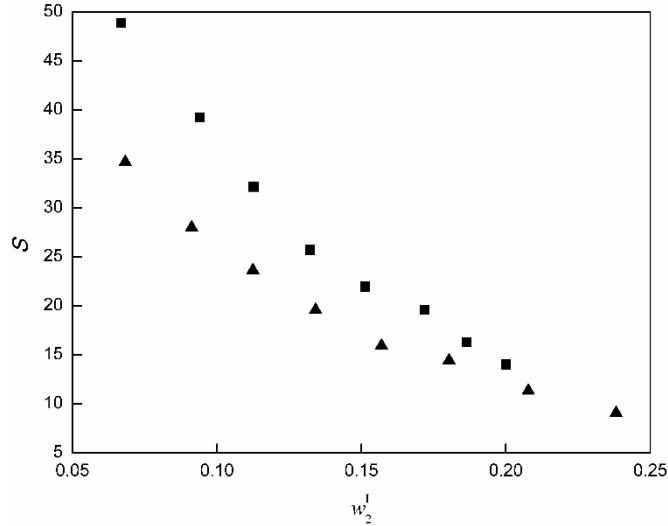


Fig. 5. The selectivity (S) for the ternary system of water + TFP + ILs. (▲), water + TFP + [HMIM][OTf]; (■), water + TFP + [OMIM][OTf].

Meanwhile, all the values of β and S are higher than unity, meaning that the adopted ILs can separate TFP from its aqueous solution. The calculated results of β and S for [OMIM][OTf] are bigger than those of [HMIM][OTf], which indicates that [OMIM][OTf] has the best extraction capacity compared to [HMIM][OTf]. Also, the extraction ability of the ILs increases with increasing the alkyl chain length of cations.

3.3 LLE data correlation

In this work, the experimental data on liquid-liquid equilibrium was fitted using the NRTL model [27] and the formula is presented as follows:

$$\ln \gamma_i = \frac{\sum_j x_j \tau_{ji} G_{ji}}{\sum_j x_j G_{ji}} + \sum_j \frac{x_j G_{ij}}{\sum_k x_k G_{kj}} \left(\tau_{ij} - \frac{\sum_k x_k \tau_{kj} G_{kj}}{\sum_k x_k G_{kj}} \right) \quad (3)$$

$$\tau_{ij} = \frac{\Delta g_{ij}}{RT},$$

$$G_{ij} = \exp(-\alpha \cdot \tau_{ij})$$

where x_i , γ_i , T and Δg_{ij} represent mole fraction of component i , activity coefficient of component i , temperature and binary interaction parameters, respectively; α represents the non-randomness factor and was set to 0.2.

Moreover, to regress the NRTL thermodynamic model parameters, the nonlinear least-squares optimization technique was used. The objective function is given as:

$$OF = \sum_{k=1}^M \sum_{j=1}^2 \sum_{i=1}^3 (w_{ijk}^{exp} - w_{ijk}^{cal})^2 \quad (4)$$

where the subscripts i, j, k and M refer to component, phase, tie-line and tie line number; w^{exp} and w^{cal} represent the measured data and calculated values in mass fraction.

For evaluating the difference between the experimental data and the correlated results, $RMSD$ was adopted and is given as follows:

$$RMSD = \left[\frac{\sum_{k=1}^M \sum_{j=1}^2 \sum_{i=1}^3 (w_{ijk}^{exp} - w_{ijk}^{cal})^2}{6M} \right]^{1/2} \quad (5)$$

The calculated results of $RMSD$ and the parameters of the NRTL model are presented in Table 4. Meanwhile, the correlated values are plotted and compared with the LLE data in Figs. 2 and 3. As listed in Table 4, the $RMSD$ values are less than 3.95%, meaning the experimental measured data and the correlated values are in agreement.

In addition, a tool GUI-MATLAB presented by ReyesLabarta [38, 39] was adopted to check the optimized parameters of the NRTL model to ensure that the correlated results and the experimental data have a good coherence. The validation results are presented in the Supplementary Materials, which shows the optimized NRTL parameters are coherent consistency [40].

Table 4

Regressed binary interaction parameters of the NRTL model, the $RMSD$ values for the ternary systems water + TFP + ILs at 298.15 K and 101.3 kPa.

$i-j$	Interaction parameter		α	$RMSD$ /%
	Δg_{ij} (kJ/mol)	Δg_{ji} (kJ/mol)		
water (1) + TFP (2) + [HMIM][OTf] (3)				
1-2	1.478	0.582	0.2	3.39
1-3	1.995	-0.331		
2-3	-0.158	-0.862		

	water (1) + TFP (2) + [OMIM][OTf] (3)			
1-2	1.296	-0.455		
1-3	2.163	-0.223	0.2	3.95
2-3	-1.765	-0.862		

4. Interaction analysis

To investigate the interactions between ILs, TFP and water, the hydrogen bond lengths, interaction energy and electron density were calculated using the Dmol³ in the Material Studio (MS). In our previous work [41-43], the detailed processes of the quantum chemical calculation were presented. For the calculation of “Geometry Optimization”, the structures were drawn with ball and stick and the DNP 4.4 basis set was used for GGA/VWN-BP. To get the hydrogen bond lengths, the structures of ILs were put together with TFP or water and the “Cutoff Global” was changed to “5.5000 angstrom”, then the “Geometry Optimization” was performed. For calculation of the electron densities and the interaction energies between ILs, TFP and water, the “Total density” and “Deformation density” were selected from the “Electron densities”, and the “Energy” calculation was performed with “Calculate BSSE correction”.

The counterpoise correction method [44], which can avoid the Basis Set Superposition Error (BSSE) and ensure the accuracy of the calculated results, was adopted in the calculation of interaction energy. The equations are given as follows:

$$\Delta E_{interaction} = E_{AB} - E_A - E_B + E_{BSSE} \quad (6)$$

$$E_{BSSE} = E_A - E_{(A,AB)} + E_B - E_{(B,AB)} \quad (7)$$

where E_{AB} represents the energy of the complex of AB in the A, B basis set, E_A is the energy of A in the A basis set, E_B is the energy of B in the B basis set; $E_{(A,AB)}$ and $E_{(B,AB)}$ stand for the energy of A and B in the A, B basis set.

4.1 Bond lengths and the interaction energies of ILs - TFP and ILs - water

The hydrogen bonds between [HMIM][OTf], [OMIM][OTf] and TFP / water are plotted in Fig. 6. The interaction energy values are list in Table 5.

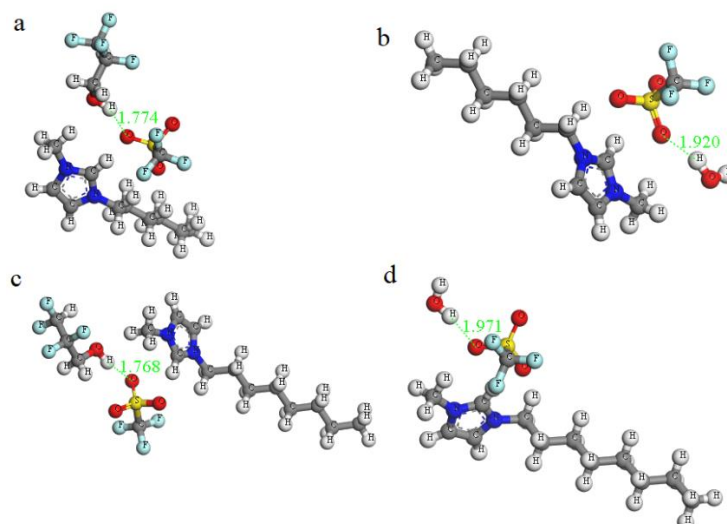


Fig. 6. Bond lengths for [HMIM][OTf] with TFP (a) and water (b), and [OMIM][OTf] with TFP (c) and water (d).

Table 5

Interaction energy of ILs - TFP and ILs - water

System	$E(\text{hartree}^a)$	$E(\text{kJ/mol})$	$\Delta E(\text{kJ/mol})$
TFP	-589.645		
water	-76.084		
[HMIM][OTf]	-1457.692		
[OMIM][OTf]	-1535.397		
[HMIM][OTf] + TFP	-2055.487	-5397201.480	-43.532
[HMIM][OTf] + water	-1540.399	-4044706.978	-30.390
[OMIM][OTf] + TFP	-2134.138	-5603720.390	-53.379
[OMIM][OTf] + water	-1619.044	-4251208.963	-27.977

^a 1hartree = 27.211eV = 627.509 kcal·mol⁻¹ = 2625.753 kJ·mol⁻¹

As shown in Fig.6, the N–H···O hydrogen bond exists in the systems ILs + TFP and ILs + water. Moreover, the bond lengths for [HMIM][OTf] - TFP, [OMIM][OTf] - TFP, [HMIM][OTf] - water and [OMIM][OTf] - water are 1.774 Å, 1.768 Å, 1.920 Å and 1.971 Å, respectively. [OMIM][OTf] has the shortest bond length with TFP, which indicates that [OMIM][OTf] has better extract capability than [HMIM][OTf]. In another word, with increasing the alkyl chain length of cations in ILs, the hydrogen bond lengths between the TFP and ILs decrease. As presented in Table 5, the calculation of the interaction energies between [OMIM][OTf] / [HMIM][OTf] with

TFP are -53.379 kJ/mol and -43.532 kJ/mol and those of [OMIM][OTf] / [HMIM][OTf] with water are -27.977 kJ/mol and -30.390 kJ/mol, respectively. [OMIM][OTf] has the biggest interaction energy with TFP and the least interaction energy with water, which indicates that [OMIM][OTf] is the suitable extractant compared to [HMIM][OTf]. Meanwhile, the interaction energy values between the ILs and TFP increases with increasing the alkyl chain length of cations in ILs.

4.2 Electron Densities between the ILs and TFP / water

The Dmol³ in the Material Studio were used to calculate the total and deformation electron densities for ILs and TFP / water. The calculated results are shown in Figs. 7-9, respectively.

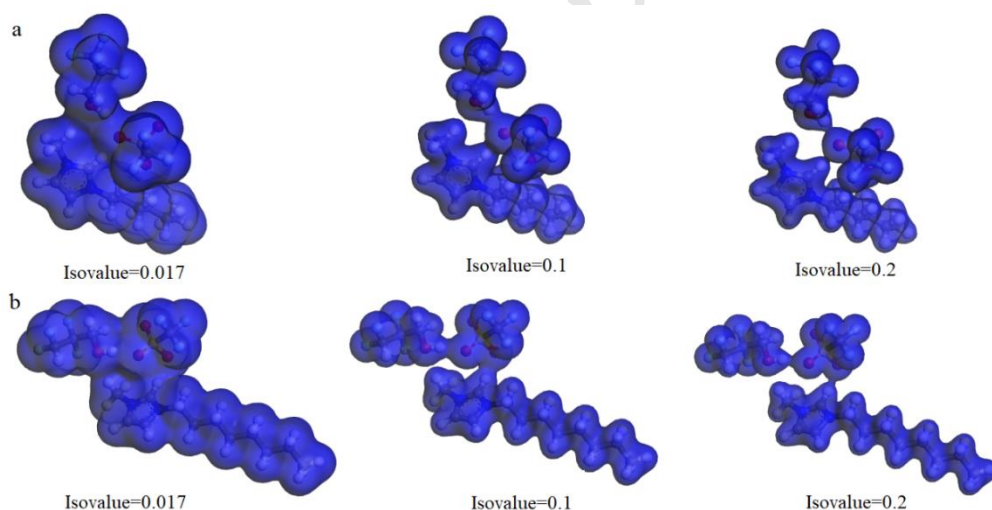


Fig. 7. Total electron density maps of different isovalues for [HMIM][OTf] (a) and [OMIM][OTf] (b) with TFP

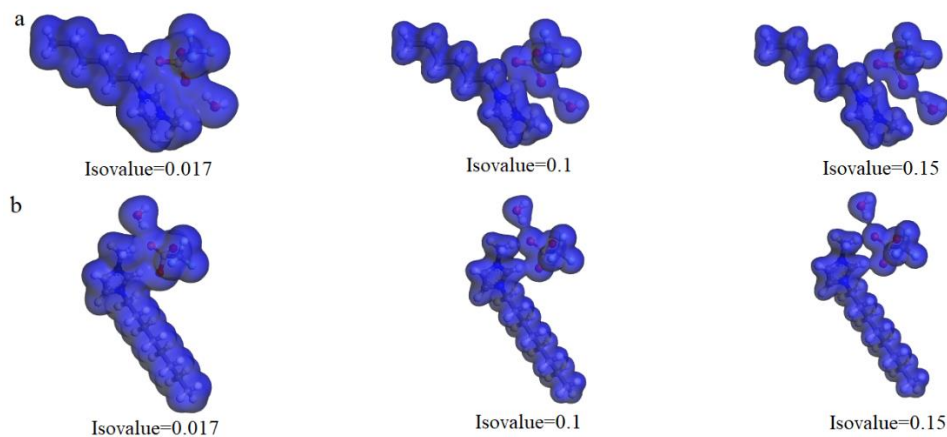


Fig. 8. Total electron density maps of different isovalues for [HMIM][OTf] (a) and [OMIM][OTf] (b) with water.

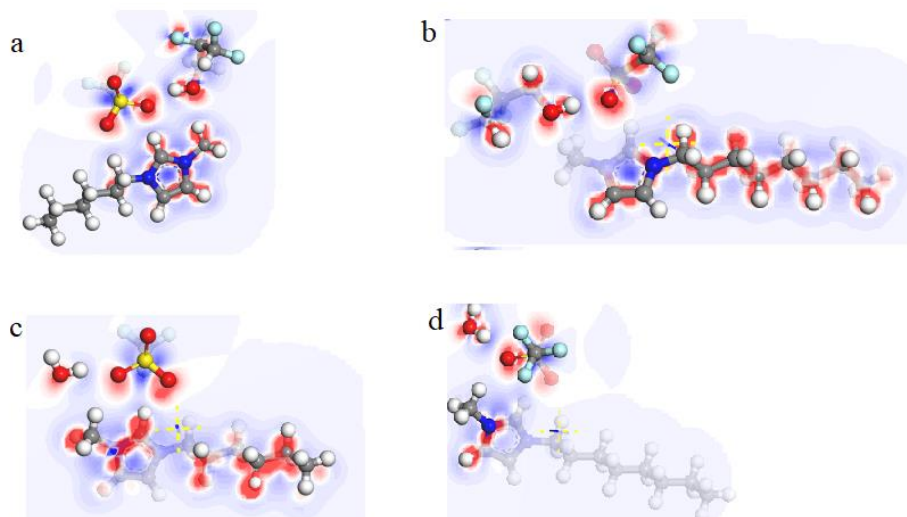


Fig. 9. Deformation electron density maps for [HMIM][OTf] (a) / [OMIM][OTf] (b) with TFP and [HMIM][OTf] (c) / [OMIM][OTf] (d) with water.

Figs. 7 and 8 are the total electron density of [HMIM][OTf] / [OMIM][OTf] with TFP / water and Fig. 9 is the deformation electron density of [HMIM][OTf] / [OMIM][OTf] with TFP / water, which are adopted to validate the formation of the hydrogen bonds between the ILs and TFP / water. As shown in Figs. 7 and 8, when the isovalue is 0.2, the hydrogen bonds appear between the anions of [HMIM][OTf] / [OMIM][OTf] and TFP. In the meantime, when the isovalue is 0.15, the hydrogen bonds appear between the anions of [HMIM][OTf] / [OMIM][OTf] and water. Moreover, as the deformation electron density shown in Fig. 9, the hydrogen bond $O\cdots H$ can be easily conformed between the anions of ILs and TFP / water. The bonding effect existed between the H atom in TFP / water and O atom in the anions of the ILs with the electron loss zone around the H atom in blue, and the received electron zone around the O atom in red.

4. Conclusion

For separation of the azeotrope TFP and water by liquid-liquid extraction, the ILs [HMIM][OTf] and [OMIM][OTf] were adopted as the extraction solvents. The experimental data on liquid-liquid equilibrium for the mixtures (water + TFP + [HMIM][OTf]) and (water + TFP + [OMIM][OTf]) were measured at the temperature

of 298.15 K. Furthermore, the values of β and S increase with increasing the alkyl chain length of cations. Meanwhile, according to the calculation of the bond lengths and interaction energies between the ILs and TFP, [OMIM][OTf] has less bond length and bigger interaction energy with TFP than [HMIM][OTf]. Also, as the analysis of the total and deformation electron densities, the ILs extraction capacity increase with increasing the cation alkyl chain lengths. Therefore, [OMIM][OTf] was more suitable than [HMIM][OTf] for extracting TFP from its aqueous mixture. The values fitted by the NRTL model showed an agreement with the determined data with the *RMSD* values less than 3.95%.

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Note

The authors declare no competing financial interest.

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Journal Pre-proof

Declaration of interests

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

The authors declare the following financial interests/personal relationships which may be considered as potential competing interests:

Highlights

- Two ionic liquids [HMIM][OTf] and [OMIM][OTf] were adopted to separate the azeotrope TFP and water.
- The LLE data for the ternary systems water + TFP + ILs were measured and correlated by the NRTL model.
- The hydrogen bond length, interaction energy, total and deformation electron densities were calculated.
- The influence of the alkyl chain length of cations on phase behavior was explored.