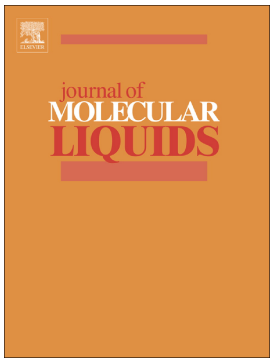

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PII: S0167-7322(17)32167-0
DOI: doi: 10.1016/j.molliq.2017.08.014
Reference: MOLLIQ 7722

To appear in: *Journal of Molecular Liquids*

Received date: 17 May 2017
Revised date: 4 August 2017
Accepted date: 5 August 2017

Please cite this article as: Xiaohua Li, Qing Zhou, Xingmei Lu, Suojiang Zhang , Densities and viscosities of binary mixtures of magnetic ionic liquids 1-alkyl-3-methylimidazolium tetrachloroferrate with ethyl acetate at temperatures (293.15 to 323.15)K, *Journal of Molecular Liquids* (2017), doi: 10.1016/j.molliq.2017.08.014

Densities and viscosities of binary mixtures of magnetic ionic liquids 1-alkyl-3-methylimidazolium tetrachloroferrate with ethyl acetate at temperatures (293.15 to 323.15) K

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Abstract: The physicochemical properties of the binary mixtures of magnetic ionic liquids (MILs) are essential for industrial process designs of their applications. In this work, three MILs were synthesized and characterized, including 1-butyl-3-methylimidazolium tetrachloroferrate ([Bmim][$FeCl_4$]), 1-hexyl-3-methylimidazolium tetrachloroferrate ([Hmim][$FeCl_4$]) and 1-octyl-3-methylimidazolium tetrachloroferrate ([Omim][$FeCl_4$]). Densities and viscosities of binary mixtures of these MILs with ethyl acetate (EA) were determined over the whole range of compositions at temperatures (293.15 to 323.15) K at 5 K intervals. The data of densities as a function of temperature were fitted with linear equation and viscosities were correlated with Vogel−Fucher−Tammann (VFT) equation. Results showed that the densities and viscosities of the binary mixtures decreased significantly with the IL concentration decreasing and with temperature increasing. Excess molar volumes (V^E) and viscosity deviations ($\Delta\eta$) were calculated and fitted well with the Redlich-Kister equation. The negative V^E and $\Delta\eta$ over the entire composition range indicated that there were stronger interactions between MILs and EA than those among MILs and among EA.

Keywords: Densities; Viscosities; Magnetic ionic liquids; Excess molar volumes; Viscosity deviations; Molecular interactions

1. Introduction

Magnetic ionic liquids (MILs) as a subclass of ionic liquids (ILs) have attracted considerable attention over the past decade, as they can combine the unique properties of ILs with magnetic, photo-physical or catalytic properties that originate from the metal incorporated in the complex anion.[1] Since the first MIL [Bmim][$FeCl_4$] was synthesized by Hayashi in 2004, more MILs have been reported in the literatures.[2-5] The paramagnetic properties are mainly induced by the transition metal containing anions, lanthanide complexes in anions or organic radical ions. For example, Del Sesto presented a series of MILs with transition metal (such as iron Fe(III), cobalt Co(II) and manganese Mn(II)) containing anions.[6] Mudring subsequently explored dysprosium based MILs with luminescence and strong response to magnetic fields.[7]

Among all these MILs, 1-alkyl-3-methylimidazolium tetrachloroferrate has been extensively studied in various application areas. As the solvent and oxidant, [Bmim][$FeCl_4$] can be used in the polymerization of conducting polymers, leading to the formation of uniform nanospheres with relatively narrow size distributions (50-100 nm).[8-10] This MIL also exhibits high catalytic activity for varied reactions, such as synthesis of 1,2-azidoalcohols, esterification of oleic acid to biodiesel and depolymerization of poly(ethylene terephthalate).[11-13] Furthermore, [Bmim][$FeCl_4$] has also been successfully applied as solvent to extract asphaltenes from coal direct liquefaction residues and [Hmim][$FeCl_4$] can effectively extract triazine herbicides from vegetable oils.[14, 15] On the grounds of magnetic property of MIL, they have the potential to open up new application areas because of their easy separation and efficient recyclability.

Despite the wide applications of MILs in the laboratory, they have not been implemented

at commercial scales yet, partially due to their high viscosities. Although it is true that the viscosity could be decreased by forming magnetic anions, still MILs have typically several orders of magnitude higher viscosity than the conventional organic solvent. A combination of the MILs with other low viscous components can be considered as an alternative. Ethyl acetate (EA) is one organic solvent with low viscosity, low cost, low toxicity and agreeable odor and it can be applied as solvents in liquid-liquid extraction, such as aromatics removal from pyrolytic oil fractions.[16, 17] Thus using EA as co-solvent is one option in MILs applications to reduce the viscosity. EA has been employed as a dispersing solvent for the extracting solvent MIL in the technique of dispersive liquid-liquid microextraction, and further used as diluent for MIL phase to reduce its viscosity prior to analysis.[18] The densities and viscosities of some pure MILs have been studied by several researchers and the results were summarized in a review paper.[1] To the best of our knowledge, no study has been reported for the binary or tertiary mixtures of MILs and organic solvents. Yet investigation on the physicochemical properties of the binary mixtures of MILs is essential for further application of MILs and also for industrial process designs.

In the present work, three MILs [Bmim][$FeCl_4$], [Hmim][$FeCl_4$] and [Omim][$FeCl_4$] were synthesized and characterized with ^{1}H NMR and Raman spectroscopy. The densities and viscosities of three binary systems, [Bmim][$FeCl_4$] + EA, [Hmim][$FeCl_4$] + EA and [Omim][$FeCl_4$] + EA, were measured over the whole range of compositions at temperatures (293.15 to 323.15) K at atmospheric pressure. The molar volume and the thermal expansion coefficient of the pure MILs were calculated from the experimental densities. The densities and viscosities of these mixtures as a function of temperature were correlated using linear equation and VFT equations, respectively. In the end, the excess

molar volumes (V^E) and viscosity deviations ($\Delta\eta$) were calculated and fitted to the Redlich-Kister equation. The intermolecular interactions were discussed as well.

2. Experimental

2.1. Materials. Ethyl acetate (> 99.5%), Iron(III) chloride (anhydrous, 98%), 1-chlorobutane (> 98%), 1-chlorohexane (> 98%) and 1-chlorooctane (> 98%) were supplied by Chemical Reagent Beijing Company Limited. 1-methylimidazole (>98%) was obtained from Beijing Donghua Rio Tinto Technology Development Company Limited.

2.2. Preparation of MILs [Bmim][$FeCl_4$], [Hmim][$FeCl_4$] and [Omim][$FeCl_4$]. [Bmim][$FeCl_4$] was prepared via two steps.[2] Firstly, the intermediate 1-butyl-3-methylimidazolium chloride ([Bmim]Cl) was synthesized by reacting 1-methylimidazole (0.20 mol) with 1-chlorobutane (0.24 mol) at 343.15 K for 48 h. The product was then washed with acetone for three times and dried in vacuum. Subsequently, the purified [Bmim]Cl was mixed with equimolar of $FeCl_3$ under N_2 atmosphere and stirred at room temperature for 12 h, leading to a dark brown liquid product. [Hmim][$FeCl_4$] and [Omim][$FeCl_4$] were prepared similarly, but 1-chlorobutane was replaced by 1-chlorohexane and 1-chlorooctane, respectively.

2.3. Characterization. The intermediates 1-alkyl-3-methylimidazolium chloride, including [Bmim]Cl, [Hmim]Cl and [Omim]Cl were characterized with ^{1}H NMR on a Brucker-ARX-600 Nuclear Magnetic Resonance spectrometer, using dimethyl sulfoxide-d_6 (DMSO-d_6) as solvent with tetramethylsilane (TMS) as the internal standard. A LabRAM HR 800 Raman spectrometer was used to detect the Raman spectra of MILs. The water content of MILs was determined by a thermogravimetric analyzer (TGA) in a nitrogen atmosphere at a heating rate of 10 °C/min.

2.4. Apparatus and Procedure. The binary mixtures of [Bmim][$FeCl_4$] + EA, [Hmim][$FeCl_4$] + EA and [Omim][$FeCl_4$] + EA were prepared by using an electronic analytical balance (Mettler Toledo ML204) with an accuracy of ± 0.1 mg and later were converted to mole fraction.

The densities of all the binary mixtures as well as the pure compounds were measured using a vibrating-tube densimeter (Anton Paar DMA 5000) with an uncertainty of ± 0.00005 g/cm^3. The temperature was controlled with two integrated Pt-100 platinum thermometers with an uncertainty of ± 0.001 K. The densities for all the samples were measured for three times and the average values were reported with an accuracy of 0.01 %.

The viscosities of all the binary mixtures and pure MILs were determined using an Anton Paar AMVn Measuring Assembly with an uncertainty of ± 0.005 mPa·s. The viscosities of EA were measured with a Capillary viscometer with an uncertainty of ± 0.01 mPa·s. All the viscosities were measured for four times and the average values were reported with an accuracy of 2 %.

The melting and glass transition points of pure MILs were obtained using a Mettler-Toledo differential scanning calorimetry DSC1 by heating from -100 to 150 °C at a rate of 10 °C/min in an atmosphere of nitrogen.

3. Results and Discussion

3.1. Characterization of MILs. The cationic structures of the intermediates [Bmim]Cl, [Hmim]Cl and [Omim]Cl and their purities were primarily confirmed with the ^{1}H NMR spectra. The data of ^{1}H NMR spectra are presented in Table 1 and the results show that the aimed intermediates have been synthesized successfully, as the ratio of the integral peak area are in agreement with the ratio of the number of the hydrogen atoms at different

chemical shift, and there are no additional peaks appearing.

Table 1. The data of ^{1}H NMR spectra for the intermediates of MILs

Name	Data of ^{1}H NMR spectra (600 MHz, DMSO-d_6, δ, ppm)
[Bmim]Cl	0.89-0.92 ppm (t, 3H), 1.26 (m, 2H), 1.76 (m, 2H), 3.85 (s, 3H), 4.16-4.18 (t, 2H), 7.71 (s, 1H), 7.78 (s, 1H), 9.15 (s, 1H)
[Hmim]Cl	0.86 ppm (t, 3H), 1.27 (m, 6H), 1.76-1.79 (m, 2H), 3.87 (s, 3H), 4.16-4.18 (t, 2H), 7.75 (s, 1H), 7.81 (s, 1H), 9.30 (s, 1H).
[Omim]Cl	0.86 ppm (t, 3H), 1.24-1.28 (m, 10H), 1.78 (m, 2H), 3.86 (s, 3H), 4.16 (t, 2H), 7.73 (s, 1H), 7.80 (s, 1H), 9.26 (s, 1H).

Since the MILs can disturb the NMR signals, their anion structures were characterized with Raman spectra and the results are shown in Figure 1. The strong band at 330 cm^{-1} was reported and assigned to the symmetric Fe–Cl stretch vibration of $FeCl_4^-$.[2] Thus, it can be confirmed that the aimed MILs have been successfully synthesized.

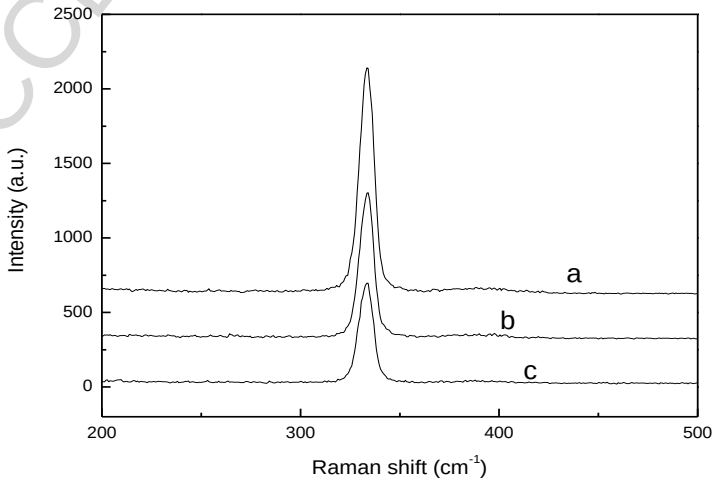


Figure 1. Raman spectra of MILs. (a) [Bmim][$FeCl_4$]; (b) [Hmim][$FeCl_4$]; (c) [Omim][$FeCl_4$]

To determine the water content of the synthesized MILs, an equipment TGA was employed by measuring the weight loss of the MILs, where the samples were heated from 20 to 700 °C. According to the TGA curves shown in Figure S1 to S3 in the Supporting Information, the water contents in all the three MILs were negligible (< 0.1 wt%), because no obvious weight loss was observed when heating to 100 °C. Furthermore, Figures S1 to S3 also indicate that these MILs start to decompose at 300 °C. On the basis of the ^{1}H NMR spectra for the intermediates, the negligible water content and the purity of the starting materials, it is concluded that the purity of the synthesized MILs were > 98 wt%. We assume that all the impurities in the MIL were from the impurities in the starting material iron(III) chloride.

The thermal property of the studied MILs were measured by DSC technique. The results showed that [Bmim][$FeCl_4$] has a melting point of -8.29 °C, while no melting point was observed for [Hmim][$FeCl_4$] and [Omim][$FeCl_4$]. But the glass transition points were detected, which are -85.70 °C, -83.50 °C and -83.01 °C for [Bmim][$FeCl_4$], [Hmim][$FeCl_4$] and [Omim][$FeCl_4$], respectively.

3.2. Densities and excess molar volumes. The densities of pure MILs and EA were determined and compared with the literature data to confirm the procedure and reproducibility of our measured data. Densities from this work and literatures are displayed in Table 2. The small deviations shown in Table 2 indicate that the experimental results are consistent with the literature data and hence the methods used in this work are valid.

Table 2. Comparison of measured densities of [Bmim][$FeCl_4$], [Hmim][$FeCl_4$], [Omim][$FeCl_4$] and EA with literature values

Compounds		Density ($g \cdot cm^{-3}$)		Deviation
	T/K	This work	Literature	(%)
[Bmim][$FeCl_4$]	293.15	1.36907	1.38[19]	0.79
			1.3700[20]	0.07
[Hmim][$FeCl_4$]	293.15	1.30812	1.33[19]	1.65
[Omim][$FeCl_4$]	293.15	1.24472	1.28[19]	2.76
EA	298.15	0.89455	0.89437[21]	0.02
	303.15	0.88841	0.88826[21]	0.02
	313.05	0.87600	0.87588[21]	0.01

Density values were measured for binary systems [Bmim][$FeCl_4$] + EA, [Hmim][$FeCl_4$] + EA and [Omim][$FeCl_4$] + EA at temperature (293.15 to 323.15) K and atmospheric pressure. The results are shown in Figure 2 and the values are collected in Table 3. It is observed that for pure MILs, [Bmim][$FeCl_4$] has the biggest density and [Omim][$FeCl_4$] exhibits the smallest one at constant temperature. This is probably because that elongating the alkyl chain length increases the free volume of the MILs and hence reduces the density. Also, the same trend is viewed for the binary mixtures. At fixed composition and temperature, [Bmim][$FeCl_4$] + EA always displays the highest densities, followed by [Hmim][$FeCl_4$] + EA and [Omim][$FeCl_4$] + EA over the whole composition range.

Table 3. Experimental densities (ρ) for binary mixtures of [Bmim][$FeCl_4$] + EA, [Hmim][$FeCl_4$] + EA and [Omim][$FeCl_4$] + EA

T (K)

x_1 [a]	293.15	298.15	303.15	308.15	313.15	318.15	323.15
			ρ (g/cm^3) for [Bmim][$FeCl_4$] + EA				
0.0000	0.90065	0.89455	0.88841	0.88222	0.87600	0.86971	0.86338
0.1002	1.01568	1.01021	1.00472	0.99922	0.99377	0.98842	0.98359
0.1999	1.09575	1.09072	1.08567	1.08060	1.07551	1.07034	1.06504
0.3007	1.16065	1.15586	1.15108	1.14631	1.14155	1.13679	1.13203
0.3999	1.21022	1.20562	1.20104	1.19648	1.19192	1.18774	1.18283
0.5000	1.24913	1.24467	1.24023	1.23580	1.23139	1.22699	1.22259
0.6001	1.28157	1.27720	1.27287	1.26855	1.26424	1.25996	1.25568
0.7000	1.30905	1.30477	1.30052	1.29629	1.29207	1.28787	1.28368
0.7973	1.33135	1.32714	1.32296	1.31878	1.31463	1.31049	1.30637
0.9000	1.35063	1.34647	1.34234	1.33822	1.33413	1.33005	1.32599
1.0000	1.36907	1.36498	1.36090	1.35685	1.35281	1.34880	1.34481
			ρ (g/cm^3) for [Hmim][$FeCl_4$] + EA				
0.0930	1.00256	0.99713	0.99169	0.98625	0.98080	0.97550	0.97000
0.1851	1.07305	1.06804	1.06302	1.05801	1.05299	1.04795	1.04318
0.2815	1.12937	1.12466	1.11995	1.11525	1.11055	1.10586	1.10117
0.3770	1.17113	1.16662	1.16212	1.15762	1.15329	1.14883	1.14436
0.4719	1.20303	1.19866	1.19430	1.18995	1.18571	1.18140	1.17709
0.5799	1.23293	1.22867	1.22443	1.22021	1.21618	1.21200	1.20782
0.6752	1.25522	1.25106	1.24692	1.24278	1.23867	1.23457	1.23049
0.7764	1.27460	1.27051	1.26645	1.26239	1.25835	1.25432	1.25031
0.8869	1.29226	1.28825	1.28426	1.28027	1.27630	1.27235	1.26841
1.0000	1.30812	1.30417	1.30023	1.29630	1.29240	1.28850	1.28462
			ρ (g/cm^3) for [Omim][$FeCl_4$] + EA				
0.0999	0.99989	0.99455	0.98920	0.98383	0.97845	0.97303	0.96762
0.1970	1.06297	1.05811	1.05324	1.04838	1.04350	1.03862	1.03373

0.2987	1.11013	1.10562	1.10110	1.09657	1.09203	1.08737	1.08243
0.3989	1.14309	1.13889	1.13468	1.13047	1.12626	1.12205	1.11784
0.4986	1.16943	1.16526	1.16112	1.15699	1.15279	1.14840	1.14423
0.6004	1.19115	1.18715	1.18316	1.17918	1.17520	1.17124	1.16728
0.6958	1.20757	1.20366	1.19976	1.19587	1.19199	1.18812	1.18426
0.7939	1.22151	1.21770	1.21388	1.21008	1.20628	1.20249	1.19872
0.8777	1.23167	1.22791	1.22416	1.22041	1.21667	1.21295	1.20924
1.0000	1.24472	1.24104	1.23738	1.23371	1.23005	1.22640	1.22276

[a] x_1 is mole fraction of MILs.

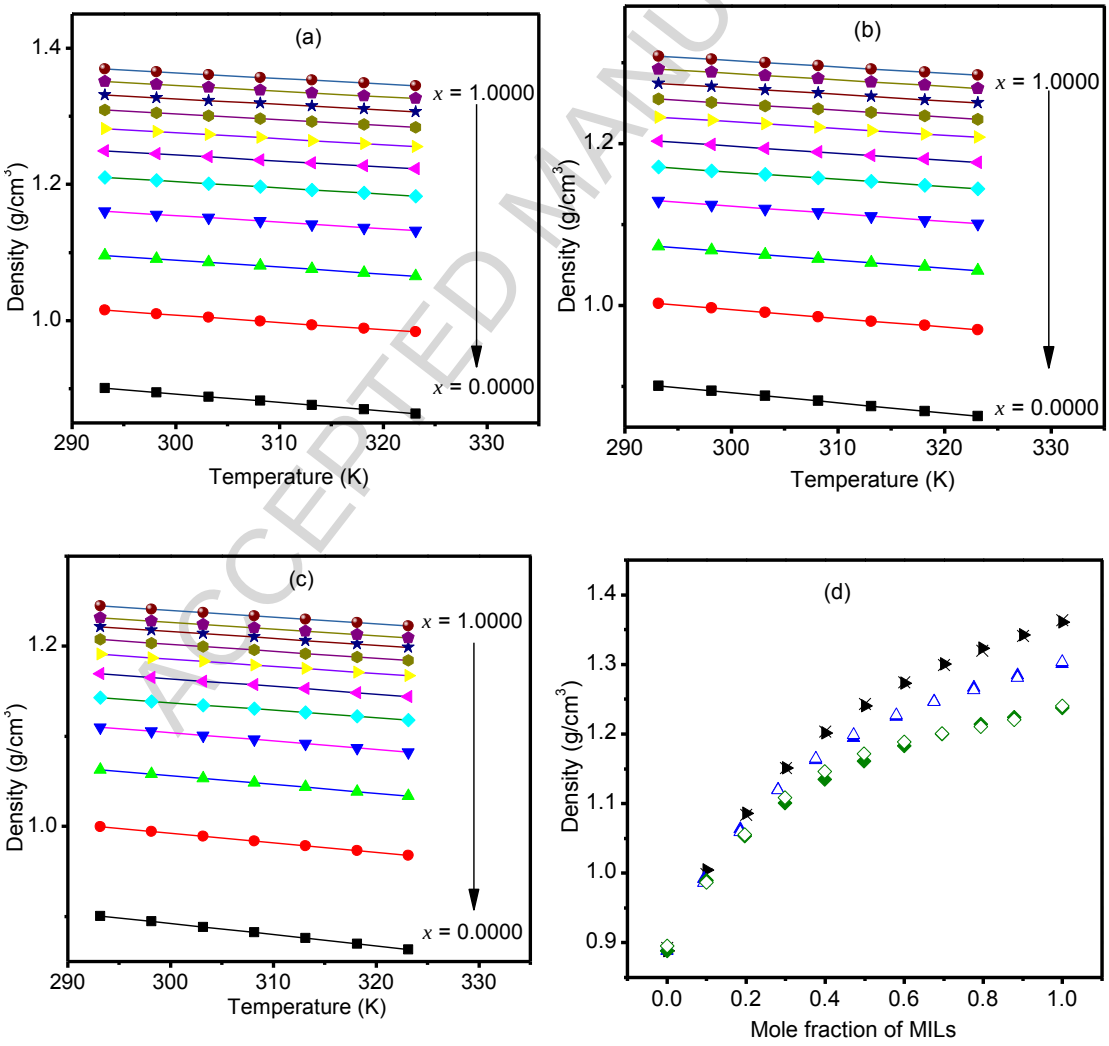


Figure 2. Densities of the binary mixtures as a function of temperature and the comparison of experimental and calculated data using equation (1) at 303.15 K. (a) [Bmim][$FeCl_4$] + EA; (b) [Hmim][$FeCl_4$] + EA; (c) [Omim][$FeCl_4$] + EA; (d) Comparison of calculated and experimental data. In figure (a), (b) and (c), the mole fractions of MILs (x) decrease from top = 1.0000 to bottom x = 0.0000. In figure (d): ► and × are experimental and calculated data for [Bmim][$FeCl_4$] + EA; ▲and Δ are experimental and calculated data for [Hmim][$FeCl_4$] + EA; ♦ and ◊ are experimental and calculated data for [Omim][$FeCl_4$] + EA

For all these three binary mixtures, their densities are gradually increased as the mole fraction of MILs increases at constant temperature. Most importantly, their densities are reducing linearly with temperature increasing, as demonstrated in Figure 2. The following equations (1) were used to correlate the density with temperature and the mole fraction of MILs.[22]

$$\rho = \alpha T + \beta$$
$$\alpha = Ax^3 + Bx^2 + Cx + D \qquad (1)$$
$$\beta = Ex^3 + Fx^2 + Gx + H$$

where ρ is the density of mixtures; T is the Kelvin temperature; α and β are the slope and y-intercept of the linear graph of density versus temperature as shown in Figure 2; x is the mole fraction of MILs and A, B, C, D, E, F, G and H are determined from polynomial equations where α and β are correlated with experimental x.

For all these three binary mixtures, α and β are expressed in terms of mole fraction of MILs x and the parameters A to H are shown in Table 4. These equations can be used to predict the density of mixtures at certain temperature and compositions. The deviations

between the calculated densities using equation (1) and the experimental data are very small as shown in Figure 2 (d). The highest deviation at 303.15 K is 1.0 % among all three binary mixtures. Unfortunately, we did not examine any clear relations between the parameter A to H and the alkyl chain length of MILs.

Table 4. Parameters for correlation of densities with temperature and mole fraction of MILs for three binary mixtures

Binary mixtures	$A*10^3$	$B*10^3$	$C*10^3$	$D*10^3$	E	F	G	H
[Bmim][$FeCl_4$] + EA	0.805	-1.758	1.376	-1.227	0.234	-0.645	0.754	1.265
[Hmim][$FeCl_4$] + EA	0.943	-2.032	1.541	-1.229	0.224	-0.583	0.632	1.266
[Omim][$FeCl_4$] + EA	1.000	-2.170	1.673	-1.229	0.254	-0.594	0.533	1.268

The molar volume (V_m) of MILs at 293.15 K were calculated from their densities using the following equation (2):

$$V_m = M / \rho \qquad (2)$$

where M is the molar mass of pure MIL and ρ is the density of pure MIL at 293.15 K. The calculated V_m for [Bmim][$FeCl_4$], [Hmim][$FeCl_4$] and [Omim][$FeCl_4$] are 246, 279 and 316 cm^3/mol respectively. The results show the average molar volume increment per CH_2 group of 17.5 cm^3/mol, which perfectly matches the range of values found in the literature for this group in other cation families.[23]

The density of MILs is dependent on the temperature. The linear equations were fitted for lnρ over the investigated temperatures, which are shown in equation (3) to (5) for [Bmim][$FeCl_4$], [Hmim][$FeCl_4$] and [Omim][$FeCl_4$], respectively. For these three equations, the correlation coefficients are all 1.0000, which indicates the fittings are very

well.

$$\ln[\rho/(g/cm^3)] = 0.3171 - 2.9803 \cdot 10^{-3} T \qquad (3)$$

$$\ln[\rho/(g/cm^3)] = 0.2716 - 3.0215 \cdot 10^{-3} T \qquad (4)$$

$$\ln[\rho/(g/cm^3)] = 0.2219 - 2.9670 \cdot 10^{-3} T \qquad (5)$$

The isobaric thermal expansion coefficients (α_p) for MILs can be defined as the temperature derivatives of ($\ln \rho$) as expressed in equation (6).

$$\alpha_p = \frac{1}{V}\left(\frac{\partial V}{\partial T}\right)_p = -\left(\frac{\partial \ln \rho}{\partial T}\right)_p \qquad (6)$$

where V is the molar volume of the MILs, ρ is the density and T is the temperature. The α_p were calculated from the slop of the linear fit of MILs. Therefore, for [Bmim][$FeCl_4$], [Hmim][$FeCl_4$] and [Omim][$FeCl_4$], the α_p are $2.9803 \cdot 10^{-3}$ K^{-1}, $3.0215 \cdot 10^{-3}$ K^{-1} and $2.9670 \cdot 10^{-3}$ K^{-1}, respectively. This result demonstrates that these MILs exhibited similar thermal expansion properties at atmospheric pressure, in spite of different alkyl chain length in the cation.

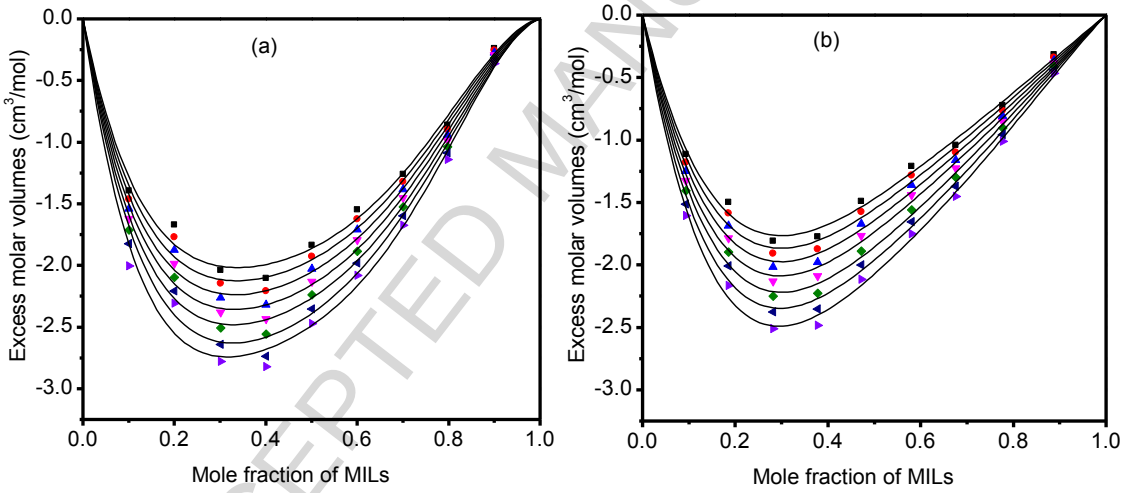
The excess molar volumes (V^E) were calculated from the experimental values using the following equation (7):

$$V^E = \frac{x_1 M_1 + x_2 M_2}{\rho} - \left(\frac{x_1 M_1}{\rho_1} + \frac{x_2 M_2}{\rho_2}\right) \qquad (7)$$

where ρ_1, ρ_2 and ρ are the densities of the pure MILs, EA and their binary mixtures; x_1 and x_2 are the mole fractions; M_1 and M_2 are molecular weights of the pure MILs and EA.

The values of V^E for all studied binary mixtures are collected in Table S1 in the supplementary information and are drawn in Figure 3. All the V^E exhibit negative deviations from ideality over the entire composition range, indicating that the volumes

contract upon mixing. It is believed that the negative V^E arises from interactions between unlike molecules, such as dipole-dipole interaction, dispersion force or hydrogen bonding.[24] Therefore, there are stronger interactions between MILs and EA as compared to those among MILs or among EA. All the V^E are more negative at higher temperature, because the H-bonding between MILs and EA tends to strengthen upon heating.[25] The values of V^E become more negative from [Omim][$FeCl_4$] to [Bmim][$FeCl_4$], implying that the interactions between MILs and EA are strengthened as the carbon chains are shortened in the cation of MILs. In addition, the minimum V^E is observed at $x \approx 0.4$ for [Bmim][$FeCl_4$] + EA and at $x \approx 0.3$ for the other two binary mixtures.



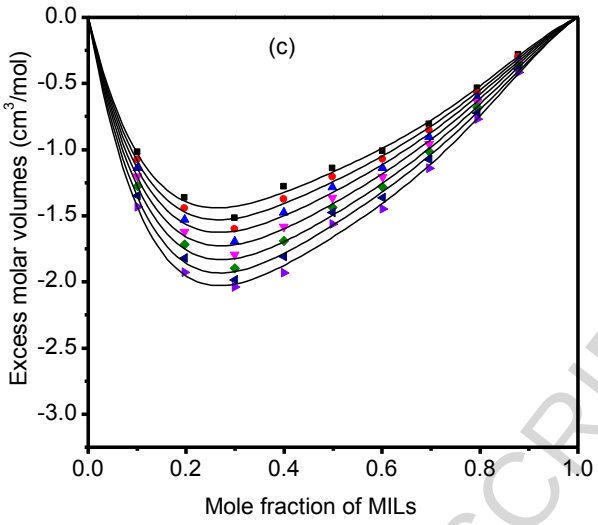


Figure 3. Excess molar volumes as a mole function of MILs at different temperatures for three binary systems. (a) [Bmim][$FeCl_4$] + EA; (b) [Hmim][$FeCl_4$] + EA; (c) [Omim][$FeCl_4$] + EA. Symbols: ■, 293.15 K; ●, 298.15 K; ▲, 303.15 K; ▼, 308.15 K; ♦, 313.15 K; ◄, 318.15 K; ►, 323.15 K. The symbols represent experimental values and the solid curves represent the data calculated from the Redlich-Kister equation.

3.3. Viscosities and viscosity deviations. The viscosities of pure MILs and EA together with their binary mixtures are measured at temperatures (293.15 to 323.15) K at 5 K intervals over the full range of compositions. All the data are presented in Table 5. It is shown that at fixed temperature, the viscosities of all studied binary mixtures are increasing significantly as the mole fraction of MILs increases. Whereas at constant composition, the viscosities are decreasing as the temperature increases.

Table 5. Experimental viscosities (η) for binary mixtures of [Bmim][$FeCl_4$] + EA, [Hmim][$FeCl_4$] + EA and [Omim][$FeCl_4$] + EA

x_1 [a]	T (K)

	293.15	298.15	303.15	308.15	313.15	318.15	323.15
				η (mPa·s) for [Bmim][$FeCl_4$] + EA			
0.0000	0.46	0.43	0.41	0.39	0.37	0.35	0.33
0.1002	1.17	1.09	1.02	0.97	0.91	0.86	0.82
0.1999	2.37	2.19	2.01	1.86	1.75	1.66	1.57
0.3007	4.32	3.92	3.56	3.26	2.99	2.76	2.56
0.3999	7.33	6.53	5.84	5.26	4.76	4.34	3.98
0.5000	11.15	9.78	8.64	7.69	6.88	6.19	5.63
0.6001	16.31	14.09	12.31	10.84	9.63	8.65	7.79
0.7000	22.98	19.72	16.92	14.65	12.81	11.32	10.08
0.7973	30.79	26.28	22.35	19.21	16.68	14.58	12.88
0.9000	41.33	34.20	28.72	24.45	21.04	18.34	16.08
1.0000	56.56	46.00	37.95	31.87	27.01	23.24	20.16
				η (mPa·s) for [Hmim][$FeCl_4$] + EA			
0.0930	1.14	1.07	1.01	0.95	0.89	0.85	0.80
0.1851	2.30	2.11	1.95	1.80	1.68	1.57	1.47
0.2815	4.29	3.87	3.51	3.20	2.93	2.70	2.50
0.3770	7.45	6.62	5.93	5.34	4.84	4.42	4.05
0.4719	11.71	10.22	9.02	8.01	7.18	6.46	5.85
0.5799	18.13	15.53	13.48	11.79	10.40	9.26	8.30
0.6752	26.64	22.42	19.08	16.45	14.33	12.60	11.15
0.7764	36.57	30.27	25.46	21.68	18.64	16.23	14.24
0.8869	51.89	42.15	34.86	29.26	24.83	21.38	18.51
1.0000	73.92	58.96	47.89	39.56	33.07	28.06	24.02
				η (mPa·s) for [Omim][$FeCl_4$] + EA			
0.0999	1.47	1.38	1.29	1.21	1.14	1.07	1.02
0.1970	3.56	3.24	2.97	2.72	2.52	2.33	2.16
0.2987	7.50	6.65	5.94	5.33	4.81	4.37	3.99

0.3989	13.82	11.97	10.48	9.22	8.17	7.31	6.60
0.4986	23.21	19.68	16.88	14.61	12.77	11.24	9.97
0.6004	37.15	30.95	26.07	22.20	19.08	16.49	14.40
0.6958	58.20	47.60	39.75	33.32	28.28	24.27	20.98
0.7939	85.97	69.55	56.28	46.86	39.40	33.42	28.43
0.8777	111.83	91.12	73.83	59.83	49.32	41.48	35.08
1.0000	166.99	133.16	105.98	84.71	68.30	55.87	46.60

[a] x_1 is mole fraction of MILs.

The viscosity reductions are more dramatic for pure MILs than for pure EA. In addition, at the same temperature, the viscosity of the MIL containing longer alkyl chain in cation are relatively high, following the order: [Omim][$FeCl_4$] > [Hmim][$FeCl_4$] > [Bmim][$FeCl_4$]. This same trend is also observed for their binary mixtures.

The Vogel-Fulcher-Tamman (VFT) method represented in equation (8) was used to fit the temperature dependence of viscosity data for the studied binary mixtures.[26]

$$\eta = A\exp[B/(T - T_0)] \qquad (8)$$

where η is the viscosity in mPa·s, T is temperature in K and A, B, T_0 are adjustable parameters. The best fitted parameters are presented in Table 6. The correlation coefficient R^2 is 1.0000 for all those fittings.

Table 6. Fitted parameters A, B and T_0 for the viscosities of binary mixtures based on VFT equation.

x_1 [a]	A (mPa·s)	B (K)	T_0 (K)
	[Bmim][$FeCl_4$] + EA		
0.0000	0.003	2260	-150
0.1002	0.134	332	140

0.1999	0.485	134	209
0.3007	0.109	663	113
0.3999	0.145	636	131
0.5000	0.148	689	134
0.6001	0.338	494	166
0.7000	0.104	894	128
0.7973	0.047	1240	102
0.9000	0.403	543	176
1.0000	0.366	587	177
		[Hmim][$FeCl_4$] + EA	
0.0930	0.012	1620	-63
0.1851	0.138	447	134
0.2815	0.134	562	131
0.3770	0.198	539	145
0.4719	0.210	579	149
0.5799	0.263	561	161
0.6752	0.301	559	169
0.7764	0.318	574	172
0.8869	0.349	580	177
1.0000	0.309	637	177
		[Omim][$FeCl_4$] + EA	
0.0999	0.040	946	31
0.1970	0.079	758	94
0.2987	0.111	717	123
0.3989	0.170	650	145
0.4986	0.181	691	151
0.6004	0.101	927	136
0.6958	0.147	874	147

0.7939	0.200	818	158
0.8777	0.003	2521	54
1.0000	0.001	3071	40

[a] x_1 is mole fraction of MILs.

The viscosity deviations ($\Delta\eta$) were calculated for all three binary mixtures according to the equation (9):

$$\Delta\eta = \eta - (x_1\eta_1 + x_2\eta_2) \qquad (9)$$

where η represents viscosity of mixtures; x_1. x_2 are mole fractions and η_1. η_2 are viscosities of MILs and EA. respectively.

Experimentally acquired $\Delta\eta$ are collected in Table S2 and shown in Figure 4 as a function of mole fraction of MILs at different temperatures from 293.15 to 323.15 K. The $\Delta\eta$ are negative for all three binary systems over the entire composition range and all minimum values are located at $x_1 \approx 0.6$. On the contrary to V^E. as the temperature increases. the $\Delta\eta$ are less negative. meaning more similar as ideal systems for all these binary mixtures. Also $\Delta\eta$ for [Omim][$FeCl_4$] + EA are the most negative and those for [Bmim][$FeCl_4$] + EA are the least negative. implying that $\Delta\eta$ becomes particularly strong as the cationic alkyl chain length of MILs increases.

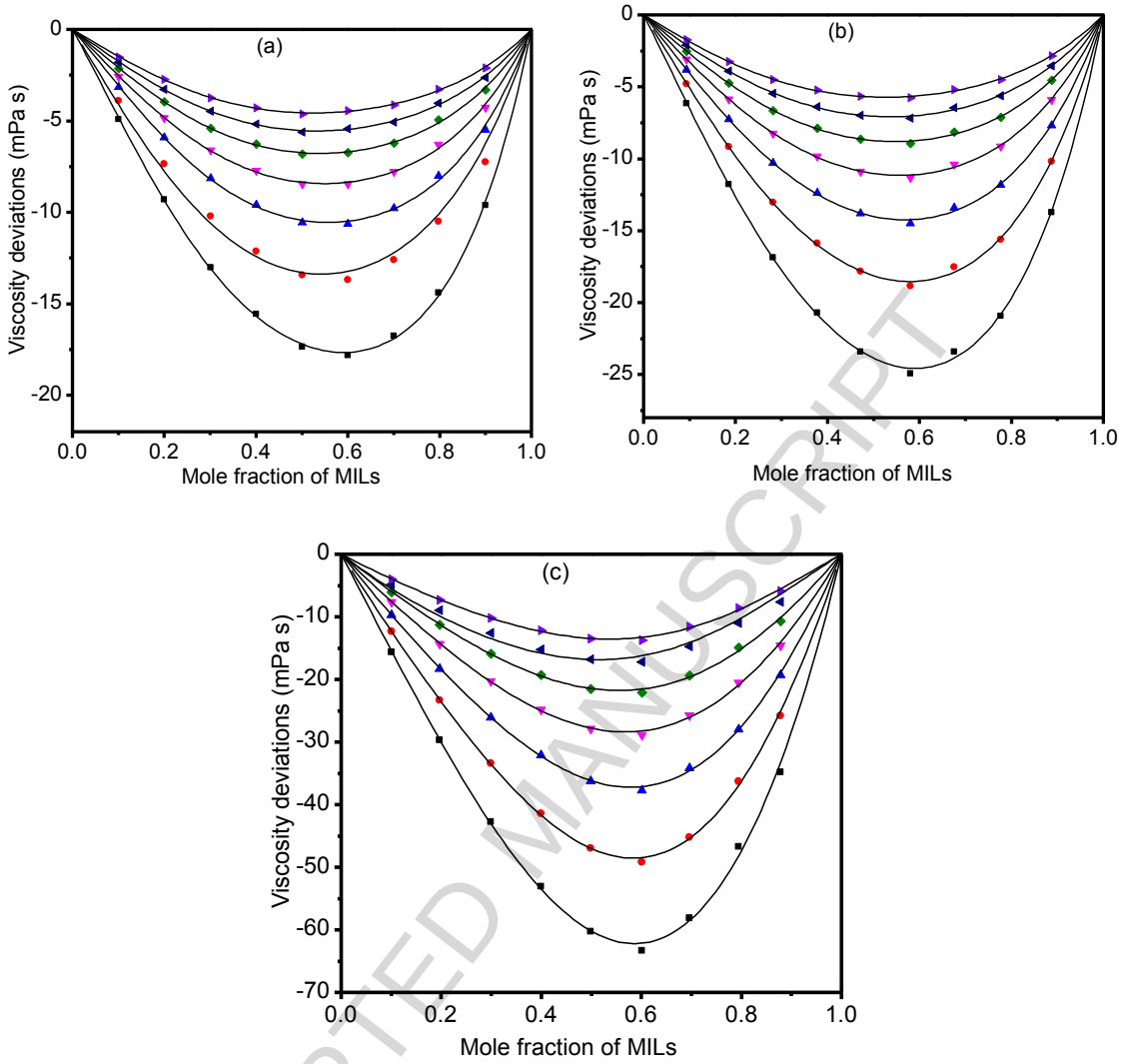


Figure 4. Viscosity deviations as a mole function of MILs at different temperatures for three binary systems. (a) [Bmim][$FeCl_4$] + EA; (b) [Hmim][$FeCl_4$] + EA; (c) [Omim][$FeCl_4$] + EA. Symbols: ■. 293.15 K; ●. 298.15 K; ▲. 303.15 K; ▼. 308.15 K; ♦. 313.15 K; ◄. 318.15 K; ►. 323.15 K. The symbols represent experimental values and the solid curves represent the data calculated from the Redlich-Kister equation.

3.4. Correlation excess properties with Redlich-Kister equation. All values of V^E and $\Delta\eta$ were fitted with the Redlich-Kister polynomial equation (10) and the standard deviation

σ was correlated by the equation (11):[27, 28]

$$Y = x_1(1-x_1)\sum_{i=0}^{3} A_i(2x_1-1)^i \qquad (10)$$

$$\sigma = [\frac{\sum(Y_{exp}-Y_{cal})^2}{n-p}]^{\frac{1}{2}} \qquad (11)$$

where Y denotes V^E or $\Delta\eta$; x_1 is mole fraction of MILs; A_i and i are equation coefficients and the degree of the polynomial expansion. respectively; n is the number of experimental data. and p is the number of coefficients of the Redlich-Kister equation.

The values of the parameters A_i and the standard deviations σ are presented in Table 7. From σ values for these mixtures and the solid curves representing the data calculated from the Redlich-Kister equations in Figure 3 and 4. it can be concluded that the polynomial equations calculated from the experiment data are acceptable for both excess molar volumes and viscosity deviations.

Table 7. Fitted parameters of equation (10) and standard deviations (σ) for three binary systems [Bmim][$FeCl_4$] + EA. [Hmim][$FeCl_4$] + EA and [Omim][$FeCl_4$] + EA

T (K)	293.15	298.15	303.15	308.15	313.15	318.15	323.15
			[Bmim][$FeCl_4$] (1) + EA (2)				
			V^E (cm^3/mol)				
A_0	-7.45	-7.82	-8.22	-8.63	-9.06	-9.57	-9.95
A_1	3.68	3.94	4.21	4.48	4.75	5.16	5.07
A_2	-1.91	-2.10	-2.29	-2.50	-2.76	-2.92	-3.64
A_3	5.05	5.22	5.40	5.59	5.90	6.00	7.61
σ	0.11	0.11	0.12	0.12	0.12	0.14	0.16

$\Delta\eta$ (mPa·s)

A_0	-68.82	-53.19	-41.75	-33.45	-26.99	-22.13	-18.24
A_1	-19.96	-12.16	-7.99	-5.53	-3.65	-2.49	-1.56
A_2	-15.66	-9.63	-6.69	-5.03	-3.43	-2.59	-1.98
A_3	-18.76	-14.88	-10.87	-8.23	-5.96	-4.64	-3.81
σ	0.19	0.26	0.20	0.15	0.11	0.07	0.06

[Hmim][$FeCl_4$] (1) + EA (2)

V^E (cm^3/mol)

A_0	-5.88	-6.21	-6.57	-6.95	-7.43	-7.85	-8.30
A_1	4.81	5.08	5.35	5.64	5.94	6.19	6.55
A_2	-3.25	-3.46	-3.70	-3.95	-4.01	-4.37	-4.80
A_3	1.30	1.39	1.52	1.70	1.90	2.37	2.70
σ	0.07	0.07	0.07	0.08	0.07	0.08	0.07

$\Delta\eta$ (mPa·s)

A_0	-95.43	-72.50	-56.03	-44.06	-34.94	-28.18	-22.83
A_1	-30.79	-20.38	-13.58	-9.03	-5.80	-3.68	-2.07
A_2	-15.50	-11.14	-8.00	-5.95	-4.62	-3.37	-2.82
A_3	-16.38	-13.25	-10.17	-8.04	-6.55	-5.13	-4.52
σ	0.27	0.22	0.16	0.13	0.11	0.09	0.08

[Omim][$FeCl_4$] (1) + EA (2)

V^E (cm^3/mol)

A_0	-4.67	-4.97	-5.29	-5.63	-5.98	-6.28	-6.64
A_1	3.33	3.60	3.89	4.17	4.45	4.65	4.68
A_2	-3.63	-3.79	-3.94	-4.10	-4.35	-4.74	-4.99
A_3	3.44	3.44	3.45	3.51	3.61	3.87	4.52
σ	0.05	0.05	0.05	0.05	0.05	0.06	0.06

$\Delta\eta$ (mPa·s)

A_0	-240.85	-188.05	-144.78	-111.21	-85.86	-67.31	-53.83

A_1	-89.85	-71.03	-51.05	-33.74	-21.71	-14.60	-10.17
A_2	-3.45	2.76	3.42	5.49	8.80	11.89	10.38
A_3	-0.80	13.48	10.52	5.66	6.01	10.15	8.64
σ	1.12	0.56	0.38	0.44	0.43	0.35	0.29

4. Conclusions

The densities and viscosities of three binary mixtures for [Bmim][$FeCl_4$] + EA. [Hmim][$FeCl_4$] + EA and [Omim][$FeCl_4$] + EA were measured over the entire composition range from 293.15 K to 323.15 K at 5 K intervals and at atmospheric pressure. The results showed that densities and viscosities presented a decreasing trend with temperature increasing or with mole fraction of EA increasing. Therefore. adding low viscous organic solvent EA to MIL indeed can obtain desirable physicochemical properties of binary mixtures. The excess molar volume V^E and viscosity deviations $\Delta\eta$ were calculated and fitted well with Redlich-Kister polynomial equation. The negative V^E and $\Delta\eta$ indicated the interactions between MILs and EA were stronger than those among pure MILs and among pure EA.

Acknowledgements

This research was supported financially by the National Natural Scientific Fund of China (No.21376242. No.21336002. No.21476234). Key Research Program of Frontier Sciences.CAS(QYZDY-SSW-JSC011) and the Fund of State Key Laboratory of Multiphase Complex Systems. IPE. CAS (No.MPCS-2015-A-05).

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Highlights

- Densities and viscosities of three binary systems were decreasing with temperature or mole fraction of EA increasing.
- Negative excess molar volumes implies that the interactions between MILs and EA are stronger than that among pure compounds
- As the alkyl chain length in cation of MILs increases, the density of MIL decreases and the viscosity increases