

Synthesis of 1,3-Dimethylimidazolium Chloride and Volumetric Property Investigations of Its Aqueous Solution

L. Dong · D. X. Zheng · Z. Wei · X. H. Wu

Received: 18 January 2009 / Accepted: 16 September 2009 / Published online: 1 October 2009
© Springer Science+Business Media, LLC 2009

Abstract By investigating the vapor pressure of the solvent and the affinity between ionic liquids (ILs) and the solvent, it is proposed that 1,3-dimethylimidazolium chloride ([Mmim]Cl) has the potential to be used as a novel absorbent species with the absorption cycle working fluid. Adopting a high-pressure reaction kettle, the method of gas–liquid phase reaction was used to synthesize [Mmim]Cl under the conditions of 348.15 K and 0.7 MPa. The densities of [Mmim]Cl aqueous solutions were measured for mass fractions in the range from 20 % to 90 % at 293.15 K, 298.15 K, 303.15 K, 308.15 K, 313.15 K, and 318.15 K with a digital vibrating-tube densimeter. The excess volume, the apparent molar volume, the partial molar volume, and the apparent molar expansibility of this system were investigated, and the influences of variations of the cation and anion on the density of several IL aqueous solutions are discussed.

Keywords Density · 1,3-Dimethylimidazolium chloride · Ionic liquid · Working fluid

1 Introduction

The main freedom in designing absorption systems lies in the choice of working fluids and in the design of cycle configuration. Thus, a crucial fraction of fixed and variable costs for absorption processes are defined by absorbent and refrigerant properties. Although many innovative working fluids have been suggested over the last decades, only two meet the prevailing industrial requirements, i.e., water/lithium-

L. Dong · D. X. Zheng (✉) · Z. Wei · X. H. Wu
School of Chemical Engineering, Beijing University of Chemical Technology, Heping street,
Beijing 100029, China
e-mail: dxzh@mail.buct.edu.cn

bromide ($\text{H}_2\text{O}/\text{LiBr}$) and ammonia/water ($\text{NH}_3/\text{H}_2\text{O}$) [1]. However, this situation for the working fluids shows a number of drawbacks. In the late 1950s, some pioneering studies proposed new working fluids for the absorption refrigeration cycle, using fluoroalkane refrigerants with organic absorbents. A thorough search for improving the absorbent species, e.g., for the replacement of LiBr, has led us to consider a recently rediscovered and vastly expanded class of interesting liquids, known as ionic liquids (ILs) [2].

The combination of ILs and a refrigerant to be used for the absorption refrigeration cycle has been proposed which has several advantages to make it appropriate. The IL does not evaporate, thus it is environment friendly.

They are thermally stable and can be operated over a wide range of temperatures in which other working fluids need to be cascaded [3]. They are able to dissolve gases such as carbon dioxide, which makes them suitable for use in absorption refrigeration with natural working fluids. Their physical properties can be tailor-made to a certain extent since there is a broad choice of anions and cations that can be combined to give different absorbent species with special features.

In the most recent decade, many scientists had introduced ILs as an absorbent species to overcome the problems of the existing working fluids and to improve the overall efficiency of absorption refrigeration cycles. Shiflett and Yokozeki [4–6] had thought about H_2O , TFE, and R134a as refrigerants with ILs as the absorbent species for absorption cooling cycles. Kim et al. [7] investigated $[\text{Bmim}]\text{Br} + \text{TFE}$ and $[\text{Bmim}]\text{BF}_4 + \text{TFE}$ as potential working fluids for the absorption cycles. The $[\text{Bmim}]\text{Br} + \text{TFE}$ system was found to be more favorable than $[\text{Bmim}]\text{BF}_4 + \text{TFE}$ based on the behavior of the vapor pressure.

However, it is noted that more thermophysical properties are required for application feasibility assessment and engineering design. Several studies investigated the thermodynamic properties of a wide variety of ILs and their systems with other solvents. Lu [8], Zhou [9], and Zhang et al. [10] presented some studies on densities and volumetric properties for aqueous solutions of IL $[\text{Emim}]\text{SE}$, $[\text{Bmim}]\text{BF}_4$, and $[\text{Emim}]\text{BF}_4$ for different temperature ranges, respectively.

The ILs selected as an absorbent should be very hygroscopic, because water is generally chosen as a refrigerant for air conditioning. The hydrophilic property of ILs was influenced by three factors: the organic cation, the length of the side chain, and the anion. Two important cation groups are those based on imidazolium and pyridinium. A wide range of imidazolium-based ILs has been studied, incorporating many different anions in an effort to demonstrate the potential specifically to tailor the properties of ILs for specific applications. For haloid salts, they are hydrophilic and miscible with water. Huddleston et al. [11] indicated for a series of 1-alkyl-3-methylimidazolium cations, increasing the length of the alkyl chain increases the hydrophobicity, whereas the densities of the ILs decrease. And the simple halide salts have significantly lower densities than the PF_6^- ILs. The experimental results of binary systems indicated that the ILs studied can lower the vapor pressure of the solvent due to the affinity between the IL and solvent, while the depreciation depended on the type and content of IL involved. It was shown that the effect of ILs on the vapor pressure lowering followed the order, i.e., with a decrease of alkyl chain length, the hydrophilicity of ILs increases [12, 13]. In a previous study, the saturated vapor pressures of $[\text{Mmim}]\text{Cl}$

aqueous solution have been investigated [14]. The properties of [Mmim]Cl aqueous solutions show the potential to be used as an alternative working fluid of an absorption cooling cycle.

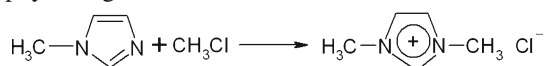
The ILs have a one-step synthesis method, two-step method, and for the more complex ILs, even a multi-step method, the choice of method depends largely on the structure of the target ILs. Among various ILs known heretofore, the ILs with such anions as halides or alkylphosphates seem more competitive since they can be produced via a single-step reaction with very high yield using 1-methylimidazole and trialkylphosphate or alkyl halides as feedstocks [15]. Such types of ILs prepared include [Emim]Br and [Bmim]Br. As a result of raw materials (chloromethane is gaseous under normal temperature), [Mmim]Cl investigated in this study was not obtained using a conventional approach but a special synthesis method concluding in a high-pressure reaction kettle. Such a method based on several procedures differ from the others in very mild operating conditions and results in the formation of high-purity colorless chloride ILs.

The aim of this article is to present research results about [Mmim]Cl as a novel absorbent species of an absorption cycle working fluid, which involves the synthesis of [Mmim]Cl, the measurement of densities for the water and [Mmim]Cl system in the concentration range from 20 mass% to 90 mass% at different temperatures, and data modeling studies.

2 Experimental

2.1 Synthesis

1-Methylimidazole was obtained from Shanghai Titan Chem. Co., and chloromethane was purchased from Beijing Gaisi Chem. Gases Center. The purity was checked by gas chromatography, being more than 99.98 %.



1-Methylimidazole was freshly distilled under reduced pressure before use. In a 500 mL high-pressure reaction kettle with a magnetic stirrer, 1-methylimidazole was placed under vacuum. A large excess of the appropriate chloromethane was slowly mixed with the intensively stirred 1-methylimidazole. Then, the reactants were heated at 75 °C for 24 h with magnetic stirring. After the reaction completion, the excess chloromethane was removed by distillation under a reduced pressure, resulting in a slightly off-white solid product that showed no original reactants by NMR spectroscopy. The crude product was recrystallized from acetonitrile/ethyl acetate three times. And the product was dried at 100 °C for 24 h under a vacuum of approximately 1 kPa. They were then sealed and stored in a desiccator. The product is solid at 298.15 K and represents colorless crystals, mp of 124 °C to 128 °C. The chemical shift for the ¹H NMR spectrum (D₂O, δ ppm, 600 MHz) appears as follows: δ = 8.640 (s, 1H, H2(Im)), 7.410 (s, 2H, H4, H5(Im)), 3.880 (s, 6H, 2NCH₃). Impurity peaks were not observed in the ¹H NMR spectrum, and there is a solvent peak at δ = 4.695 in the

Table 1 Comparison of measured densities for two pure compounds with literature values

Component	T (°C)	ρ_{exp} ($\text{g} \cdot \text{cm}^{-3}$)	ρ_{lit} [16] ($\text{g} \cdot \text{cm}^{-3}$)	$ \rho_{\text{exp}} - \rho_{\text{lit}} $ ($\text{g} \cdot \text{cm}^{-3}$)	$100 \rho_{\text{exp}} - \rho_{\text{lit}} /\rho_{\text{lit}}$ (%)
Water	29.81	0.99558	0.99570	0.00012	0.012
	34.68	0.99401	0.99414	0.00013	0.013
	39.75	0.99239	0.99231	0.00008	0.008
Acetonitrile	35.00	0.76598	0.76585	0.00013	0.017

¹HNMR spectrum. The chemical shift of other peaks corresponded to the structure of [Mmim]Cl. The purity of the product [Mmim]Cl was determined to be greater than 99.4% by differential scanning calorimetry.

2.2 Density Measurement

The densities of the [Mmim]Cl aqueous solutions were measured with an Anton Paar DMA 55 digital vibrating-tube densimeter with an uncertainty of $1 \times 10^{-5} \text{ g} \cdot \text{cm}^{-3}$. Ethanol was used for rinsing the cell tube between measurements. Before each series of measurements, the instrument was calibrated with pure water and air. The densimeter was thermostated by a circulating-water bath with an uncertainty of 0.01 K. All of the [Mmim]Cl aqueous solutions composed of water and [Mmim]Cl were prepared by mass, and were prepared with deionized water and partially degassed. The balance was manufactured by Xiangyi Precision Science Ins. Co. with an uncertainty of 0.1 mg.

To validate and demonstrate current approaches, the measured densities of water and acetonitrile together with literature values are shown in Table 1. The subscripts exp and lit of the character ρ denote the experimental and literature values, respectively. Literature values of the density for water and acetonitrile were obtained from the CRC Handbook of Chemistry and Physics [16]. The calibration experiments indicated the average relative deviation and the maximum relative deviation are 0.0125% and 0.017%, respectively, using acetonitrile. Each density measurement was replicated three times, with the standard deviation being reported as the uncertainty in Sect. 3 below.

3 Results and Discussion

3.1 Excess Volume

The densities for the $\text{H}_2\text{O}(1) + [\text{Mmim}]\text{Cl}(2)$ system, as a function of water content over the temperature range from 293.15 K to 318.15 K are presented in Table 2.

Density data were regressed by the following equation:

$$\rho = \sum_{n=0}^2 A_n w^n + T \sum_{n=0}^2 B_n w^n + T^2 \sum_{n=0}^2 C_n w^n \quad (1)$$

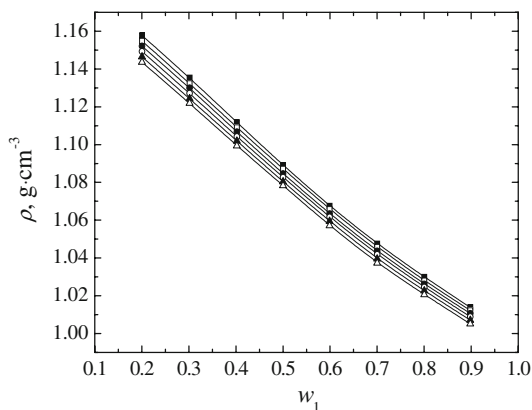
where ρ is the density of [Mmim]Cl aqueous solutions; T is the absolute temperature; w is the mass fraction of water; and A_n , B_n , and C_n are regression coefficients

Table 2 Experimental densities for the H₂O(1) + [Mmim]Cl(2) system (w_1 is mass fraction of water)

w_1	ρ (g · cm ⁻³)					
	293.15 K	298.15 K	303.15 K	308.15 K	313.15 K	318.15 K
0.20045	1.15778	1.15479	1.15215	1.14931	1.14646	1.14359
0.30148	1.13529	1.13240	1.12993	1.12715	1.12433	1.12185
0.40195	1.11177	1.10903	1.10669	1.10422	1.10107	1.09834
0.50008	1.08904	1.08714	1.08455	1.08268	1.08038	1.07858
0.59922	1.06756	1.06577	1.06334	1.06163	1.05944	1.05708
0.70034	1.04752	1.04581	1.04370	1.04180	1.03952	1.03712
0.80030	1.03053	1.02798	1.02615	1.02453	1.02266	1.02105
0.89800	1.01407	1.01220	1.01057	1.00886	1.00720	1.00565

Table 3 Coefficients of equation for densities for the H₂O(1) + [Mmim]Cl(2) system

n	A_n	B_n	C_n
0	1.65643	-0.00231	2.71×10^{-6}
1	-2.03824	0.01114	-1.75×10^{-5}
2	1.58588	-0.00991	1.61×10^{-5}

Fig. 1 Variation of density versus mass fraction of water for the H₂O(1) + [Mmim]Cl(2) system. ■, 293.15 K; □, 298.15 K; ●, 303.15 K; ○, 308.15 K; ▲, 313.15 K; △, 318.15 K; —, calculated

listed in Table 3. Equation 1 is valid from 293.15 K to 318.15 K; the average relative deviation and the maximum relative deviation between experimental and calculated values are 0.067 % and 0.178 %, respectively, and a fitting coefficient $R^2 = 0.99986$. It was found that Eq. 1 can represent well the experimental results as shown in Fig. 1.

From the graphical illustration of density data in Fig. 1, it can be readily observed that an increase in the content of water or temperature causes the density to decrease and approach that of water. With the addition of water, the densities of [Mmim]Cl aqueous solutions decline sharply at mass fractions in the range from 20 % to 90 %. An increase in temperature results in a slight decrease in density. Therefore, the physical properties of ILs can be adjusted to meet the needs of applications for hydrophilic ILs, e.g., [Mmim]Cl, by adding water or changing the temperature.

The excess properties, which depend on the composition and/or temperature, are of great importance in understanding the nature of molecular aggregation that exists in binary systems. On the measured densities for the $\text{H}_2\text{O}(1) + [\text{Mmim}]\text{Cl}(2)$ system, the excess volume V^E was obtained by using the following equations [17]:

$$\begin{aligned} V^E &= x_1 (\bar{V}_1 - V_1) + x_2 (\bar{V}_2 - \bar{V}_2^\infty) = V - (x_1 V_1 + x_2 \bar{V}_2^\infty) \\ &= \frac{x_1 M_1 + x_2 M_2}{\rho} - \left(\frac{x_1 M_1}{\rho_1} + x_2 \bar{V}_2^\infty \right) \end{aligned} \quad (2)$$

where ρ , ρ_1 are the densities of aqueous solutions and water, respectively; x_1 , x_2 are mole fractions of water and $[\text{Mmim}]\text{Cl}$, respectively; M_1 , M_2 are the molar masses of water and $[\text{Mmim}]\text{Cl}$, i.e., 18.0148 and 132.59, respectively; \bar{V}_1 , \bar{V}_2 are the partial molar volumes of water and $[\text{Mmim}]\text{Cl}$, respectively; and \bar{V}_2^∞ is the partial molar volume of $[\text{Mmim}]\text{Cl}$ at infinite dilution.

The partial molar volume of component i , is expressed as

$$\bar{V}_i = V - \sum_{k \neq i} \left[x_k (\partial V / \partial x_k)_{T, p, x_{l \neq i, k}} \right] \quad (3)$$

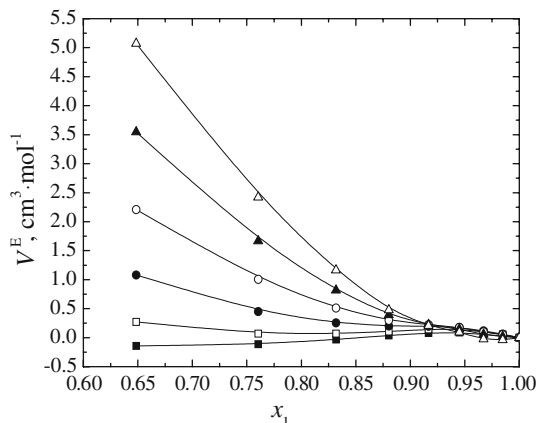
Also, the partial molar volume of $[\text{Mmim}]\text{Cl}$ is given by

$$\bar{V}_2^\infty = (\bar{V}_2)_{x_1 \rightarrow 1} = [V - x_1 dV/dx_1]_{x_1 \rightarrow 1} \quad (4)$$

The results for the excess volume versus the mole fraction of water is plotted in Fig. 2.

The values of the excess volume decreases with the mole fraction of water from 298.15 K to 313.15 K when $x_1 > 0.65$ or so, which corresponds to mass fractions of w_1 from 0.2 to 0.9, however, the excess volume increases with the mole fraction of water at 293.15 K. Comparatively, V^E increases slightly with an increase in temperature from 293.15 K to 313.15 K.

Fig. 2 Excess volume versus mole fraction of water for the $\text{H}_2\text{O}(1) + [\text{Mmim}]\text{Cl}(2)$ system. ■, 293.15 K; □, 298.15 K; ●, 303.15 K; ○, 308.15 K; ▲, 313.15 K; △, 318.15 K



3.2 Apparent Molar Volume

The apparent molar volumes, V_φ , were determined from the solution densities using the following expression:

$$V_\varphi = \frac{M_2}{\rho} - \frac{1000(\rho - \rho_1)}{m\rho\rho_1} \quad (5)$$

where m is the molality. In Fig. 3, it can be readily observed that the apparent molar volume decreases with an increase in molality and shows a small temperature effect in the range from 293.15 K to 318.15 K.

3.3 Partial Molar Volume

The partial molar volume, \bar{V}_2 , is an important thermodynamic property of solution and is calculated conveniently from the apparent molar volume:

$$\begin{aligned} \bar{V}_2 &= V_\varphi + n_2 \left(\frac{\partial V_\varphi}{\partial n_2} \right)_{T,p,n_1} \\ \bar{V}_2 &= V_\varphi + m \left(\frac{\partial V_\varphi}{\partial m} \right)_{T,p} \end{aligned} \quad (6)$$

where $m \left(\frac{\partial V_\varphi}{\partial m} \right)_{T,p}$ may be obtained from taking the partial derivative of Eq. 5 with respect to m at constant T and p . The values of \bar{V}_2 calculated from Eq. 6 are listed in Table 4.

Fig. 3 Apparent molar volumes plotted against molalities for the water (1) + [Mmim]Cl (2) system. ■, 293.15 K; □, 298.15 K; ●, 303.15 K; ○, 308.15 K; ▲, 313.15 K; △, 318.15 K

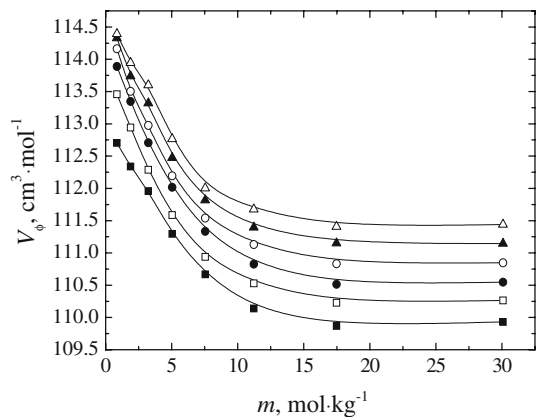


Table 4 Partial molar volume for the H₂O(1) + [Mmim]Cl(2) system at molality *m*

<i>m</i> (mol · kg ⁻¹)	\bar{V}_2 (cm ³ · mol ⁻¹)					
	293.15 K	298.15 K	303.15 K	308.15 K	313.15 K	318.15 K
0.8567	112.3179	113.0365	113.4205	113.4209	113.6063	113.8360
1.8820	111.7937	111.9877	112.3891	112.6143	113.0391	113.4199
3.2271	110.9296	110.8396	111.3061	111.7070	112.1349	112.5123
5.0443	109.5601	109.9167	110.3339	110.2289	110.3028	110.4667
7.5395	109.2368	109.5254	109.7433	110.2493	110.6012	110.6206
11.2216	109.0288	109.7791	109.8417	110.3115	110.5250	111.1940
17.4746	109.8408	109.6940	110.1756	110.3987	110.9918	110.7470
30.0832	108.6946	111.2950	110.4672	111.2710	110.3477	113.3409

3.4 Apparent Molar Expansibility

The apparent molar expansibility of the solute is expressed as [18]

$$\begin{aligned}\phi E &= \left[(\partial V / \partial T)_p - n_1 \left(\partial V_1^0 / \partial T \right)_p \right] / n_2 \\ &= (\alpha V - \alpha_0 n_1 V_1^0) / n_2\end{aligned}\quad (7)$$

where α and α_0 are the coefficients of thermal expansion of the solution and of the pure solvent given by

$$\alpha = -(\partial \ln \rho / \partial T)_p \quad (8)$$

and

$$\alpha_0 = -(\partial \ln \rho_1 / \partial T)_p \quad (9)$$

respectively. In order to obtain the values of α and α_0 , the experimental values of ρ_1 and ρ at constant composition of the solution were fit with the following empirical equation:

$$\rho = A_1 + A_2/T + A_3T \quad (10)$$

The values of the parameters A_i in Eq. 10 are listed in Table 5. According to Eqs. 8 and 9, the values of α and α_0 are listed in Table 6. The apparent molar expansibility was calculated from the density and their temperature coefficients by

$$\phi E = 1000 (\alpha - \alpha_0) / m\rho_1 + \alpha V_\varphi \quad (11)$$

Therefore, the values of ϕE calculated from Eq. 11 are listed in Table 7.

Table 5 Values of the parameters A_i , in Eq. 10 at temperatures from 293.15 K to 318.15 K at molality m

m (mol · kg ⁻¹)	A_1 (kg · m ⁻³)	A_2 (kg · m ⁻³ · K ⁻¹)	A_3 (kg · m ⁻³ · K ⁻¹)
0.0000	1.87701	-119.773	-0.0016
0.8567	1.35263	-4.4926	-0.00061
1.8820	1.20706	13.1199	-0.0004
3.2271	1.69052	-64.4277	-0.00122
5.0443	0.99744	33.0239	-0.00007
7.5395	1.43972	-38.1009	-0.00083
11.2216	1.71950	-83.9376	-0.00132
17.4746	0.52649	93.5039	0.00063
30.0832	0.91465	30.2006	-0.00001

Table 6 Coefficient of thermal expansion of aqueous solutions and of pure solvent at 293.15 K to 318.15 K at molality m

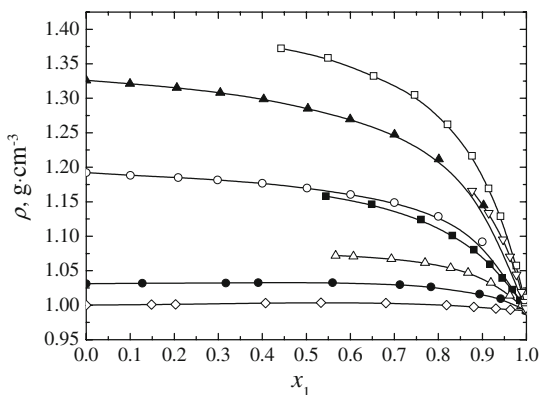
m (mol · kg ⁻¹)	$\alpha \times 10^4$ (K ⁻¹)					
	293.15 K	298.15 K	303.15 K	308.15 K	313.15 K	318.15 K
0.0000	2.06	2.53	2.98	3.40	3.81	4.20
0.8567	4.81	4.84	4.87	4.89	4.92	4.94
1.8820	4.87	4.84	4.81	4.78	4.75	4.72
3.2271	4.23	4.46	4.68	4.90	5.11	5.31
5.0443	4.17	4.06	3.96	3.86	3.76	3.67
7.5395	3.63	3.77	3.91	4.04	4.17	4.30
11.2216	3.28	3.60	3.90	4.19	4.47	4.74
17.4746	4.45	4.10	3.78	3.46	3.16	2.88
30.0832	3.56	3.45	3.35	3.25	3.15	3.06

Table 7 Apparent molar expansibility at temperatures from 293.15 K to 318.15 K at molality m

m (mol · kg ⁻¹)	$\phi E \times 10^{-6}$ (m ³ · mol ⁻¹ · K ⁻¹)					
	293.15 K	298.15 K	303.15 K	308.15 K	313.15 K	318.15 K
0.8567	0.376	0.325	0.277	0.231	0.186	0.144
1.8820	0.204	0.178	0.152	0.128	0.104	0.082
3.2271	0.114	0.110	0.106	0.102	0.098	0.095
5.0443	0.088	0.076	0.064	0.052	0.041	0.031
7.5395	0.061	0.058	0.056	0.054	0.051	0.049
11.2216	0.047	0.049	0.052	0.054	0.056	0.058
17.4746	0.063	0.054	0.046	0.039	0.031	0.024
30.0832	0.044	0.041	0.038	0.036	0.033	0.030

Fig. 4 Comparison of densities of several IL aqueous solutions at 313.15 K.

- , H₂O + [Emim]Br [19];
- ∇, H₂O + [Bmim]Br [20];
- ▲, H₂O + [Emim]BF₄ [10];
- , H₂O + [Bmim]BF₄ [9];
- , H₂O + [Mmim]Cl;
- △, H₂O + [Bmim]Cl [21];
- , H₂O + [Hmim]Cl [21];
- ◇, H₂O + [Omim]Cl [21]



3.5 Density Comparisons of Several IL Aqueous Solutions

For several 1-alkyl-3-methylimidazolium salt aqueous solutions, the impact of cation and anion variations on the density have been determined.

As shown in Fig. 4, keeping the cation constant, the densities of the [Emim]Br aqueous solution substantially exceed those of the [Emim]BF₄ aqueous solution, due to the greater mass of bromine atoms. Similarly, for the [Bmim]⁺-containing ILs aqueous solutions, the densities decrease in the order [Bmim]Br > [Bmim]BF₄ > [Bmim]Cl. Keeping the anion constant, the densities of the [Emim]Br aqueous solution and the [Emim]BF₄ aqueous solution are larger than those of the [Bmim]Br aqueous solution and the [Bmim]BF₄ aqueous solution, respectively, due to the elongated cation such as [Bmim]⁺. Likewise, for the Cl⁻-based ILs aqueous solutions, the densities decrease in the order [Mmim]Cl > [Bmim]Cl > [Hmim]Cl > [Omim]Cl.

The results show that structural variations such as changing the length of the alkyl chain in the cation and substituting the halides in the anion have a significant impact on the densities of the IL aqueous solutions. Adding CH₂ groups to the alkyl chain on the [C_nmim]⁺ cation decreases the density, and the density increases as the mass of the anion increases.

4 Conclusions

It was proposed here that [Mmim]Cl has the potential to be used as a novel absorbent species of an absorption cycle working fluid. Through synthesis of [Mmim]Cl and studies on the volumetric properties of its aqueous solution, the conclusions can be given as follows.

The method of gas–liquid phase reaction was selected to synthesize [Mmim]Cl at conditions of 348.15 K and 0.7 MPa. The structure of the product was validated by the ¹H NMR spectrum that matches the structure of [Mmim]Cl; organic impurities were not found in the synthesized products. The purity of the product [Mmim]Cl was determined to be greater than 99.4% by differential scanning calorimetry.

Using a digital vibrating-tube densimeter, the density of [Mmim]Cl aqueous solutions was measured at mass fractions in the range from 20% to 90% at 293.15 K, 298.15 K, 303.15 K, 308.15 K, 313.15 K, and 318.15 K. A polynomial dependence on composition and temperature was obtained for which the average relative deviation and the maximum relative deviation are 0.067% and 0.178%, respectively.

The excess volume, the apparent molar volume, the partial molar volume, and the apparent molar expansibility of [Mmim]Cl aqueous solutions were investigated. The results show that the water content has significant influence on the volumetric properties, and the temperature dependence of the density is significantly less than the water content. Variation of the length of the alkyl chain and substitution of the anion have significant impact on the densities of the ionic liquid aqueous solutions.

Acknowledgments This work was financially supported by the National Natural Science Foundation of China (No. 50890184) and the National Basic Research Program of China (No. 2010CB227304).

References

1. M. Seiler, P. Schwab, F. Ziegler, in *Proceedings of International Sorption Heat Pump Conference*, SAREK, Seoul, Korea, 2008, AB-040
2. M.B. Shiflett, A. Yokozeki, in *Proceedings of The 22nd International Congress of Refrigeration*, Beijing, China, 2007, ICR07-B1-1119
3. K.R. Seddon, A. Stark, M.J. Torres, *Pure Appl. Chem.* **72**, 2275 (2000)
4. M.B. Shiflett, A. Yokozeki, US 20060197053A1, 2006.9
5. M.B. Shiflett, A. Yokozeki, US 20070144186A1, 2007.6
6. M.B. Shiflett, A. Yokozeki, WO 2006/084262A1, 2006
7. K.S. Kim, B.K. Shin, H. Lee, F. Ziegler, *Fluid Phase Equilib.* **218**, 215 (2004)
8. X.M. Lu, W.G. Xu, J.S. Gui, H.W. Li, J.Z. Yang, *J. Chem. Thermodyn.* **37**, 13 (2005)
9. Q. Zhou, L.S. Wang, H.P. Chen, *J. Chem. Eng. Data* **51**, 905 (2006)
10. S.J. Zhang, X. Li, H.P. Chen, J.F. Wang, J.M. Zhang, M.L. Zhang, *J. Chem. Eng. Data* **49**, 760 (2004)
11. J.G. Huddleston, A.E. Visser, W.M. Reichert, H.D. Willauer, G.A. Broker, R.D. Rogers, *Green Chem.* **3**, 156 (2001)
12. J. Zhao, C.C. Dong, C.X. Li, *Fluid Phase Equilib.* **242**, 147 (2006)
13. J. Zhao, X.C. Jiang, C.X. Li, Z.H. Wang, *Fluid Phase Equilib.* **247**, 190 (2006)
14. J.Z. Wang, D.X. Zheng, L. Dong, Z. Wei, C. Xiong, in *5th Chinese National Chemical and Biochemical Engineering Annual Meeting*, Xi'an, China, 2008, Paper No. A001, p. 1
15. J.S. Wilkes, J.A. Levisky, R.A. Wilson, C.L. Hussey, *Inorg. Chem.* **21**, 1263 (1982)
16. C. Robert Weast (ed), *CRC Handbook of Chemistry and Physics*, 66th edn. (CRC Press, Boca Raton, FL, 1985–1986)
17. J.M. Smith, H.C. Van Ness, M.M. Abbott, in *Introduction to Chemical Engineering Thermodynamics*, 6th edn. (McGraw-Hill, New York, 2001), pp. 376–380
18. H.S. Harned, B.B. Owen, in *The Physical Chemistry of Electrolytic Solutions*, 3rd edn. (Reinhold Publishing Co., New York, 1958), pp. 358–375
19. L. Dong, D.X. Zheng, X.H. Wu, F. Li, in *Proceedings of Chinese Thermophysical Conference 2008*, Tianjin, China, 2008, Paper No. 081169, p. 153
20. M.T. Zafarani-Moattar, H. Shekaari, *J. Chem. Thermodyn.* **37**, 1029 (2005)
21. E. Gmez, B. Gonzalez, N. Domnguez, E. Tojo, J. Tojo, *J. Chem. Eng. Data* **51**, 696 (2006)