Density, Viscosity, Refractive Index and Conductivity of 1-Allyl-3-methylimidazolium Chloride + Water Mixture†

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The concentration dependence of density, viscosity, refractive index, and conductivity of aqueous solution of 1-allyl-3-methyl-imidazolium chloride ([Amim]Cl) at 298.15 K has been measured. It was shown that the density, as well as viscosity and refractive index, increased with increasing concentration of [Amim]Cl, while the conductivity increased sharply in the water-rich region and decreased in the [Amim]Cl-rich region. It was concluded that [Amim]Cl was a surfactant-like solvent, and the critical aggregation concentration of aqueous [Amim]Cl solution was obtained. The data obtained will play an important supplementary function in completion of the ionic liquids database.

Introduction

Ionic liquids (ILs) are well recognized to be a class of green solvents with some unique advantages.[1] Accordingly, ILs have replaced traditional organic solvents in many fields, among which polymer processing is concerned. Rogers et al. first demonstrated that 1-butyl-3-methyl-imidazolium ([Bmim]Cl) chloride was a good solvent for cellulose processing.[2] Afterward, 1-allyl-3-methyl-imidazolium chloride ([Amim]Cl) was discovered as an alternative solvent for cellulose processing,[3] where water generally is used as coagulant. Therefore, data on the physical properties of aqueous [Amim]Cl solutions would be useful, for example, to determine the concentration of the coagulation bath and recycling of [Amim]Cl. To our best knowledge, however, the property values on aqueous [Amim]Cl solution are rather scarce,[4] although relative studies on other ILs are abundant.[5−15] Therefore, this work describes a comprehensive study of the physicochemical properties of aqueous [Amim]Cl solution.

In our earlier papers,[7,8] the physicochemical properties of aqueous solutions of imidazolium-based ILs were investigated. As a continuation, herein we focus on the physicochemical properties of aqueous [Amim]Cl solution, such as density, refractive index, viscosity, and conductivity over the whole concentration range at 298.15 K. This work is a contribution to further improve the database on properties of ILs and their mixtures.

Experimental Section

Materials. Allyl chloride, 1-methylimidazole, ethyl acetate, and toluene were all purchased from Shanghai Chemical Reagents Company. They were of analytic grade and used as received. Doubly distilled water was used in all experiments. The synthesis of [Amim]Cl was based on the reported procedures.[3] The purity of [Amim]Cl was verified in terms of NMR analysis (> 99 %), and the Cl^{-1} mass fraction is smaller than $1.3 \cdot 10^{-4}$. The water mass fraction of ILs (< 0.18 %) was determined by the Karl Fischer titration (ZSD-2 KF Cany Precision Instruments Co., Ltd.).

Measurement of Density. Before measuring the densities, a Westphal balance (PZ-D-5) was corrected with pure water at (298.15 ± 0.1) K. The uncertainty in density was estimated to be $\pm 2.0 \cdot 10^{-6}$ g·cm^{-3}. All measurements were repeated three times, and then average values were calculated.

Measurement of Viscosity. The viscosity in low mole fraction was determined by an Ubbelohde viscometer (inner diameter = 1.0 mm). For each test, a 20 mL sample was used, and the temperature of the sample was maintained to (298.15 ± 0.1) K with an external temperature controller. The measurements were performed three times. The average values were calculated. The uncertainty in viscosity was estimated to be $\pm 2.0 \cdot 10^{-4}$ mPa·s.

When the viscosity of solution went beyond the range of the Ubbelohde viscometer, we chose a digital rotary viscometer (NDJ-8S) to continue our measurement. The final data are the average of three measurements, and the uncertainty was estimated to be $\pm 1.0 \cdot 10^{-3}$ mPa·s.

Measurement of Refractive Index. The refractive index was determined by a 2WAJ Abbe refractometer. Deionized water was used as a reference for calibration. All measurements were taken at (298.15 ± 0.1) K and repeated three times to calculate the average value. The uncertainty in refractive index was estimated to be $\pm 1.0 \cdot 10^{-4}$.

Measurement of Conductivity. The conductivity measurements were carried out with a DDSJ-308A conductometer (Shanghai Optical Instrument Factory, cell constant = 1.0 cm^{-1}) with an uncertainty of 0.5 %. The temperature of the sample was maintained at (298.15 ± 0.1) K with a DC-2006 low-temperature thermostat (Shanghai Hengping Instrument Factory). Each measurement was repeated three times, and the average values were calculated and reported. The specific conductance for pure water was 0.03 mS·cm^{-1}.

Results and Discussion

Density. The density data of [Amim]Cl aqueous solution with different compositions at T = 298.15 K were given in Table 1. The ideal molar volume was obtained from

$$V_m = X_1 V_1 + X_2 V_2 \tag{1}$$

$$d_m = (X_1 M_{w1} + X_2 M_{w2})/V_m \tag{2}$$

where V_m is molar volume calculated by the ideal molar volume equation; X is the mole fraction of the component; M_w is the

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Table 1. Experimental Density and Calculated Density of H_2O (1) + [Amim]Cl (2) at 298.15 K

100 x_2	ρ/g·cm^{-3}	d_m/g·cm^{-3}
0.0171	1.0050	0.9972
0.0362	1.0075	0.9974
0.0553	1.0010	0.9977
0.0754	1.0045	0.9979
0.1151	1.0040	0.9984
0.1575	1.0047	0.9989
0.2478	1.0030	1.0001
0.3359	1.0042	1.0011
0.4859	1.0050	1.0030
0.6386	1.0060	1.0048
0.8102	1.0070	1.0068
0.9949	1.0085	1.0089
1.1785	1.0116	1.0109
1.3730	1.0165	1.0130
1.7654	1.0172	1.0171
2.1561	1.0218	1.0210
2.5652	1.0240	1.0249
2.9730	1.0260	1.0287
3.3936	1.0292	1.0323
4.4424	1.0400	1.0408
5.5355	1.0468	1.0487
6.6464	1.0542	1.0560
7.8572	1.0618	1.0631
9.1376	1.0730	1.0698
11.4280	1.0841	1.0803
13.6948	1.0920	1.0890
16.1616	1.1000	1.0971
18.6711	1.1058	1.1041
21.1044	1.1102	1.1099
22.4487	1.1089	1.1128
32.3337	1.1278	1.1292
50.8319	1.1328	1.1467
100	1.1660	1.1660

Table 2. Viscosity, Refractive Index, and Conductivity of H_2O (1) + [Amim]Cl (2) at 298.15 K

100 x_2	η/mPa·s	n	κ/mS·cm^{-1}
0.0171	0.8974	1.3329	0.7945
0.0362	0.8946	1.3330	1.6874
0.0553	0.8979	1.3333	2.5820
0.0754	0.8954	1.3336	3.4500
0.1151	0.9008	1.3340	5.0350
0.1575	0.9038	1.3346	6.6540
0.2478	0.9234	1.3360	9.6900
0.3359	0.9356	1.3375	12.3650
0.4859	0.9802	1.3400	16.5480
0.6386	0.9919	1.3421	26.5600
0.8102	1.0435	1.3452	30.2500
0.9949	1.0606	1.3470	32.8800
1.1785	1.0932	1.3495	36.8800
1.3730	1.1289	1.3520	39.3700
1.7654	1.1932	1.3574	46.5200
2.1561	1.2521	1.3635	53.2900
2.5652	1.3222	1.3676	59.7500
2.9730	1.3941	1.3730	62.2700
3.3936	1.4726	1.3775	71.5400
4.4424	1.6769	1.3888	68.3000
5.5355	1.8997	1.3995	76.6400
6.6464	2.1658	1.4084	79.2200
7.8572	2.4752	1.4176	74.6700
9.1376	3.1181	1.4315	72.0200
11.4280	3.8670	1.4464	64.800
13.6948	4.8056	1.4574	56.7200
16.1616	5.9742	1.4673	49.1700
18.6711	7.4412	1.4742	41.2800
21.1044	7.9004	1.4831	39.1300
22.4487	8.5184		38.1600
32.3337	18.0000		26.3400
50.8319	48.0000		0.0974
100	821.0000		0.0695

molecular weight; and d_m is the density calculated by eq 2. Subscripts m, 1, and 2 denote, respectively, binary mixture, liquid 1, and liquid 2.

The experimental values of densities were compared with the value calculated by the ideal formula. It is shown that there is no distinct difference, especially in the low concentration region (see Figure 1). This is in line with our previous results,[7,8] as well as the results of other research groups.[9−13]

Viscosity. The experimental data of viscosity were given in Table 2. The curves of the viscosity of solution versus mole fraction of [Amim]Cl was shown in Figure 2, where the inset shows that viscosity of solution increases significantly with the concentration of IL, and the increase will be even sharper at higher concentrations of IL. This phenomenon, to some extent, reflects that the cluster behavior of IL in aqueous solution has changed with the increasing concentration.

Other researchers found that the decrease of the viscosity of ILs by the addition of cosolvents followed a different pattern depending on the nature of the cosolvents, possibly due to

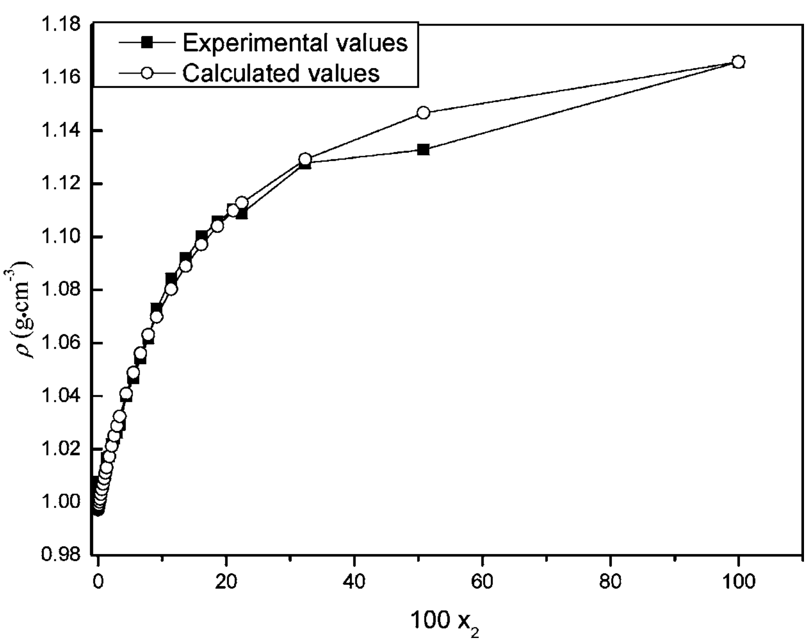

Figure 1. Comparison of the experimental density with the values calculated by the ideal formula.

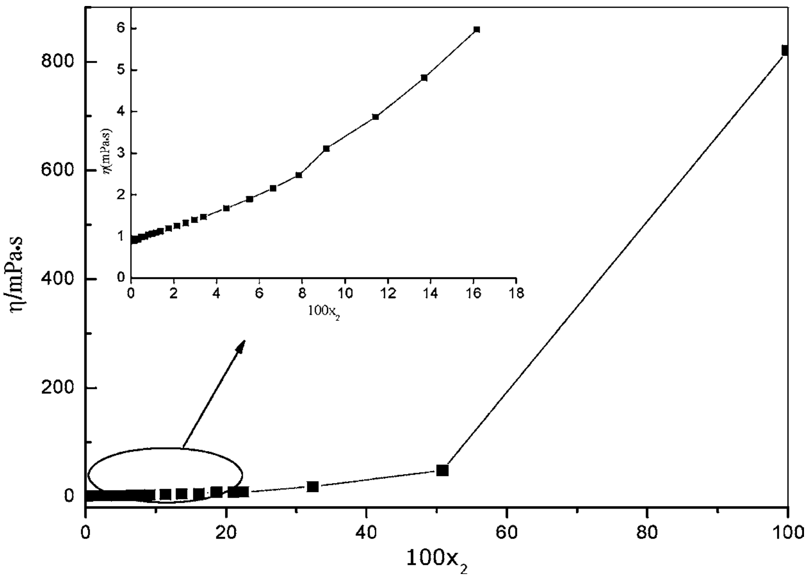

Figure 2. *x* dependence of η of H_2O (1) + [Amim]Cl (2) at $T = 298.15$ K.

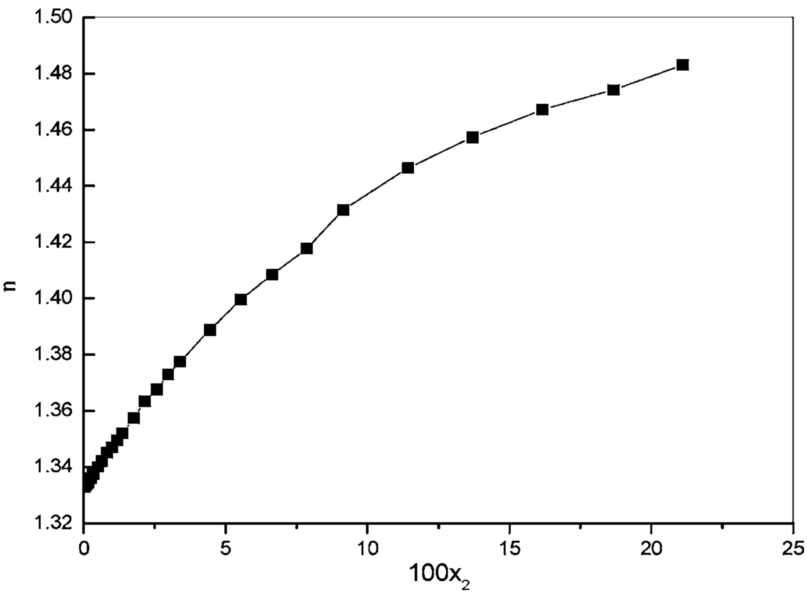

Figure 3. *x* dependence of *n* of H_2O (1) + [Amim]Cl (2) at $T = 298.15$ K.

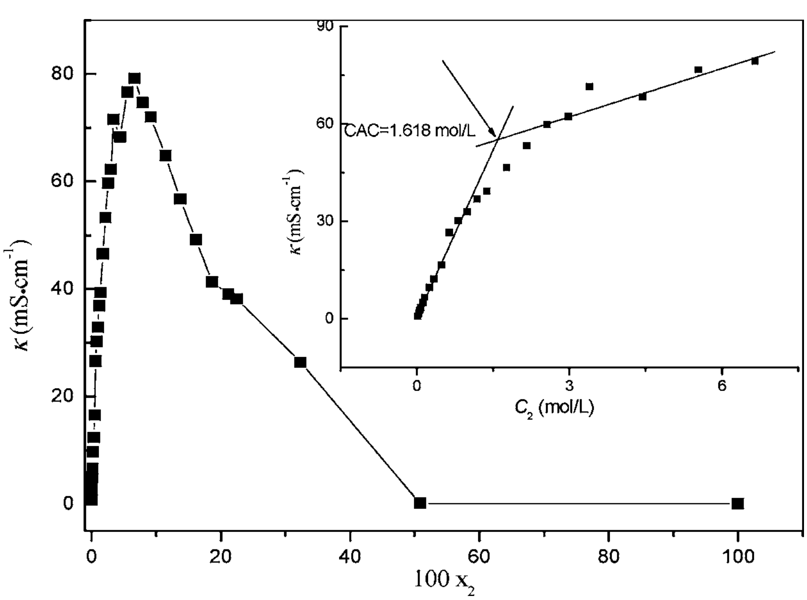

Figure 4. *x* dependence of κ of H_2O (1) + [Amim]Cl (2) at $T = 298.15$ K. Inset shows the CAC of aqueous [Amim]Cl solution.

differences in polarities which led to different interactions with the ions in the ILs.[14]

Refractive Index. The refractive index of aqueous [Amim]Cl solution as a function of mole fraction at 298.15 K was given in Table 2. From Figure 3, the refractive index of the solution increases with [Amim]Cl because the refractive index of [Amim]Cl is larger than that of water. It is worthy to note that the refractive index increases much faster at the water-rich region. This may ascribed to the fact that the chaotropic effect of [Amim]Cl on water network structure is more pronounced. In our previous work, the relationship between concentration and refractive index among four kinds of different ILs was discussed with the ion structure.[8]

Conductivity. Figure 4 shows the relationship between the conductivity of aqueous solution and the mole fraction of [Amim]Cl. As shown in Figure 4, mixtures of ionic liquids and water display the classical properties of concentrated saline solutions, with a maximum conductivity. The conductivity increases sharply in the water-rich region and decreases linearly in the [Amim]Cl-rich region after the maximum. This can be ascribed to two effects: (i) increase of viscosity and therefore reduction of the mobility of the charge carriers and (ii) reduction of the number of charge carriers due to aggregate formation. The latter become dominant at higher concentration, thus leading to a strong decrease of conductivity. This is consistent with our previous results.[7,8]

Additionally, the critical aggregation concentration (CAC) was obtained from the intersect point ($CAC = 1.618\ mol \cdot L^{-1}$) shown in the inset in Figure 4. This value is somewhat higher than that of other imidazolium-based ILs obtained by the same method.[16−18] As a watershed, after CAC, aggregation will be found in the solution, at the same time, some properties of the solution may change greatly.

Conclusion

In this work, the physicochemical properties of aqueous [Amim]Cl solution were measured at room temperature, such as density, viscosity, refractive index, and conductivity. Density increases with increasing mole fraction of [Amim]Cl, and the same trend was observed in the case of viscosity and refractive index. However, the conductivity increases sharply in the water-rich region and decreases linearly in the [Amim]Cl-rich region, whereby [Amim]Cl was considered as a surfactant-like solvent. These phenomena were discussed via water−ionic liquid interactions.

In summary, our investigation of physicochemical properties of IL is very important to understand the interactions between ILs and water. Meanwhile, the present results will enrich the database of physical and chemical properties of ILs.

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