

The Aggregation Behavior of Short Chain Hydrophilic Ionic Liquids in Aqueous Solutions

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ABSTRACT: In this paper, aggregation behaviors of aqueous solutions of short chain hydrophilic Ionic Liquids (ILs), 1 - allyl - 3 - methylimidazolium chloride ([Amim]Cl), 1 - ethyl - 3 - methylimidazolium chloride ([Emim]Cl), 1 - butyl - 3 - methylimidazolium chloride ([Bmim]Cl), 1 - butyl - 3 - methylimidazolium tetrafluoroborate ([Bmim]BF₄) were investigated using conductivity and laser light scattering. The measurements of conductivity and light scattering were conducted over the whole liquid range, and the Critical Aggregation Concentration (CAC) of aqueous ILs solution determined with the conductivity, was in the order of 2.35mol/L([Amim]Cl) > 2.32mol/L([Emim]Cl) > 2.29mol/L([Bmim]Cl) < 2.54mol/L([Bmim]BF₄). The CAC value of [Bmim]BF₄ determined with conductivity was consistent with the result of light scattering. In addition, we proposed aggregation model for illustrating the structural change in the aqueous ILs solutions.

KEY WORDS: Ionic liquid, Aggregation behavior, Conductivity, Light scattering.

INTRODUCTION

Nowadays, the study of Ionic Liquids (ILs) as the potential "green" and "designable" solvents is booming because of their extremely low volatility and toxicity[1]. They are widely used as media for organic and inorganic reactions [2,3], polymerization [4], and chemical separation [5]. Recently, ILs were found to exhibit surfactant-like properties. *Seoud et al* investigated the micelle formation of 1-alkyl-3-methylimidazolium chlorides[6]. *Vanyur et al* studied the surface property of 1-alkyl-3-methylimidazolium bromides by conductivity measurements and fluorescent probes [7]. *Baker et al* used the pyrrolidinium-based ILs as surfactants[8].

Nevertheless, less attention was paid to the hydrophilic ILs with short chain. The earlier work of *Liu* showed that the surface tension of aqueous [Bmim]BF₄ solution decreased rapidly in dilute solution and almost

did not change in concentrated solution[9]. This work inspired us to do a systematic research of aqueous solution of hydrophilic ILs with short chain. Therefore, the conductivity and light scattering behavior of 1 - allyl - 3 - methylimidazolium chloride ([Amim]Cl), 1 - ethyl - 3 - methylimidazolium chloride ([Emim]Cl), 1 - butyl - 3 - methylimidazolium chloride ([Bmim]Cl), and 1 - butyl - 3 - methylimidazolium tetrafluoroborate ([Bmim]BF₄) aqueous solutions were investigated using conductivity and laser light scattering over the whole liquid range [10-12]. In addition, we proposed aggregation model for illustrating the structural change in the aqueous ILs solutions.

EXPERIMENTAL SECTION

Materials

Chlorobutane (≥ 99 %), 1-methylimidazole (≥ 99 %),

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ethyl acetate (99 %), acetone (99 %) and NaBF_4 (≥ 99 %) were all purchased from Shanghai Chemical Reagents Company. They are of analytic grade and used as received. Doubly distilled water was used in all experiments. The chlorobutane and 1-methylimidazole were distilled before use. The ethyl acetate, acetone and sodium tetrafluoroborate were used as supplied.

Synthesis of ILs

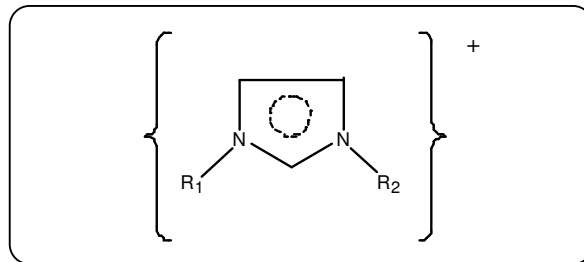
[Amim]Cl, [Emim]Cl, [Bmim]Cl and [Bmim]BF₄ were prepared based on the reported procedures [13-15], and their molecular structures could be seen in Theme 1. [Bmim]BF₄ was dried under vacuum at 373.15 K for 24 h. The purity of the ILs was verified in terms of NMR analysis ($> 99\%$), and the Cl^- content is smaller than 130 ppm. The water content of [Bmim]BF₄ (0.18 %) was determined by the Karl Fischer titration (ZSD-2 KF with an uncertainty of 0.05 %, Cany Precision Instruments Co., Ltd.).

Measurement of conductivity

The conductivity measurements were carried out with a DDSJ-308A conductometer (Shanghai Optical Instrument Factory, cell constant = 1.0 cm^{-1}). The uncertainty of the measurements was $1 \times 10^{-6} \text{ mS} \cdot \text{cm}^{-1}$. The temperature of the sample was maintained at $298.15 \pm 0.05 \text{ K}$ with a DC-2006 low temperature thermostat (Shanghai Hengping Instrument Factory). All aqueous solutions to be studied were freshly prepared. Each measurement was repeated thrice and the average values were calculated and reported. It was estimated that the uncertainty of the conductivity data was less than 3%. The specific conductance for pure water is $0.03 \text{ mS} \cdot \text{cm}^{-1}$.

Light scattering measurement

A commercialized spectrometer equipped from Brookhaven Instruments Corporation (BI-200SM Goniometer) was used to perform both Static Light Scattering (SLS) and Dynamic Light Scattering (DLS) over a scattering angular range of 20 - 120° . A solid-state laser polarized at the vertical direction (CNI Changchun GXC-III, 532 nm, 100 Mw) operating at 532 nm was used as the light source, and a BI-TurboCorr Digital Correlator was used to collect and process data [16]. In LLS, we measured the density fluctuation-induced-intensity fluctuation via a time correlation function. The Laplace inversion of each precisely measured intensity-intensity



Theme 1: Cation of ionic liquid. $R_1 = \text{CH}_3$; $R_2 = \text{C}_3\text{H}_7$, C_2H_5 , C_4H_9 for [Amim]⁺, [Emim]⁺, [Bmim]⁺.

time correlation function $G^{(2)}(\tau)$ resulted in a characteristic line-width distribution $G(\Gamma)$. The CONTIN Laplace inversion algorithm in the correlator was used. The average line width, $\bar{\Gamma}$, was calculated according to $\bar{\Gamma} = \int \Gamma G(\Gamma) d\Gamma$. The polydispersity index, PDI, was defined as $\text{PDI} = \mu_2 / \bar{\Gamma}^2$ with $\mu_2 = \int (\Gamma - \bar{\Gamma})^2 G(\Gamma) d\Gamma$. $\bar{\Gamma}$ is a function of both C and q , which can be expressed as

$$\bar{\Gamma} / q^2 = D(1 + k_d C) \left[1 + f (R_g q)^2 \right] \quad (1)$$

With D , k_d , f being the translational diffusive coefficient, the diffusion second virial coefficient, and a dimensionless constant, respectively. D can be further converted into the hydrodynamic radius R_h by using the Stokes-Einstein equation:

$$D = k_B T / 6\pi\eta R_h \quad (2)$$

Where k_B , T , η are the Boltzmann constant, the absolute temperature, and the viscosity of the solvent, respectively. Using a modern LLS instrument, we can measure R_h down to a size about 1 nm because of a fast correlator and a powerful laser. All the LLS measurements were conducted at $30.0 \pm 0.1^\circ \text{C}$.

RESULTS AND DISCUSSION

Conductivity

The effect of mole fraction (x %) of ILs on the conductivity of their aqueous solutions shows a distinct trend, shown in Fig. 1. Mixtures of ILs and water display the classical properties of concentrated surfactant solutions, with a maximum conductivity [17]. The conductivity increases sharply in the water-rich region and decreases linearly in the ILs-rich region. This can be

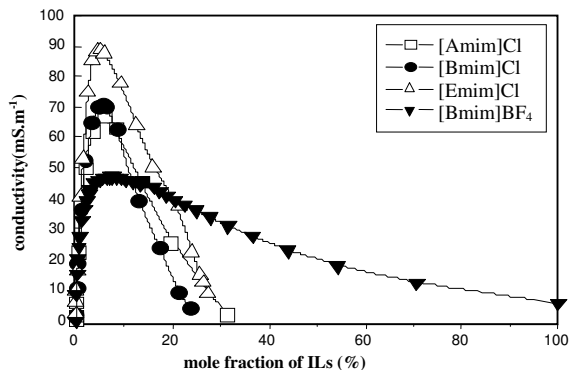


Fig. 1: Concentration dependence of conductivity for aqueous ILs solution.

ascribed to two effects: i) increase of viscosity and therefore reduction of the mobility of the charge carriers; ii) reduction of the number of the charge carriers due to aggregate formation [9,18]. The latter becomes dominant at higher concentration, thus leading to a strong decrease of conductivity. The critical concentrations of the mixtures are 5.9771 for [Amim]Cl (2.35mol/L), 5.1280 for [Emim]Cl (2.32mol/L), 5.5022 for [Bmim]Cl (2.29mol/L), 8.2690 for [Bmim]BF₄ (2.54mol/L). The order of [Amim]Cl (2.35mol/L) > [Emim]Cl (2.32mol/L) > [Bmim]Cl (2.29mol/L) is ascribed to the fact that the shorter the side chain of ILs, the larger value the CAC [9]. In addition, the reason for [Bmim]BF₄ (2.54mol/L) > [Bmim]Cl (2.29mol/L) is that the anion BF₄⁻ is weakly hydrated than Cl⁻ [19].

The Kohlraush's law for aqueous solution of salt,

$$\Lambda_m = \Lambda_m^\infty (1 - \beta\sqrt{c}) \quad (3)$$

Where Λ_m , Λ_m^∞ , β , c are the equivalent conductivity, the molar conductivity at infinite dilution, constant for a certain system and concentration respectively.

The equivalent conductivity and ionization degree α were calculated according to the following.

$$\Lambda_m = \frac{\kappa}{M} \quad (4)$$

$$\alpha = \frac{\Lambda_m}{\Lambda_0} \quad (5)$$

For the studied aqueous ILs solutions here, the ionization degree decreases sharply at water-rich region and decreases gently at IL-rich region (see Fig. 2),

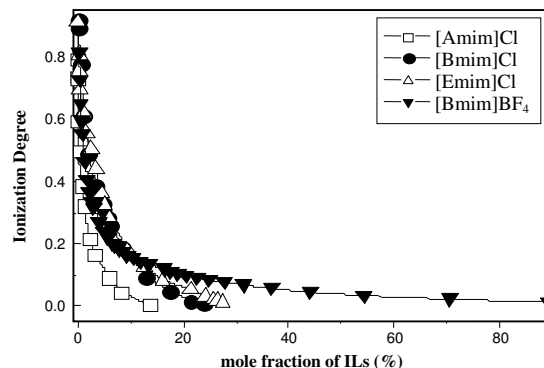


Fig. 2: Concentration dependence of ionization degree for aqueous ILs solutions.

which may indicate two regions of differing aggregate nature. Bowers [20] found the critical aggregation point of aqueous solution of [Omim]I and [Omim]Cl using the same method, which is not valid for their aqueous [Bmim]BF₄ solution, instead they determined the CAC of aqueous [Bmim]BF₄ solution with surface tension measurement.

Light scattering

For better understanding the aggregation behavior of aqueous ILs solution, DLS and SLS measurements of aqueous [Bmim]BF₄ solution were conducted at 532 nm with a commercial Brookhaven instrument laser light-scattering spectrometer [18]. Fig. 3 shows the concentration dependence of average characteristic line-width of relaxation and averaged intensity of scattered light. The time averaged intensity of scattered light reflects the fluctuation in the mixture. Both pure water and pure ionic liquid have homogeneous structure. It is well known that [Bmim]BF₄ is macroscopically 100% miscible with water in any molar ratio [18]. However, Fig. 3 clearly showed that when the [Bmim]BF₄ was added, the fluctuation and the intensity of scattered light increased obviously. That means, the mixture of [Bmim]BF₄ and water is not microscopically as homogeneous as we thought. Besides, the increasing of free charge, because of addition of [Bmim]BF₄, makes the motion of ions faster and results in the fluctuation increasing. The critical concentration determined by average characteristic line-width of relaxation is very close to the critical concentration determined by intensity of scattered light.

Fig. 4 shows intensity-intensity time correlation functions of aqueous [Bmim]BF₄ solutions at different concentrations. The time correlation function of pure ILs, pure water, the dilute solution ($x\% = 0.0850$) and the concentrated solution ($x\% = 87.8066$) within the delay time window is almost flat and structure-less, like the baseline parallel to the x-axis. However, it is very different when the critical concentration is 6.4085 ($x\%$), where shows a dominant relaxation in the mixture which means the mixture is not homogeneous. It proved the existence of aggregation directly. This critical concentration matches data of conductivity

Fig. 5 shows that the average characteristic line width obtained from measured time correlation function is a linear function of the square of the scattering vector (q), and the extrapolation of $q \rightarrow 0$ passes through the origin, which is a characteristic of diffusive relaxation [21]. The average mutual diffusion coefficient D (112987273.1 cm²/s) is derived from the slope of the line.

Proposed model of the aggregation

By combining the light scattering and conductance results, we proposed a schematic model [9] to explain the changes of the solution properties of aqueous ILs solution over the whole concentration ranges, which is shown in Fig. 6. In the diluted solution, IL ionizes to free ions, no to aggregates (see Fig. 6 (a)). The aggregation occurs with the further addition of IL (see Fig. 6 (b)). There is a maximum of aggregations and free ions at the critical concentration (see Fig. 6 (c)). The imidazolium cation is hydrophobic while the anions are hydrophilic. Because of this "hate-love" structure, the anions are positioned at the aggregate surface. Furthermore, the alkyl chain on the cation is positioned at the center of the aggregate which was proved by NMR.[22] Because the intensity of scattered light is independent with the detected angle, the aggregates are spheric. When the concentration is beyond the CAC, the IL can not ionize to free anions and cations. The free ions and aggregations decrease (see Fig. 6 (d)).

Absorption at interfaces is one way of avoiding the entropically unfavorable contact between water and the hydrophobic part which was confirmed by Baldelli.[23] Self-association into structures with marked hydrophobe-hydrophile separation is another way of achieving this. The self-association of ILs in aqueous solution is strongly

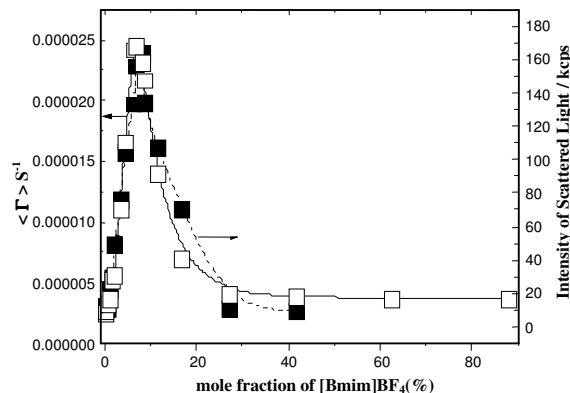


Fig. 3: Concentration dependence of average characteristic line-width and light intensity of relaxation in mixture of [Bmim]BF₄ and water.

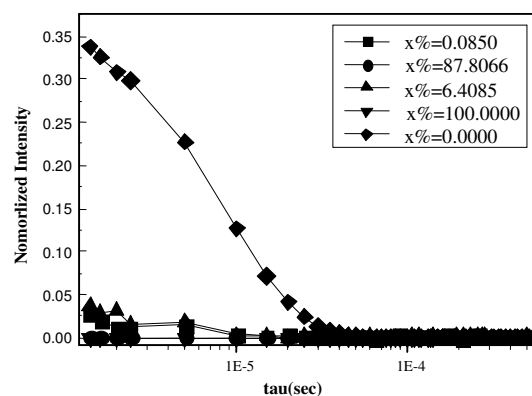


Fig. 4: Intensity-intensity time correlation function of aqueous [Bmim]BF₄ solutions at different concentration.

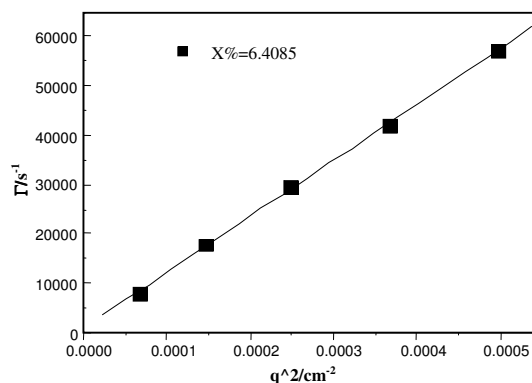


Fig. 5: Scattering vector (q) dependence of average characteristic line-width of relaxation in aqueous [Bmim]BF₄ solutions at concentration of $x\% = 6.6085$.

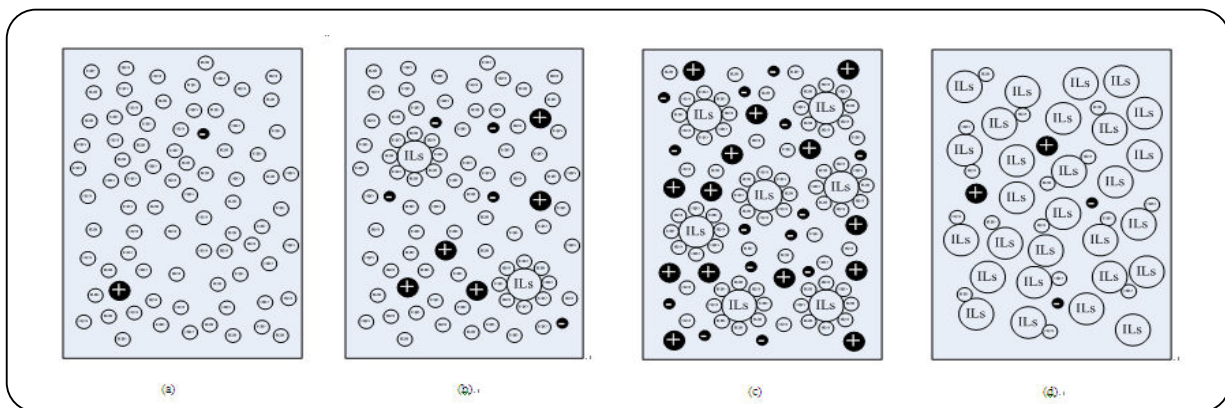


Fig. 6: The schematic model of the aggregation of ionic liquids in aqueous solution \odot : ionic liquid \circ : H_2O \oplus : free cation \ominus : free anion

cooperative and starts generally with the formation of roughly spherical aggregate around a fairly well defined concentration (CAC).

Absorption at interfaces is one way of avoiding the entropically unfavorable contact between water and the hydrophobic part which was confirmed by Baldelli.[23] Self-association into structures with marked hydrophobe-hydrophile separation is another way of achieving this. The self-association of ILs in aqueous solution is strongly cooperative and starts generally with the formation of roughly spherical aggregate around a fairly well defined concentration (CAC).

CONCLUSIONS

In summary, we investigated the conductivity and laser light scattering of four short chain imidazolium-based ILs in aqueous solution, whereby their aggregation behavior was studied. The critical aggregation concentration of different ILs, determined with different techniques, was in fairly good agreement. Our results demonstrated that the four ILs had surfactant-like properties, whose critical concentrations are in the order of $2.35\text{mol/L}([\text{Amim}]\text{Cl}) > 2.32\text{mol/L}([\text{Emim}]\text{Cl}) > 2.29\text{mol/L}([\text{Bmim}]\text{Cl}) < 2.54\text{mol/L}([\text{Bmim}]\text{BF}_4)$. The model of aggregation in the aqueous solution indicates the structural change in the mixture. It is very important to understand the interactions between ILs and water. It is helpful to the bottom-up design of the ILs and its further applications.

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