

## Salt Effect on the Aggregation Behavior of 1-Decyl-3-methylimidazolium Bromide in Aqueous Solutions

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Received: November 16, 2009; Revised Manuscript Received: December 14, 2009

Understanding of the specific salt effect on the aggregation behavior of ionic liquids (ILs) is relevant to multiple applications. In this work, the influence of a series of 15 salts on the aggregation behavior of [C<sub>10</sub>mim]Br in aqueous solutions has been investigated by conductivity, fluorescence, and dynamic light scattering. It was shown that NaCl, NaBr, NaI, CH<sub>3</sub>CO<sub>2</sub>Na, NaSCN, NaNO<sub>3</sub>, NaBrO<sub>3</sub>, NaClO<sub>3</sub>, C<sub>6</sub>H<sub>5</sub>COONa, Na<sub>2</sub>CO<sub>3</sub>, Na<sub>2</sub>SO<sub>4</sub>, Na<sub>2</sub>C<sub>4</sub>H<sub>4</sub>O<sub>6</sub>, and Na<sub>3</sub>CH<sub>5</sub>O<sub>7</sub> have salting-out effect, whereas FeBr<sub>3</sub> and AlBr<sub>3</sub> have salting-in effect on the aggregation of [C<sub>10</sub>mim]Br in aqueous solutions. The effect of anions of the added sodium salts on the critical aggregation concentration (CAC), degree of anionic binding ( $\beta$ ), and aggregation number ( $N_{\text{agg}}$ ) of the IL basically follows the Hofmeister series, and the CAC values decrease but the  $\beta$  and  $N_{\text{agg}}$  values increase with increasing concentration of the salts. Hydrophobicity of the anions is suggested to play important roles in the salt effect on the aggregation of [C<sub>10</sub>mim]Br in aqueous solutions. Furthermore, the IL aggregates were found to grow slowly as the increase of the salt concentrations under studied static conditions, and resulting in the increased aggregation number of the IL. These results are expected to be useful in the applications of ionic liquids.

### Introduction

Ionic liquids (ILs) have gained great attention for their promising role as alternative media in catalysis, separation, and electrochemical processes due to their unique chemical and physical properties.<sup>1–3</sup> Knowledge of the aggregation behavior of ILs is a vital part for understanding how these compounds participate as components in the practical applications. In recent years, a number of research publications indicated aggregates formation of ILs in aqueous solutions.<sup>4–17</sup> It was found that the aggregation behavior of ILs can be regulated and controlled by designing the alkyl chain length, cationic structure, and anionic type of the ILs. Literature survey reveals that aggregation behavior of ILs can also be tuned by the addition of some inorganic salts, but the related investigation is very limited. In this context, Rebelo et al.<sup>18</sup> found that the addition of salts (NaCl, Na<sub>2</sub>SO<sub>4</sub>, tetrabutylammonium bromide) affected significantly the critical aggregation concentration (CAC) of [C<sub>10</sub>mim]Cl and [C<sub>12</sub>mim]Cl in aqueous solutions, and the CAC values decreased with increasing ionic strength of the added salts. Dong et al.<sup>19</sup> studied the effect of sodium halide on the CACs of [C<sub>10</sub>mim]Br, [C<sub>12</sub>mim]Br, and [C<sub>12</sub>mim][BF<sub>4</sub>] in water, and it was reported that the effect of anions decreased in the order I<sup>−</sup> > Br<sup>−</sup> > Cl<sup>−</sup>. Therefore, a systematical study on the effect of the salt nature on the aggregation behavior of ILs is necessary from the viewpoint of fundamental and applied aspects.

Considering our preliminary investigation that influence of inorganic cations of the added salts on the aggregation behavior of ILs is marginal, this work aims to study the regulated and controlled effect of a large series of inorganic/organic anions on the aggregation behavior of 1-decyl-3-methylimidazolium

bromide ([C<sub>10</sub>mim]Br) in aqueous solutions. Toward this end, 13 sodium salts (NaCl, NaBr, NaI, CH<sub>3</sub>CO<sub>2</sub>Na, NaSCN, NaNO<sub>3</sub>, NaBrO<sub>3</sub>, NaClO<sub>3</sub>, C<sub>6</sub>H<sub>5</sub>COONa, Na<sub>2</sub>CO<sub>3</sub>, Na<sub>2</sub>SO<sub>4</sub>, Na<sub>2</sub>C<sub>4</sub>H<sub>4</sub>O<sub>6</sub>, Na<sub>3</sub>CH<sub>5</sub>O<sub>7</sub>) and 2 bromides (FeBr<sub>3</sub> and AlBr<sub>3</sub>) were selected, and conductivity, fluorescence probe, and dynamic light scattering are combined to study the salt effect on the aggregation of [C<sub>10</sub>mim]Br. The results have been discussed from the influence of the nature and concentration of salt on the critical aggregation concentration (CAC), the degree of anionic binding at the aggregates surface ( $\beta$ ), the standard Gibbs energy of aggregation ( $\Delta G_{\text{m}}^{\circ}$ ), the aggregation number ( $N_{\text{agg}}$ ), and aggregate size of the ionic liquid in aqueous solutions.

### Experimental Section

**Materials.** 1-Methylimidazole (99%) was purchased from Shanghai Chem. Co.; 1-bromodecane (99%), NaCl (99.9%), NaBr (99%), NaI (99%), CH<sub>3</sub>CO<sub>2</sub>Na (99%), NaSCN (98%), NaNO<sub>3</sub> (99%), NaBrO<sub>3</sub> (99.5%), NaClO<sub>3</sub> (99%), C<sub>6</sub>H<sub>5</sub>COONa (99%), Na<sub>2</sub>CO<sub>3</sub> (99.95%), Na<sub>2</sub>SO<sub>4</sub> (99%), Na<sub>2</sub>C<sub>4</sub>H<sub>4</sub>O<sub>6</sub>·2H<sub>2</sub>O (>99%), Na<sub>3</sub>CH<sub>5</sub>O<sub>7</sub>·2H<sub>2</sub>O (99%), FeBr<sub>3</sub> (98%), and AlBr<sub>3</sub> (98%) were from Alfar Aser. All the salts were used without further purification except for the consideration of crystal water in the sample preparation. Pyrene (99%) and benzophenone (99%) were from Fluka and Czechoslovakia, respectively. [C<sub>10</sub>mim]Br ionic liquid was synthesized by the procedure described in the literature.<sup>20</sup> A water sample with room temperature conductivity of  $1.0 \times 10^{-6} \text{ S} \cdot \text{cm}^{-1}$  was used throughout the experiments. Dilute stock solution of pyrene was prepared by dissolving the pyrene in methanol in an amber-glass vial and stored in a refrigerator at 277 K. Samples for fluorescence measurements were prepared in the following procedure: appropriate aliquots of probe stock solutions were transferred into vials and evaporated under ultra-high-purity hydrogen, and then the ionic liquid was added.

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**Experimental Methods.** Mixtures were prepared by mass on the molality concentration scale. Solution conductivities were determined on a Wayne-Kerr 6430B Autobalance Bridge fitted with a Shanghai DJS-1 electrode. The solution in the conductivity cell was stirred magnetically. The conductance cell was equipped with a water circulating jacket, and the temperature was controlled at  $298.15 \pm 0.01$  K with a HAAKE V26 temperature thermostat (Thermo Electron, Germany). The cell was calibrated with aqueous KCl solutions at different concentrations, and a cell constant of  $0.996 \text{ cm}^{-1}$  was determined. The uncertainty in conductivities measurements is about  $\pm 0.02\%$ .

Steady-state fluorescence measurements were carried out with a Cary Eclipse fluorophotometer (Varian, America). Both excitation and emission band slits were fixed at 5 nm. The excitation wavelength was selected at 335 nm, while the emission spectra were scanned from 350 to 450 nm. The first and the third vibronic peaks of pyrene appear at 373 and 383 nm, respectively. The measurements were conducted at  $298 \pm 1$  K. At the excitation wavelength of 335 nm, the effect of the ionic liquid fluorescence on the first and the third vibronic peaks of pyrene was negligible. All the data were acquired using the quartz cells with 1 cm path length. All fluorescence spectra were background subtracted using an appropriate blank.

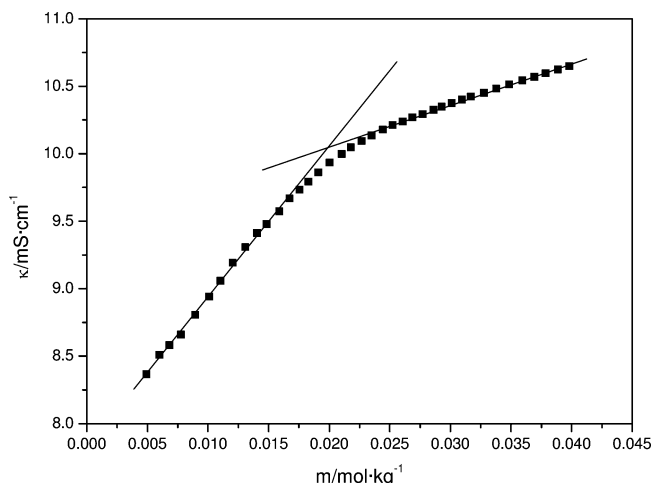
For the investigation of the IL aggregation number in aqueous salt solutions, steady-state fluorescence quenching technique was used in the present work. For this purpose, pyrene and benzophenone were used as a fluorescence probe and a quencher, respectively. The pair of pyrene/benzophenone assured that the residence time of the quencher into the aggregates is longer than the fluorescence lifetime of the probe.<sup>21,22</sup> The concentration of pyrene was kept constant at  $5 \times 10^{-7} \text{ mol L}^{-1}$ , while the quencher concentration was varied from 0 to  $1.5 \times 10^{-3} \text{ mol L}^{-1}$ , assuring a Poisson distribution.<sup>23,24</sup>

The dynamic light scattering (DLS) experiments were performed on a Nano ZS-90 particle size analyzer (Malvern, U.K.). Light of  $\lambda = 633$  nm from a solid-state He–Ne laser (4.0 mW) was used as the incident beam. All sample solutions were filtered through a  $0.22 \mu\text{m}$  hydrophilic PVDF membrane filter. All measurements were made at  $298.2 \pm 0.1$  K and at  $90^\circ$  scattering angle. At least three measurements were taken for each solution, and reproducibility of the aggregate sizes was found to be within  $\pm 3\%$ .

During the experiments, it was observed that the aqueous IL solution become turbid when the concentration of NaSCN is higher than 0.1 mol/kg. Thus, in the case of NaSCN, our studies on the IL aggregation were limited at the concentrations less than 0.1 mol/kg.

## Results and Discussion

**Salt Effect on CAC of the Ionic Liquid.** Typical experimental conductivities ( $\kappa$ ) at 298.15 K for aqueous solutions of  $[\text{C}_{10}\text{mim}]\text{Br}$  in the presence of 0.1 mol/kg  $\text{NaNO}_3$  are shown in Figure 1 as a function of IL concentrations in the range of interest. The concentration corresponding to the inflection observed in the curve is considered to be the critical aggregation concentration (CAC) of  $[\text{C}_{10}\text{mim}]\text{Br}$  in aqueous 0.1 mol/kg  $\text{NaNO}_3$  solution, and the CAC value can be calculated by solving the two linear equations below and above the inflection. Similar situations have been found for the ionic liquid in the presence of other salts at different concentrations. CAC values thus obtained are given in Table 1. As it is expected, a pronounced effect of the anions was observed on CAC of  $[\text{C}_{10}\text{mim}]\text{Br}$ . These values increase in the sequence:  $\text{SCN}^- < \text{I}^- < \text{C}_6\text{H}_5\text{COO}^- < \text{ClO}_3^- < \text{NO}_3^- \approx \text{C}_4\text{H}_4\text{O}_6^{2-} < \text{C}_6\text{H}_5\text{O}_7^{3-} <$



**Figure 1.** Concentration dependence of the conductivities for aqueous  $[\text{C}_{10}\text{mim}]\text{Br}$  solutions in the presence of 0.1 mol/kg  $\text{NaNO}_3$ .

$\text{Br}^- < \text{SO}_4^{2-} < \text{CO}_3^{2-} < \text{Cl}^- < \text{BrO}_3^- < \text{CH}_3\text{COO}^-$ . In other words, ability of the anions to promote aggregation of the IL was found to increase in the order:  $\text{SCN}^- > \text{I}^- > \text{C}_6\text{H}_5\text{COO}^- > \text{ClO}_3^- > \text{NO}_3^- \approx \text{C}_4\text{H}_4\text{O}_6^{2-} > \text{C}_6\text{H}_5\text{O}_7^{3-} > \text{Br}^- > \text{SO}_4^{2-} > \text{CO}_3^{2-} > \text{Cl}^- > \text{BrO}_3^- > \text{CH}_3\text{COO}^-$ . This anionic effect correlates well with the Hofmeister series, which provides an adequate qualitative description for the salt effect in several physical behaviors.<sup>25,26</sup> The trend observed for the CACs of  $[\text{C}_{10}\text{mim}]\text{Br}$  in aqueous salt solutions is actually analogous to those found for conventional ionic surfactants such as dodecyltrimethylammonium bromide (DTAB) and hexadecyltrimethylammonium bromide (TTAB).<sup>26</sup> Similar trend was also reported recently for the anion effect on the solubility of  $[\text{C}_4\text{mim}][\text{Tf}_2\text{N}]$  ionic liquid in water.<sup>27</sup>

It is known that the position of an anion in the Hofmeister series can be correlated with its charge and hydration radius. An increased hydration radius of the anions is usually accompanied by an increased polarizability. A high polarizability would enhance the binding of the anions at the aggregate surface and decrease the electrostatic repulsion between the head groups of the IL, thus increasing the tendency of the IL aggregation and then lowering its CAC value. On the basis of this rationale, we have examined the relationship between the CACs of  $[\text{C}_{10}\text{mim}]\text{Br}$  in the presence of 0.1 mol/kg for 1–1 salts and the effective hydrodynamic radius ( $R_h$ ) of their anions collected in Table 2. It can be seen from Figure 2 that there is an approximately linear relationship between CAC of the IL and  $R_h$  of anions of the added salts. The hydrodynamic radius of the anions can thus be considered to be a better correlation parameter for CAC of the IL. Generally, larger sized hydrophobic anions are weakly hydrated and highly polarizable and can bind more efficiently at the surface of the aggregates. Therefore, hydrophobicity of anions of the added salts plays an important role in the salt effect of the IL aggregation in aqueous solutions.

It is interesting to note that there is a close linear relationship between CACs of  $[\text{C}_{10}\text{mim}]\text{Br}$  and concentrations of the added salt. As shown in Figure 3, the linear relationship can be described by

$$\log(\text{CAC}/\text{CAC}_0) = a - km_s \quad (1)$$

where CAC and  $\text{CAC}_0$  are the critical aggregation concentrations with and without salt,  $m_s$  is molality of the added salt, and  $a$  and  $k$  are adjusted parameters. The  $k$  values for different salts

**TABLE 1: Critical Aggregation Concentration (CAC), Degree of Anion Binding  $\beta$ , and Standard Gibbs Energies of Aggregation  $\Delta G_m^\circ$  for [C<sub>10</sub>mim]Br in Aqueous Solutions in the Presence of Different Salts at 298.15 K**

salt	$m_s^a/(\text{mol}\cdot\text{kg}^{-1})$	CAC/(mol·kg <sup>-1</sup> )			$\beta$	$\Delta G_m^\circ/(\text{kJ}\cdot\text{mol}^{-1})$
		conductivity	fluorescence	average		
NaCl	0.1	0.032	0.033	0.032	0.56	-28.7
	0.2	0.026	0.025	0.026	0.57	-29.7
	0.3	0.023	0.022	0.023	0.65	-31.8
	0.4	0.019	0.020	0.019	0.68	-33.2
	0.5	0.016	0.014	0.015	0.70	-34.4
NaNO <sub>3</sub>	0.1	0.020	0.021	0.020	0.78	-34.9
	0.2	0.017	0.015	0.016	0.78	-35.8
	0.3	0.012	0.012	0.012	0.91	-39.8
	0.4	0.011	0.0096	0.010	0.91	-40.2
	0.5	0.009	0.0076	0.0083	0.94	-41.8
CH <sub>3</sub> CO <sub>2</sub> Na	0.1	0.036	0.034	0.035	0.53	-27.9
	0.2	0.031	0.030	0.031	0.63	-30.2
	0.3	0.027	0.028	0.027	0.72	-30.5
	0.4	0.025	0.026	0.025	0.72	-32.9
	0.5	0.023	0.022	0.023	0.76	-33.9
Na <sub>2</sub> CO <sub>3</sub>	0.1	0.03	0.031	0.030	0.70	-31.8
	0.2	0.022	0.021	0.022	0.76	-34.8
	0.3	0.019	0.019	0.019	0.81	-35.8
	0.4	0.018	0.018	0.018	0.83	-36.4
	0.5	0.016	0.014	0.015	0.84	-37.2
Na <sub>2</sub> SO <sub>4</sub>	0.1	0.027	0.027	0.027	0.72	-32.6
	0.2	0.022	0.022	0.022	0.77	-34.4
	0.3	0.018	0.018	0.018	0.82	-36.3
	0.4	0.014	0.015	0.014	0.84	-37.7
	0.5	0.012	0.011	0.012	0.85	-38.7
NaBrO <sub>3</sub>	0.1	0.035	0.034	0.035	0.55	-29.4
	0.2	0.029	0.030	0.029	0.74	-33.3
	0.3	0.025	0.025	0.025	0.74	-34.7
	0.4	0.022	0.020	0.021	0.74	-35.5
	0.5	0.019	0.017	0.018	0.86	-38.9
NaClO <sub>3</sub>	0.1	0.018	0.014	0.016	0.90	-37.9
	0.2	0.012	0.01	0.011	0.97	-41.2
	0.3	0.0097	0.0090	0.094	0.98	-42.5
	0.4	0.0077	0.0079	0.078	0.99	-43.8
	0.5	0.0067	0.0056	0.0062	0.99	-44.7
NaBr	0.1	0.026	0.024	0.025	0.75	-33.3
	0.2	0.020	0.017	0.019	0.77	-34.8
	0.3	0.017	0.015	0.016	0.79	-35.9
	0.4	0.015	0.014	0.015	0.81	-36.8
	0.5	0.013	0.011	0.012	0.90	-39.4
NaI	0.1	0.0061	0.0061	0.0061	0.85	-41.8
	0.2	0.0045	0.0045	0.0045	0.93	-45.0
	0.3	0.0035	0.0033	0.0034	0.94	-46.4
	0.4	0.0030	0.0028	0.0029	0.97	-47.9
	0.5	0.0025	0.0023	0.0024	0.98	-49.1
Na <sub>3</sub> C <sub>6</sub> H <sub>5</sub> O <sub>7</sub>	0.1	0.025	0.023	0.024	0.76	-33.6
	0.2	0.019	0.017	0.018	0.78	-35.1
	0.3	0.016	0.015	0.016	0.89	-38.1
	0.4	0.012	0.011	0.012	0.89	-39.3
	0.5	0.011	0.010	0.011	0.91	-40.5
C <sub>6</sub> H <sub>5</sub> CO <sub>2</sub> Na	0.1	0.0087	0.0080	0.0084	0.88	-40.8
	0.2	0.0067	0.0069	0.0068	0.91	-42.8
	0.3	0.0056	0.0049	0.0053	0.93	-44.1
	0.4	0.0047	0.0043	0.0045	0.94	-45.1
	0.5	0.0040	0.0035	0.0038	0.96	-46.2
Na <sub>2</sub> C <sub>4</sub> H <sub>4</sub> O <sub>6</sub>	0.1	0.021	0.024	0.023	0.77	-34.6
	0.2	0.017	0.015	0.016	0.82	-36.5
	0.3	0.014	0.015	0.014	0.86	-38.4
	0.4	0.012	0.012	0.012	0.88	-39.5
	0.5	0.010	0.0093	0.0097	0.91	-40.7
NaSCN	0.02	0.010	0.012	0.011	0.49	-31.7
	0.04	0.0059	0.0062	0.0060	0.57	-35.6
	0.06	0.0048	0.0054	0.0050	0.69	-39.3
	0.08	0.0039	0.0040	0.0039	0.71	-40.6
	0.10	0.0034	0.0038	0.0036	0.80	-43.3
AlBr <sub>3</sub>	0.001	0.042	0.040	0.041	0.66	-29.6
FeBr <sub>3</sub>	0.001	0.044	0.042	0.043	0.66	-29.6

<sup>a</sup> Molality of the salts.

TABLE 2: Hydrodynamic Radius ( $R_h$ ) of the Anion<sup>a</sup>

ion	$R_h$ /(nm)
$\text{CH}_3\text{CO}_2^-$	0.217
$\text{NO}_3^-$	0.223
$\text{Cl}^-$	0.224
$\text{BrO}_3^-$	0.229
$\text{Br}^-$	0.231
$\text{ClO}_3^-$	0.233
$\text{SCN}^-$	0.242
$\text{I}^-$	0.246

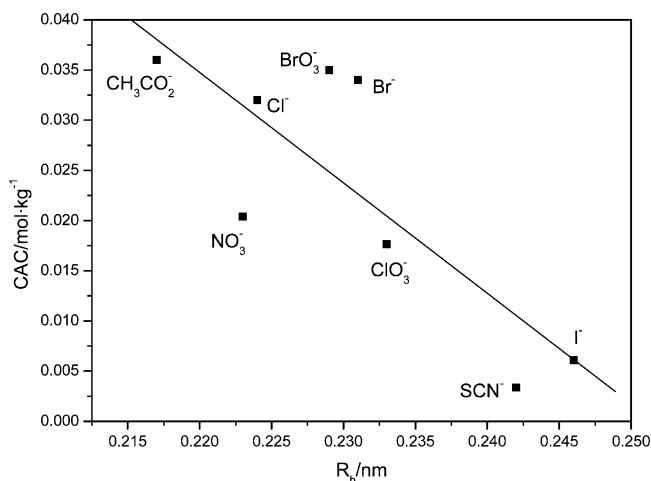
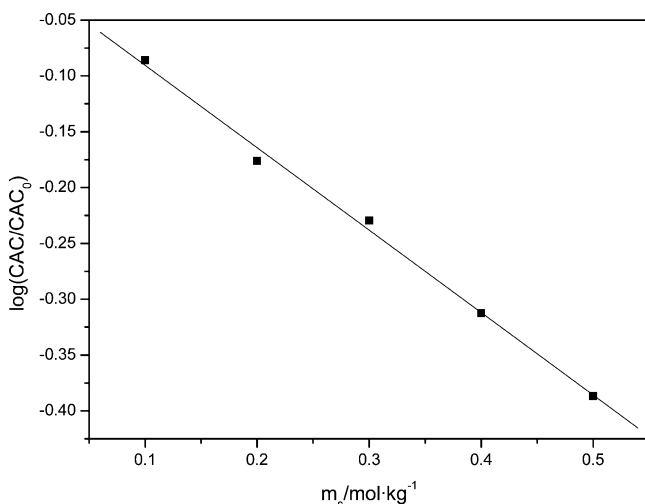
<sup>a</sup> Reference 28.

Figure 2. Relationship between critical aggregation concentration of the ionic liquid and effective hydrodynamic radii of anions of the added salts.

Figure 3. Linear plots of  $\log(\text{CAC}/\text{CAC}_0)$  for the ionic liquid versus the NaCl concentration.

are presented in Table 2. In fact, eq 1 is similar to the empirical equation of salt effect for conventional surfactants:<sup>29</sup>

$$\log \text{CAC} = \text{constant} - k_s m_s \quad (2)$$

where  $k_s$  is the salting constant, and  $k_s$  and  $k$  are equal in value. A positive  $k_s$  (or  $k$ ) indicates a salt-out effect, whereas a negative  $k_s$  (or  $k$ ) suggests a salt-in effect. Usually, the salt-out effect is entropically driven, but the salt-in effect results from the direct or indirect binding of the low charge density ions to the hydrophobic moiety of the monomer molecules of solutes.<sup>30,31</sup>

TABLE 3:  $k$  Parameter of Eq 1

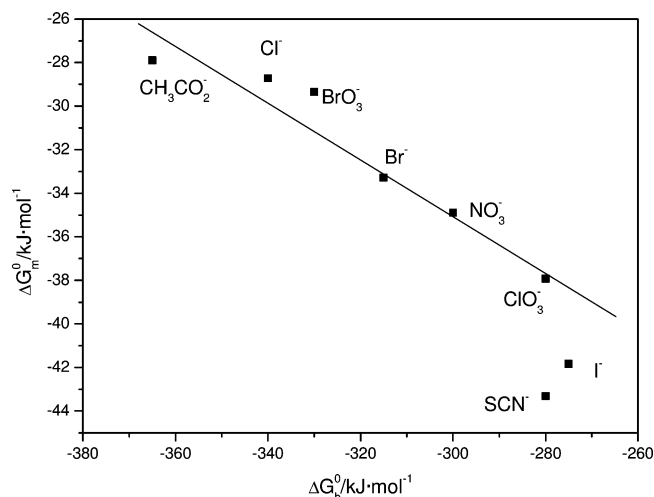
salt	$k$ /(kg/mol)
NaCl	$0.76 \pm 0.02$
$\text{Na}_2\text{SO}_4$	$0.88 \pm 0.01$
$\text{NaNO}_3$	$0.86 \pm 0.07$
$\text{CH}_3\text{CO}_2\text{Na}$	$0.49 \pm 0.02$
$\text{Na}_2\text{CO}_3$	$0.63 \pm 0.12$
$\text{NaSCN}$	$5.63 \pm 0.15$
$\text{NaBrO}_3$	$0.65 \pm 0.02$
$\text{NaClO}_3$	$1.04 \pm 0.10$
$\text{NaBr}$	$0.73 \pm 0.07$
$\text{NaI}$	$0.95 \pm 0.08$
$\text{Na}_3\text{C}_6\text{H}_5\text{O}_7$	$0.93 \pm 0.05$
$\text{C}_6\text{H}_5\text{CO}_2\text{Na}$	$0.83 \pm 0.05$
$\text{Na}_2\text{C}_4\text{H}_4\text{O}_6$	$0.77 \pm 0.05$

As can be seen from Table 3, the  $k$  values are negative for  $\text{FeBr}_3$  and  $\text{AlBr}_3$ , and they are positive for the other salts. This indicates that  $\text{FeBr}_3$  and  $\text{AlBr}_3$  weaken, but the other salts enhanced the aggregation of  $[\text{C}_{10}\text{mim}]\text{Br}$  in aqueous solutions. The degree of weakness and enhancement for the aggregation depends on the nature and concentration of the salts. Therefore, we can control the aggregation degree of the IL by choosing a right salt at a right concentration for a particular application.

Usually, the above observation that the presence of electrolytes tends to decrease CAC values of the ionic liquid can be interpreted primarily by the decrease of the electrostatic repulsions among ionic head groups of the IL due to the addition of salt. How can we understand the salt-in effect of  $\text{FeBr}_3$  and  $\text{AlBr}_3$  on the aggregation behavior of the IL? It is known that  $\text{Br}^-$  and  $\text{FeBr}_3$  (or  $\text{AlBr}_3$ ) form tetrahedral complex  $\text{FeBr}_4^-$  (or  $\text{AlBr}_4^-$ ) in aqueous solutions. Recently, a series of paramagnetic ionic liquids were prepared with 1-alkyl-3-methylimidazolium cation ( $[\text{C}_n\text{mim}]^+$ ) and tetrahalogenoferrate (III) anion ( $\text{FeBr}_4^-$  or  $\text{FeCl}_4^-$ ).<sup>32</sup> It was found that as the ratio of  $\text{FeCl}_3$  to  $[\text{C}_4\text{mim}]\text{Cl}$  was unity,  $\text{FeCl}_4^-$  was the primary anion, whereas  $\text{Fe}_2\text{Cl}_7^-$  anion was shaped at higher chloride concentrations. At a lower ratio of  $\text{FeCl}_3$  to  $[\text{C}_4\text{mim}]\text{Cl}$ , some  $\text{Cl}^-$  anions remained.<sup>33</sup> In our experiments, the concentration of  $\text{FeBr}_3$  and  $\text{AlBr}_3$  was at 0.001 mol/kg. This allows us to ensure that there is an anionic mixture of  $\text{FeBr}_4^-$  (or  $\text{AlBr}_4^-$ ) and  $\text{Br}^-$  in the most dilute IL solution. The molar number of anions was not increased in the system by the addition of  $\text{FeBr}_3$  or  $\text{AlBr}_3$ ; the only difference is that some  $\text{Br}^-$  was changed into  $\text{FeBr}_4^-$  or  $\text{AlBr}_4^-$  anion. Evidently,  $\text{FeBr}_4^-$  and  $\text{AlBr}_4^-$  anions have larger radius and less charge density compared with  $\text{Br}^-$ . So they cannot decrease effectively the electrostatic repulsion between the ionic head groups of the IL, but can interact with the hydrophobic moiety of cation of the IL, thus decreasing the tendency of the IL aggregation and then increasing its CAC.

**Salt Effects on the Degree of Anion Binding on the Aggregates Surface and Gibbs Energy of Aggregation of the Ionic Liquid.** From the plots of conductivity against concentration of the IL (Figure 1), the ratio of the slopes of the straight lines post- and pre-CAC was obtained, its difference from unity ( $\beta$ ) gives the degree of anion bound to the aggregate surface. These values are also included in Table 1, and the data allow us to evaluate the effect of salt nature on the degree of anion binding on the aggregates surface of the IL. It can be seen that the  $\beta$  values decrease in the following order:  $\text{ClO}_3^- > \text{I}^- > \text{C}_6\text{H}_5\text{COO}^- > \text{SCN}^- > \text{NO}_3^- > \text{C}_4\text{H}_4\text{O}_6^{2-} > \text{C}_6\text{H}_5\text{O}_7^{3-} > \text{Br}^- > \text{SO}_4^{2-} > \text{CO}_3^{2-} > \text{Cl}^- > \text{BrO}_3^- > \text{CH}_3\text{COO}^-$  at a given salt concentration, and increase with increasing salt concentrations for a given salt. The order of these  $\beta$  values is approximately reverse to that of CAC in the presence of different salts. This





**Figure 4.** Linear relationship between the standard Gibbs energy of aggregation ( $\Delta G_m^0$ ) of the ionic liquid and the Gibbs energy of hydration of anions ( $\Delta G_h^0$ ) of the added salts.

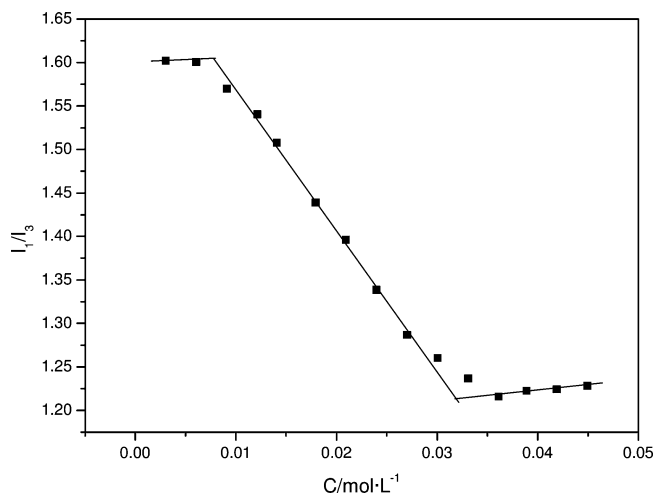
is in our expectation since the weaker anionic binding on the aggregates surface results in the less decrease of the aggregates charge, which is not favorable for the formation of aggregates by association of the amphiphilic anions. The salt concentration dependence of  $\beta$  values observed here was similar to that of cetyltrimethylammonium chloride aggregates and that of molecular dynamics simulations.<sup>34</sup> The simulations results suggested that the peak height of  $\text{Cl}^-$  in radial density distribution grows significantly with the increase of the salt concentration, indicating that more and more  $\text{Cl}^-$  anions are absorbed into the Stern layer of the surfactant head groups and thus the  $\beta$  values increase.

Based on the binding mechanisms of anions on the aggregates surface of cetyltrimethylammonium bromide (CTAB)<sup>35</sup> and cetyltrimethylammonium chloride (CTAC),<sup>36</sup> there may be two different kinds of anion binding:  $\text{SCN}^-$ ,  $\text{I}^-$ ,  $\text{ClO}_3^-$ ,  $\text{NO}_3^-$ ,  $\text{C}_4\text{H}_4\text{O}_6^{2-}$ ,  $\text{C}_6\text{H}_5\text{O}_7^{3-}$ ,  $\text{Br}^-$ ,  $\text{SO}_4^{2-}$ ,  $\text{CO}_3^{2-}$ ,  $\text{Cl}^-$ ,  $\text{BrO}_3^-$ , and  $\text{CH}_3\text{COO}^-$  are considered to be adsorbed on the surface of the aggregates due to their weakly or moderately association with the IL cation, whereas the aromatic anions, like  $\text{C}_6\text{H}_5\text{COO}^-$ , penetrate inside the aggregates with their hydrophilic groups staying in the IL headgroup region and the hydrophobic groups partially embedded into the hydrophobic core of the aggregates.

Based on the pseudophase model of micellization, the standard Gibbs energy of aggregation can be calculated from the equation:<sup>37</sup>

$$\Delta G_m^0 = (1 + \beta)RT \ln \chi_{\text{CAC}} \quad (3)$$

where  $\chi_{\text{CAC}}$  is the critical aggregation concentration expressed by mole fraction. The values of  $\Delta G_m^0$  calculated for  $[\text{C}_{10}\text{mim}]\text{Br}$  are included in Table 1 as a function of salt type and concentrations. It is clear that the effect of anions of the added salts on the standard Gibbs energy of aggregation of the IL follows the trend: the greater sized anions show the stronger effect, while the smaller sized hydrophilic anions, which have higher negative values of hydration Gibbs energy, are only weakly incorporated in the aggregation phases. Indeed, a plot of  $\Delta G_m^0$  values versus hydration Gibbs energy ( $\Delta G_h^0$ ) of the studied anions<sup>28</sup> gives a reasonable straight line (see Figure 4). Here, it should be mentioned that because data of the hydration Gibbs energy for  $\text{SO}_4^{2-}$ ,  $\text{CO}_3^{2-}$ ,  $\text{C}_6\text{H}_5\text{COO}^-$ ,  $\text{C}_4\text{H}_4\text{O}_6^{2-}$ , and  $\text{CH}_5\text{O}_7^{3-}$  are not available in the literature; they are not shown



**Figure 5.** Variation of  $I_1/I_3$  with concentrations of  $[\text{C}_{10}\text{mim}]\text{Br}$  in 0.1 mol/kg NaCl aqueous solution at 298.2 K.

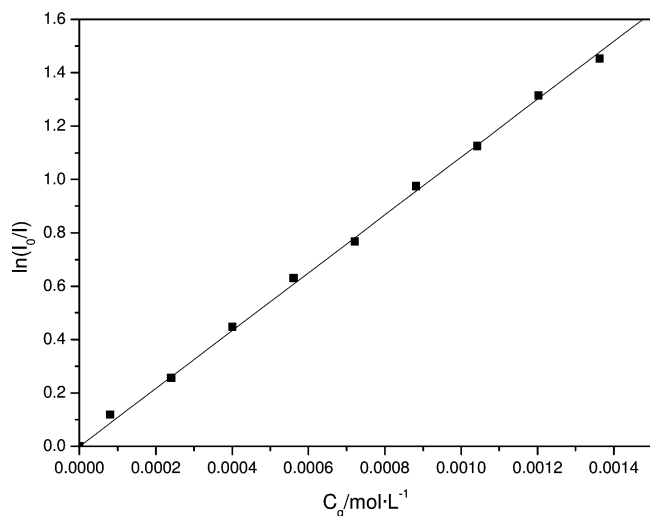
in the figure. This finding suggests that the effect of salts on the aggregation behavior of the IL is strongly related to the nature of their anions hydration. Interaction between anions of the salts and cationic moiety of the IL is stronger for hydrophobic anions than that for hydrophilic ones. However, in the presence of  $\text{AlBr}_3$  and  $\text{FeBr}_3$ , the  $\Delta G_m^0$  values are slightly larger than those in water. This suggests that the aggregation ability of  $[\text{C}_{10}\text{mim}]\text{Br}$  is weaker in aqueous salt solutions than in water.

**Salt Effect on the Aggregation Number of the Ionic Liquid.** Solvatochromic fluorescence probes are usually used to obtain various aggregation parameters, such as CAC, aggregation number, dipolarity, and microfluidity, among others. Representative fluorescence emission results of pyrene at 298.15 K are shown in Figure 5 which describes the plots of  $I_1/I_3$  ( $I_1$  and  $I_3$  refer to the intensities of pyrene emission spectra at 373 and 383 nm, respectively) versus IL concentrations. In aqueous  $[\text{C}_{10}\text{mim}]\text{Br}$  solutions with salt, the abrupt sigmoidal increase in  $I_1/I_3$  clearly indicates that aggregates of the IL were formed and pyrene preferentially resides in a more hydrophobic microenvironment of the aggregates relative to aqueous salt. CAC of the IL can be taken as the concentration that corresponds to the intersection between the linear extrapolation of the rapidly varied portion of the curve and of the relative stabilization portion at higher concentrations. These values are also listed in Table 1. It can be clearly seen that the CAC values determined from the conductivity and fluorescence probe methods are in good agreement.

Aggregation number ( $N_{\text{agg}}$ ) of the IL monomers in various aqueous salts solutions was determined from the fluorescence quenching data by using

$$\ln(I_0/I) = N_{\text{agg}} C_q / (C_t - \text{CAC}) \quad (4)$$

where  $I$  and  $I_0$  represent the intensity of pyrene fluorescence with and without quencher, and  $C_q$  and  $C_t$  are the concentrations of quencher and IL monomer, respectively. Linear plots of  $\ln(I_0/I)$  versus  $C_q$  in 0.07 mol/L of aqueous  $[\text{C}_{10}\text{mim}]\text{Br}$  and in the presence of 0.1 mol/kg  $\text{NaClO}_3$  are shown in Figure 6. The values of average aggregation number for  $[\text{C}_{10}\text{mim}]\text{Br}$  in aqueous salt solutions have been calculated from the slopes of these linear plots and the CAC values determined by the same technique, and the results are collected in Table 4. As can be seen that the effect of anions of the salts on the aggregation



**Figure 6.** Linear plot of  $\ln(I_0/I)$  for  $5 \times 10^{-7}$  mol/L of pyrene in aqueous  $[C_{10}mim]Br$  solutions in the presence of 0.1 mol/kg  $NaClO_3$  as a function of the benzophenone concentrations.

**TABLE 4: Aggregation Number,  $N_{agg}$ , of  $[C_{10}mim]Br$  in Aqueous Salt Solutions at 298.2 K**

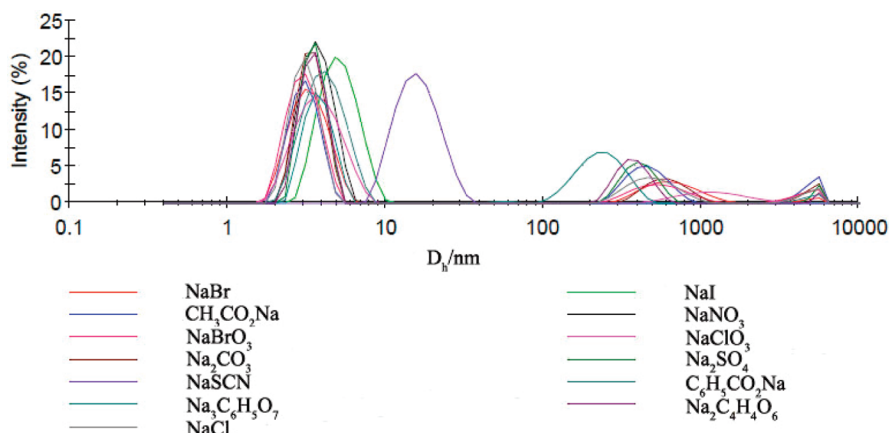
salt	$N_{agg}$				
	0.1/ (mol/kg)	0.2/ (mol/kg)	0.3/ (mol/kg)	0.4/ (mol/kg)	0.5/ (mol/kg)
NaCl	24	27	29	33	36
NaBr	28	30	37	40	47
NaI	43	48	50	53	65
NaNO <sub>3</sub>	38	41	45	47	55
NaClO <sub>3</sub>	48	55	61	63	68
NaBrO <sub>3</sub>	23	26	28	30	33
Na <sub>2</sub> CO <sub>3</sub>	25	28	30	35	38
Na <sub>2</sub> SO <sub>4</sub>	26	29	32	37	41
CH <sub>3</sub> CO <sub>2</sub> Na	20	23	25	28	30
Na <sub>2</sub> C <sub>4</sub> H <sub>4</sub> O <sub>6</sub>	34	36	42	45	50
Na <sub>3</sub> C <sub>6</sub> H <sub>5</sub> O <sub>7</sub>	30	34	40	44	47
C <sub>6</sub> H <sub>5</sub> CO <sub>2</sub> Na	41	45	47	48	60
NaSCN <sup>a</sup>	43	47	52	53	85
AlBr <sub>3</sub> <sup>b</sup>	27				
FeBr <sub>3</sub> <sup>b</sup>	32				

<sup>a</sup> The concentrations of NaSCN were 0.02, 0.04, 0.06, 0.08, and 0.1 mol/kg, respectively. <sup>b</sup> The concentration of AlBr<sub>3</sub> and FeBr<sub>3</sub> was 0.001 mol/kg.

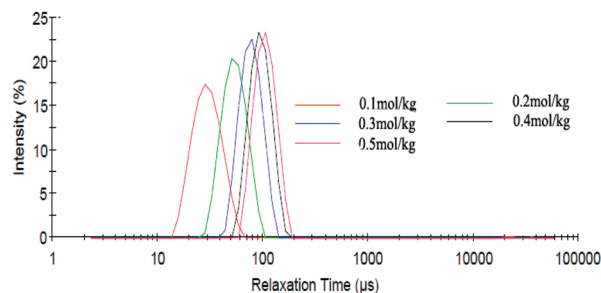
number of  $[C_{10}mim]Br$  in aqueous salt solutions decreases in the following sequence:  $SCN^- > ClO_3^- > I^- > C_6H_5COO^- > NO_3^- > C_4H_4O_6^{2-} > C_6H_5O_7^{3-} > Br^- > SO_4^{2-} > CO_3^{2-} > Cl^-$

$> BrO_3^- > CH_3COO^-$ . This sequence can be predicted by the Hofmeister series. It was also found that the aggregation number increases generally with increasing hydrophobicity of anions of the salts, indicating that the aggregation is favored by the increased hydrophobicity of anions of the added salts. A similar observation was reported earlier for the anions effect on the aggregation of some typical surfactants.<sup>38,39</sup> The trend observed here is basically the same as that observed for  $\beta$  values. This can be understood by the consideration that the higher degree of anion binding on the aggregates surface reduces the repulsive interaction between head groups of the IL, thus promoting the aggregates growth. From these results, it is evident that the nature of anion of the salts decides the change trend of CAC,  $N_{agg}$ , and  $\beta$  values of the IL. In addition, it can be seen from Table 4 that aggregation number of the IL slightly increases with the increase of salt concentration. For instance, in aqueous NaCl solutions, the aggregation number of  $[C_{10}mim]Br$  increases from 24 to 36 in the salt concentration range from 0.1 to 0.5 mol/kg. This is ascribed to the enhanced degree of anion binding on the aggregates surface with the increase of salt concentration.

**Salt Effect on the Aggregate Size of the Ionic Liquid.** For the purpose of convenient comparison, we studied the size of the  $[C_{10}mim]Br$  aggregates at the IL concentration of 0.07 mol/L and different salt concentrations by dynamic light scattering. The result indicated a significant increase in the mean hydrodynamic diameter ( $D_h$ ) of the primary aggregates of the IL from 3 to 18 nm (Figure 7) in the presence of different salts. The effect of anions of the salts on the hydrodynamic diameter of the IL aggregates under the same experimental condition was found to increase in the order:  $SCN^- > I^- > C_6H_5COO^- > ClO_3^- > C_6H_5O_7^{3-} > NO_3^- > C_4H_4O_6^{2-} > Br^- > SO_4^{2-} > CO_3^{2-} > Cl^- > BrO_3^- > CH_3COO^-$ . This sequence suggested that the aggregate size increases with increasing hydrophobicity of anions the added salts. This has been supported by our aggregation number results determined by fluorescence probe. The possible reason is that the anions with stronger hydrophobicity could have stronger ability to bind at the surface of aggregates, thus promoting formation of the IL aggregates. Therefore, more monomers are included in the IL aggregates. The aggregate solutions under study are expected to be polydisperse (see Figure 7) with, in certain cases, a noticeable fraction of very large aggregates. An interesting character is that the aggregates distribution exhibits different dispersity in different aqueous salt solutions (Figure 7). The effect of salts on the aggregate distribution was categorized into three types. The anions  $SCN^-$  and  $I^-$  belonged to class I, in which the IL aggregates are monodisperse and have relatively low polydis-



**Figure 7.** The size distribution for the aggregates of 0.07 mol/L of  $[C_{10}mim]Br$  in 0.1 mol/kg salts aqueous solutions.



**Figure 8.** DLS relaxation time distribution functions at different NaI concentration for 0.07 mol/L  $[C_{10}mim]Br$  solutions.

persity index (about 0.027).  $C_6H_5COO^-$ ,  $ClO_3^-$ ,  $NO_3^-$ , and  $Br^-$  fell in class II, in which two different sizes of the IL aggregates were observed.  $SO_4^{2-}$ ,  $CO_3^{2-}$ ,  $C_6H_5O_7^{3-}$ ,  $C_4H_4O_6^{2-}$ ,  $Cl^-$ , and  $CH_3COO^-$  constitute class III, in which the IL aggregates sizes were polydispersity which have relatively high polydispersity index (0.2–0.4). This result is related to the hydrophobic character of anions of the salts. The class I anions are usually larger in size, poorly hydrated, highly polarized and have strong binding capacity on the aggregates surface. Therefore, they can lead to dense packing of the IL molecules and make the IL aggregate monodisperse. However, the class II and III anions were fully hydrated and weakly bound to the head groups of the IL aggregates, leading to the formation of polydispersity.

Figure 8 shows the relaxation time distributions measured at the scattering angle  $\theta = 90^\circ$  for 0.07 mol/L  $[C_{10}mim]Br$  with increasing concentration of NaI. It can be seen that only one distinguished mode may be presented in the distribution. The mode is due to the collective or mutual translational diffusion of the  $[C_{10}mim]Br$  aggregates.<sup>40</sup> This mode transfers toward longer relaxation times with the increase of salt content, indicating that the aggregates are growing in size. Similar trends were observed for the other systems (not shown).

Figure 9 shows the measured average hydrodynamic diameter of the  $[C_{10}mim]Br$  aggregates as a function of the salt concentrations at a fixed IL concentration of 0.07 mol/kg. It was shown that all the salts have similar effect on the hydrodynamic diameter of the aggregates. The hydrodynamic diameter of the aggregates increases with increasing concentrations of the salts, which was supported by our result of salt concentration dependence of aggregation number of the IL. This

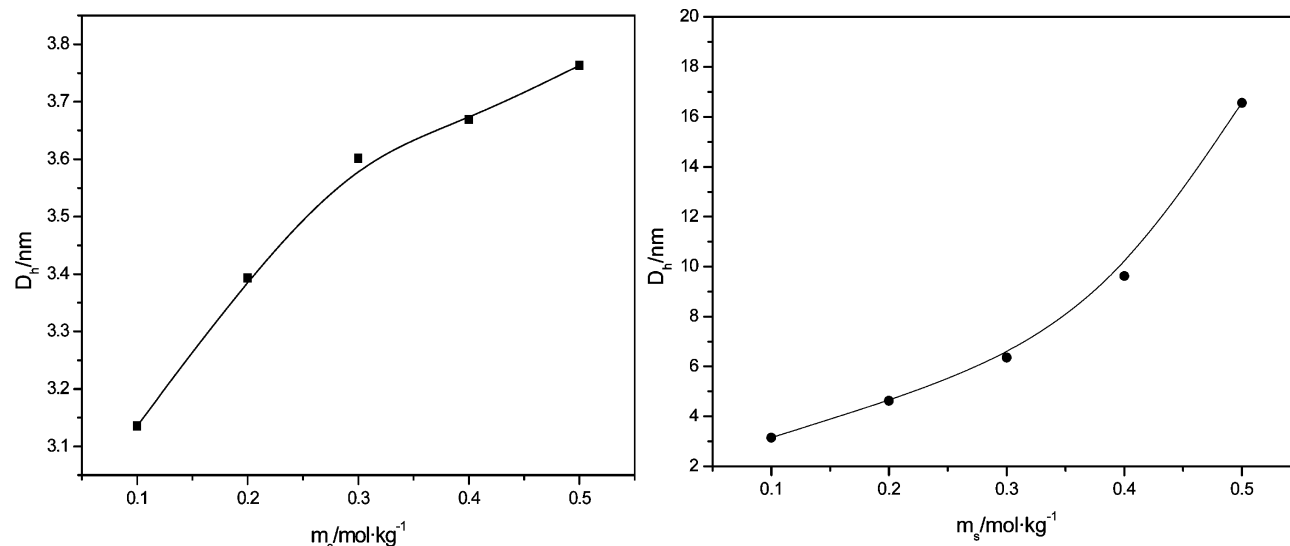
increase in the particle size is mainly due to a decrease of the headgroup repulsions because of the higher electrostatic screening at higher salt concentrations. Like the result of aggregation number of the IL in different salts solutions,  $SCN^-$  anion shows the strongest but  $Cl^-$  anion shows the weakest facilitating effect on the formation of the IL aggregates due to their difference in the hydrophobic character.

## Conclusions

In the present work, the addition of salts was found to have a remarkable influence on the aggregation behavior of  $[C_{10}mim]Br$  in aqueous solutions. The salt-in effect occurs for  $FeBr_3$  and  $AlBr_3$ , while the salt-out effect is observed for the other salts investigated. The effect of anions of the added salts on the CAC value of the IL at a given salt concentration increase in the sequence:  $SCN^- < I^- < C_6H_5COO^- < ClO_3^- < NO_3^-$ ,  $C_4H_4O_6^{2-} < C_6H_5O_7^{3-} < Br^- < SO_4^{2-} < CO_3^{2-} < Cl^- < BrO_3^- < CH_3COO^-$ . This specific effect correlates well with the Hofmeister series of the anions, and can be explained by the hydrophobicity of the anions. For a given salt, the logarithm of CAC values of the IL decrease linearly with increasing concentration of the salt, which can be described by the empirical equation of salt effect for the conventional surfactants.

Effect of the added salts on the degree of anions binding at the aggregates surface, the standard Gibbs energy of aggregation, and the aggregation number of  $[C_{10}mim]Br$  also basically follow the Hofmeister series of the anions. Values in the degree of anion binding and aggregation number of the IL increase with increasing salt concentrations to a different extent for a given salt. It was also found that the aggregates size increases with increasing hydrophobicity of anions of the salts. The results suggest that hydrophobicity of the anions plays an important role in the salt effect on the aggregation of  $[C_{10}mim]Br$  in aqueous solutions. The possible reason is that the stronger hydrophobicity of anions enhances their binding on the aggregate surface and decreases the electrostatic repulsion between the ionic head groups of the IL, thus promoting the IL aggregation, increasing the aggregation number and lowering the CAC value of the ionic liquid.

In conclusion, the aggregation behavior of ILs in aqueous solutions can be regulated by the addition of salts with different hydrophobicity at different concentrations. Therefore, we can control the aggregation degree of ILs by selecting a right salt



**Figure 9.** Effect of salts concentration on the hydrodynamic diameter of the  $[C_{10}mim]Br$  aggregates: ■, NaCl; ●, NaSCN.

at a right concentration for a particular application. It is expected that the above findings may increase the potential applications of ILs.

**Acknowledgment.** This work was partly supported by the National Natural Science Foundation of China (Grant No. 20873036), by the National Basic Research Program of China (973 Program, No. 2009CB219902), and by the Innovation Scientist and Technicians Troop Construction Projects of Henan Province (Grant No. 084200510015).

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