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Aggregation Behavior of 1-Dodecyl-3-methylimidazolium Bromide in Aqueous Solution: Effect of Ionic Liquids with Aromatic Anions

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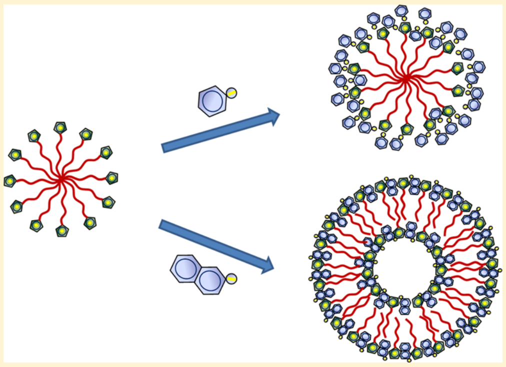
ABSTRACT: The effects of ionic liquids (ILs), 1-butyl-3-methylimidazolium methylsulfonate (bmimMsa), 1-butyl-3-methylimidazolium benzenesulfonate (bmimBsa), and 1-butyl-3-methylimidazolium 2-naphthalenesulfonate (bmimNsa), on the aggregation behavior of 1-dodecyl-3-methylimidazolium bromide (C_{12}mimBr) in aqueous solution were investigated by surface tension, dynamic light scattering measurements, and ^{1}H NMR spectroscopy. The ability to promote the surfactant aggregation is in the order bmimNsa > bmimBsa > bmimMsa. Nevertheless, only bmimNsa distinctly reduces both the CMC value and the surface tension at CMC. Due to the penetration of $C_{10}H_7SO_3^-$ anions into the surfactant aggregate, bmimNsa is found to induce a phase transition from micelles to vesicles, whereas the other ILs only slightly increase the sizes of micelles. The combined effect of intermolecular interactions, such as hydrophobic effect, electrostatic attractions, and $\pi-\pi$ stacking interactions, is supposed to be responsible for this structural transformation, in which $\pi-\pi$ stacking plays an important role.



1. INTRODUCTION

Ionic liquids (ILs) are a class of compounds composed of ions, which generally have melting points below 373 K.[1] They have attracted great attention of both academic and industrial research communities due to their unusual physicochemical properties, such as nonvolatility, nonflammability, high stability, high ionic conductivity, and easy recyclability.[2−5] ILs have been investigated and employed widely in the areas of catalysis, preparation of novel nanomaterials, organic synthesis, electrochemistry, and liquid/liquid extraction.[6] A unique advantage of ILs as solvents compared with traditional solvents is that they can be treated as environmentally benign solvents, since their nonvolatile nature can prevent atmospheric pollution.[7−10] Another distinct character of ILs is that their structures can be designed according to our needs by altering the cations and anions. On the basis of this design, a large variety of ILs with different structures have been synthesized for various applications.[11−15] Among them, 1,3-dialkylimidazolium ILs containing various anions such as BF_4^-, PF_6^-, CH_3COO^-, CF_3COO^-, $CF_3SO_3^-$, and $(CF_3SO_2)_2N^-$ have been extensively studied in the field of colloid and interface science.[16−19]

As is known universally, surfactants can self-assemble into different aggregates in aqueous solution such as micelles, vesicles, and lamellae when the surfactant concentration is above a critical micelle concentration (CMC).[20,21] These aggregates have been extensively investigated not only for their fundamental interest but also for practical applications in many fields such as nanoparticle preparation and organic or bioorganic synthesis.[22−24] The microstructures, shapes, and properties of aggregates in aqueous surfactant solutions mainly depend on the composition and types of surfactant molecules. In addition, the introduction of external additives such as salts, organic additives, and cosurfactants could modify the physicochemical properties of a given aqueous surfactant solution.[25−28] Recently, favorably modifying the physicochemical properties of aqueous surfactant solution by the utilization of ILs has attracted extensive attention. Owing to their particular properties, ILs would play unique roles in altering the properties of aqueous surfactant solution.

The effect of ILs on the aggregation behaviors of surfactants in aqueous solution has been widely studied by many researchers. Pandey et al. have systematically investigated the changes in the aggregation behavior of a series of surfactants with the addition of two 1,3-dialkylimidazolium ILs.[29−35] For example, they have shown the micelle formation of sodium dodecyl sulfate (SDS) in aqueous solution in the presence of $bmimBF_4$. Interestingly, they found that the CMC value of SDS decreases with the addition of low concentrations of $bmimBF_4$, whereas it increases with the addition of high concentrations of $bmimBF_4$. The main reason is that $bmimBF_4$ behaves similar to an electrolyte at low concentrations but as a polar cosolvent at high concentrations. Then, they studied the effect of $bmimPF_6$ on the aqueous solution of a nonionic surfactant Triton X-100, and no significant change in CMC was observed. However, the addition of $bmimBF_4$ to aqueous TX-100 solution results in increased CMC, indicating an overall unfavorable micellization process when $bmimBF_4$ is present. In many cases, addition of the IL does not alter the CMC value to a great extent, but the structure of the micelle is modified to a great extent. The aggregation

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behavior of triblock copolymer Pluornic P104 with addition of the IL 1-butyl-3-methylimidazolium bromide (bmimBr) was studied by Zheng et al. They found that very large aggregates with diameter of around 500 nm are formed at a high concentration of the IL.[36] Moreover, Sarkar et al. carried out a comparative study and established the role of the alkyl chain length of the anion of the added protic ionic liquids dimethylethanol ammonium hexanoate (DAH) and dimethylethanol ammonium formate (DAF) on the physicochemical properties of aqueous solution of a common cationic surfactant cetyltrimethylammonium bromide (CTAB).[37] It can be deduced from previous reports that ILs have significant effects on physicochemical properties of surfactant solution. Though a large number of papers have reported the effect of ILs on the aggregation behavior of surfactant in aqueous solution, most of them have focused on imidazolium ILs containing various inorganic anions; ILs with organic anions especially those with aromatic organic anions have seldom been studied. Addition of ILs with aromatic organic anions to modify physicochemical properties of aqueous surfactant solution is bound to expand the overall applications of aqueous surfactant solution.

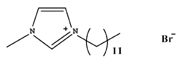
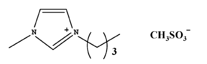
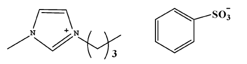
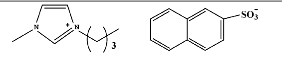
So, in this work, we have concentrated on the modifications in the physicochemical properties of aqueous solution of a cationic surfactant 1-dodecyl-3-methylimidazolium bromide (C_{12}mimBr) upon addition of two imidazolium ILs with aromatic anions, 1-butyl-3-methylimidazolium benzenesulfonate (bmimBsa) and 1-butyl-3-methylimidazolium 2-naphthalenesulfonate (bmimNsa). The effect of 1-butyl-3-methylimidazolium methylsulfonate (bmimMsa) on the aggregation behavior of C_{12}mimBr in aqueous solution was also investigated to make comparisons. The aim of this work seeks to establish the role of phenyl rings of added ILs on the physicochemical properties of aqueous C_{12}mimBr solution. We expect the addition of these ILs could generate intermolecular $\pi-\pi$ stacking between phenyl ring and imidazole headgroup of C_{12}mimBr, and this $\pi-\pi$ stacking interactions may play an important role in tuning the physicochemical properties of the surfactant solution.

2. EXPERIMENTAL SECTION

2.1. Materials. C_{12}mimBr and bmimCl were synthesized in our laboratory according to the method reported previously.[38,39] Methanesulfonic acid sodium salt (98%), benzenesulfonic acid sodium salt (98%), and 2-naphthalenesulfonic acid sodium salt (98%) were purchased from Alfa Aesar. $CDCl_3$ (99.8%) and D_2O (99.96%) were obtained from Sigma-Aldrich. Triply distilled water was used throughout the whole experiment. The ILs used in this study were synthesized in our laboratory, and the purity of the products was ascertained by ^{1}H NMR spectrum.

Synthesis of the Three ILs. Equal molar bmimCl and each sulfonate were mixed in water and stirred at 25 °C overnight. Then, the water was removed through rotary evaporation. The product is separated from the ion byproduct by extraction of the residue with dichloromethane, in which the sodium chloride is insoluble. The obtained ILs

Table 1. Names, Abbreviations, and Molecular Structures of the Cationic Surfactant and Three ILs

Name	Abbreviation	Molecular Structure
1-dodecyl-3-methylimidazolium bromide	C_{12}mimBr	
1-butyl-3-methylimidazolium methylsulfonate	bmimMsa	
1-butyl-3-methylimidazolium benzenesulfonate	bmimBsa	
1-butyl-3-methylimidazolium 2-naphthalenesulfonate	bmimNsa	

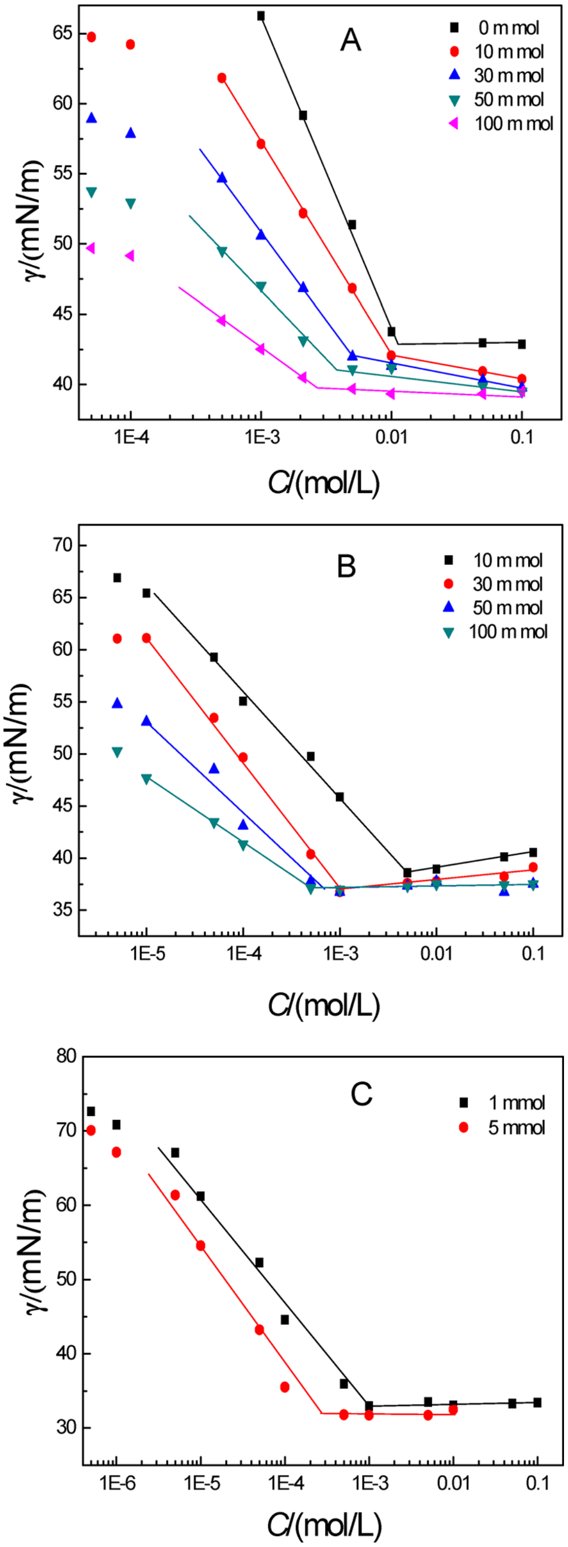


Figure 1. Surface tension curves plotted against the surfactant concentration in the presence of different IL concentrations at 25 °C: (A) bmimMsa, (B) bmimBsa, (C) bmimNsa.

Table 2. CMC and γ_{CMC} Values of Aqueous C_{12}mimBr Solutions in the Presence of Different Amounts of ILs at 25 °C

	bmimMsa					bmimBsa				bmimNsa	
C (mM)	0	10	30	50	100	10	30	50	100	1	5
CMC (mM)	11.21	9.80	5.00	3.29	2.96	4.85	1.00	0.67	0.51	1.00	0.27
γ_{CMC} (mN/m)	42.9	42.1	41.9	41.1	39.4	38.8	37.3	37.3	37.2	33.0	32.0

were then dried under vacuum conditions for 24 h. ^{1}H NMR (400 MHz, $CDCl_3$, δ-ppm) bmimMsa: 0.97 (t, 3H), 1.38 (m, 2H), 1.89 (m, 2H), 2.79 (s, 3H), 4.08 (s, 3H), 4.30 (t, 2H), 7.34 (s, 1H), 7.45 (s, 1H), 10.25 (s, 1H). For bmimBsa: 0.88 (t, 3H), 1.25 (m, 2H), 1.75 (m, 2H), 3.93 (s, 3H), 4.14 (t, 2H), 7.35 (m, 5H), 7.88 (m, 2H), 9.68 (s, 1H). For bmimNsa: 0.89 (t, 3H), 1.30 (m, 2H), 1.81 (m, 2H), 4.04 (s, 3H), 4.22 (t, 2H), 7–8 (m, 8H), 8.42 (s, 1H), 10.07 (s, 1H). The molecular structures of C_{12}mimBr and three ILs are shown in Table 1.

Sample Preparation. Certain amount of IL was dissolved in triply distilled water in a 200 mL volumetric flask. Then, the above IL solution with definite concentration was used to dissolve an appropriate amount of C_{12}mimBr in a 25 mL volumetric flask to obtain mother liquor. Finally, the mother liquor was diluted in turn by the IL solution instead of water. Then, surfactant solutions with different concentrations were prepared while the IL concentration was kept constant.

2.2. Surface Tension Measurements. Surface tension measurements were carried out on a model JYW-200B tensiometer (Chengde Dahua Instrument Co., Ltd., accuracy ±0.1 mN/m) using the ring method. Temperature was controlled at 25 ± 0.1 °C using a thermostatic bath. Each sample was equilibrated for 20 min under the test temperature to reach equilibrium before the measurement.

2.3. ^{1}H NMR Measurements. ^{1}H NMR spectra were run on a Bruker Advance 400 spectrometer equipped with a pulse field gradient module (*Z*-axis) using a 5 mm BBO probe. The instrument was operated at a frequency of 400.13 MHz at 25 ± 0.1 °C. All the samples were dissolved in D_2O, and chemical shifts were referred to the center of the HDO signal (4.700 ppm).

2.4. Dynamic Light Scattering. The micelle size distributions were determined by dynamic light scattering (DLS, DynaPro NanoStar, Wyatt Instrument Co.) with an argon-ion laser operating at 658 nm. All measurements were made at the scattering angle of 90°. The temperature was controlled with a thermostat (F31C, Julabo) with an accuracy of ±0.1 °C.

2.5. Cryogenic-Transmission Electron Microscope (Cryo-TEM). The samples were prepared in a controlled environment vitrification system (CEVS) at 25 °C. A micropipet was used to load 5 μL solutions onto a TEM copper grid, which was blotted with two pieces of filter paper, resulting in the formation of thin films suspended on the mesh holes. After waiting for about 5 s, the samples were quickly plunged into a reservoir of liquid ethane (cooled by the nitrogen) at −165 °C. The vitrified samples were then stored in the liquid nitrogen until they were transferred to a cryogenic sample holder (Gatan 626) and examined with a JEOL JEM-1400 TEM (120 kV) at about −174 °C. The phase contrast was enhanced by underfocus. The images were recorded on a Gatan multiscan CCD and processed with Digital Micrograph.

3. RESULTS AND DISCUSSION

3.1. Effect of ILs on CMC and Surface Properties. Surface tension curves of C_{12}mimBr in aqueous solution at different concentrations of bmimMsa, bmimBsa, and bmimNsa are shown in Figure 1. The surface tension versus concentration plot of pure C_{12}mimBr aqueous solution in the absence of ILs was determined and shown in Figure 1A. The CMC and γ_{CMC} values determined from the surface tension curves are listed in Table 2. The CMC values are plotted against the concentrations of the three ILs in Figure 2A. With the addition of bmimMsa, the CMC value of C_{12}mimBr decreases sharply at first and then decreases much more slowly. This result is mainly caused by the increased ionic strength as the concentration of IL is increased.[40] The enhanced ionic strength can effectively reduce the electrostatic repulsion among the head groups of C_{12}mimBr and then facilitate micelle formation. When the ionic strength is large enough, the electrostatic repulsion between the intermolecular headgroups may become almost invariable; then, the CMC value become constant.[26]

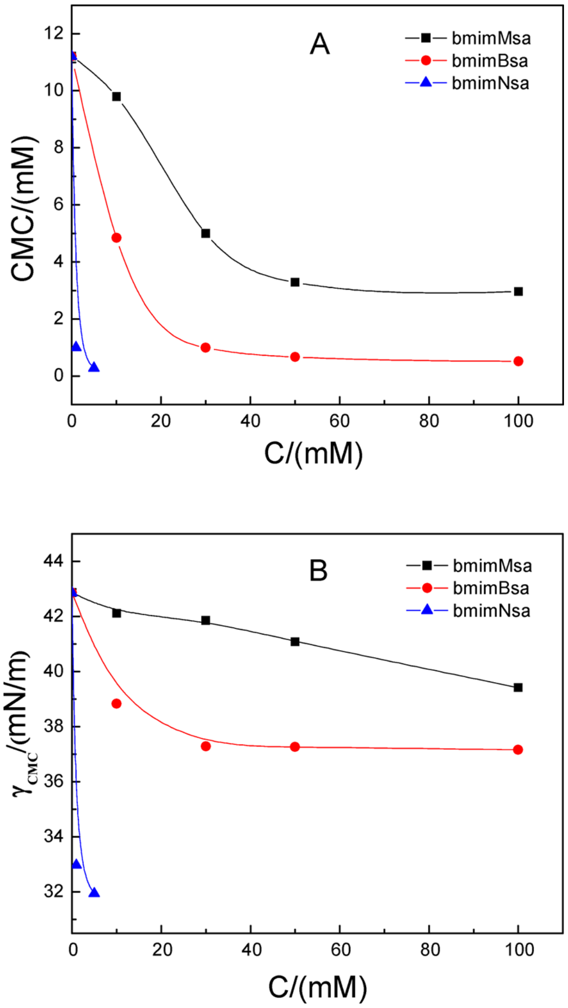


Figure 2. CMC values (A) and γ_{CMC} values (B) plotted against concentrations of different ILs.

The trend in CMC variation for aqueous solution of C_{12}mimBr upon the addition of bmimBsa is similar to that in the presence of bmimMsa. The possible reason for the similar behavior is that the two ILs affect micellization of C_{12}mimBr in the same way, in which the anions of the two ILs adsorbed at the micellar surface. However, the addition of bmimBsa reduces the CMC value of C_{12}mimBr in a higher magnitude compared with bmimMsa. That is, the introduction of benzene ring makes IL more effective to promote the micellization of C_{12}mimBr. The electrostatic repulsion among the head groups of C_{12}mimBr can be significantly reduced due to the electrostatic attraction and the π–π stacking interaction between bmimBsa and the surfactant.[41]

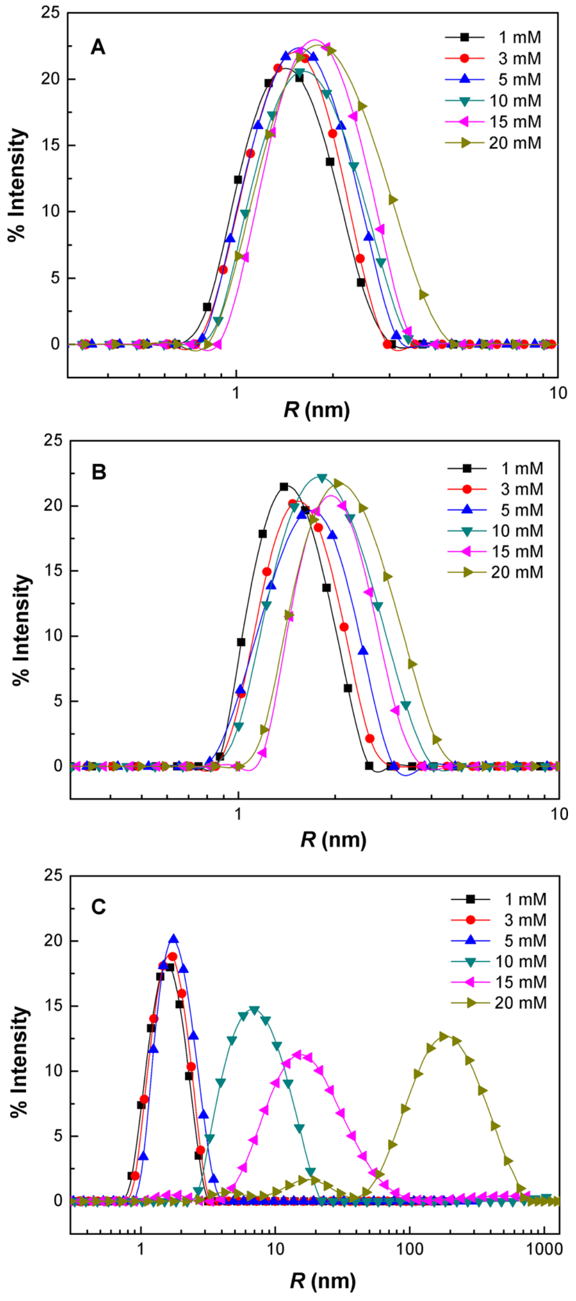


Figure 3. Size distributions of 20 mM C_{12}mimBr at different IL concentrations at 25 °C.

Consequently, the CMC value of C_{12}mimBr in the presence of bmimBsa is much lower than that in the presence of bmimMsa with the same concentration.

With the addition of bmimNsa, even a small amount can effectively reduce the CMC value of C_{12}mimBr. The CMC value reaches 0.27 mM when the bmimNsa concentration is 5 mM, which is much lower than that in the presence of bmimBsa. Thus, the ability of reducing CMC is in the order bmimNsa > bmimBsa > bmimMsa. That is to say, IL with more phenyl rings is more efficient to promote the aggregation of C_{12}mimBr in aqueous solution. It is mainly because the hydrophobicity of the anion is enhanced with increasing numbers of phenyl ring. As a result, IL with more phenyl rings is more likely to penetrate into micelles in aqueous solution and lead to stronger intermolecular interactions. Interestingly, something different appears when the concentration of bmimNsa is increased to 10 mM or even higher. A series of phase changes can be observed as the concentration of C_{12}mimBr varied. For C_{12}mimBr concentrations lower than bmimNsa, white thick precipitates at the bottom are observed, which is a salting-out phenomenon.[42] The equal molar C_{12}mimBr and bmimNsa causes the solution to be translucent and slightly bluish, and this sample contains vesicles as described below. When the concentration of C_{12}mimBr is higher than bmimNsa, the vesicle phase disappears and the solutions become transparent. This unexpected result can be owing to the strong binding of counterions between bmimNsa and C_{12}mimBr which will be discussed in detail below.

To investigate the effect of ILs on the surface activity, the surface tension value at CMC (γ_{CMC}) is plotted against the IL concentration in Figure 2B. It is obvious that bmimMsa and

Table 3. Sizes of Aggregates in Aqueous C_{12}mimBr Solution in the Presence of Different Amounts of ILs

	R (nm)					
ILs	1 mM	3 mM	5 mM	10 mM	15 mM	20 mM
bmimMsa	1.43	1.54	1.59	1.64	1.76	1.80
bmimBsa	1.42	1.55	1.72	1.81	1.96	2.09
bmimNsa	1.60	1.66	1.71	6.96	16.24	192.18

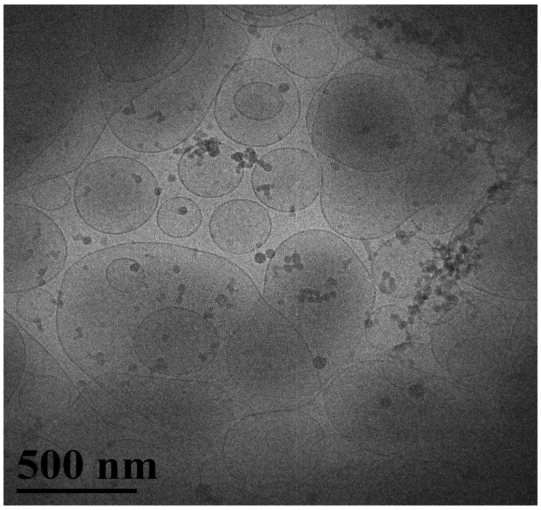
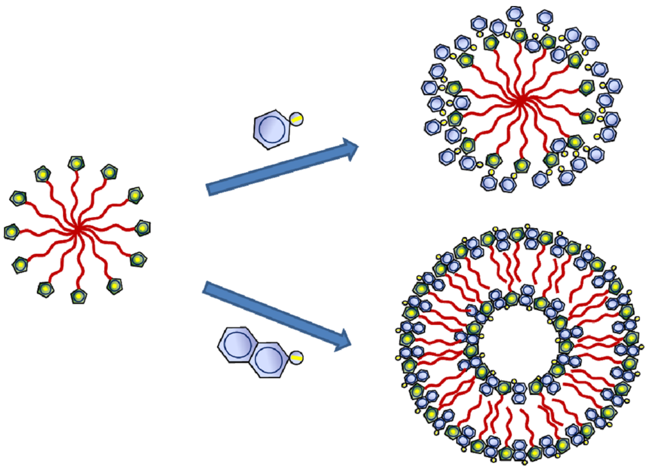


Figure 4. Cryo-TEM image of 20 mM C_{12}mimBr/20 mM bmimNsa.

Scheme 1. Proposed Schematic Illustration of Micellar Change in the Presence of bmimBsa and bmimNsa



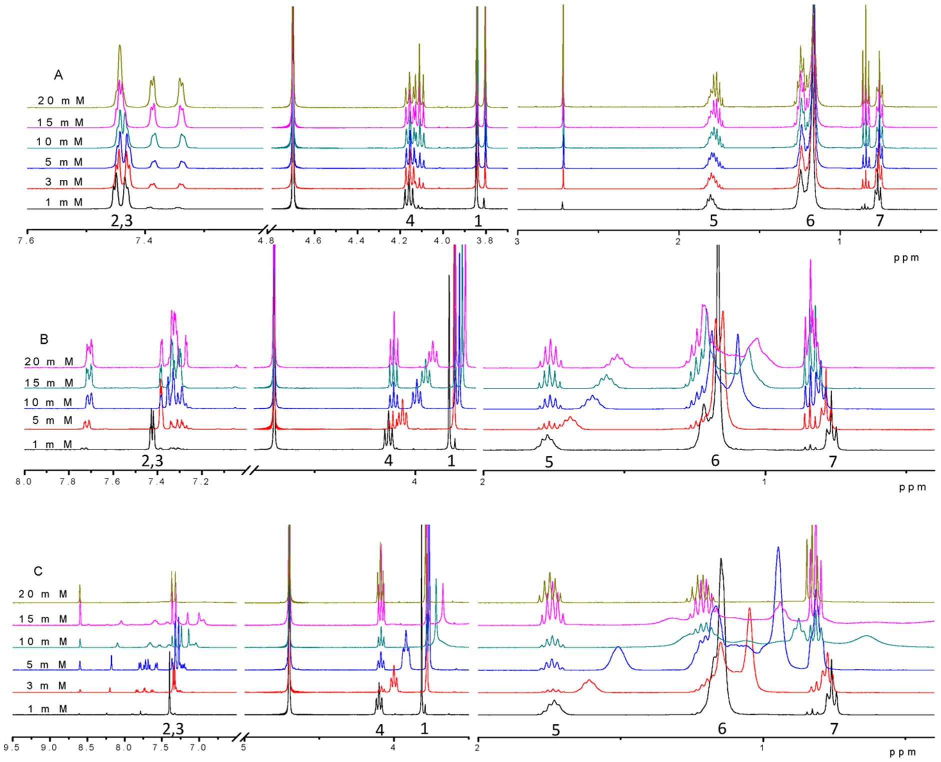


Figure 5. ^{1}H NMR spectra of 20 mM C_{12}mimBr with various concentrations of ILs at 25 °C.

bmimBsa almost do not affect the γ_{CMC} value; however, the addition of bmimNsa can reduce the γ_{CMC} greatly. That is to say, only bmimNsa can distinctly reduce the surface tension of aqueous C_{12}mimBr solution. In addition, the decrease in γ_{CMC} value also indicates that the presence of $C_{10}H_7SO_3^-$ can enhance the close packing of the C_{12}mimBr molecules at air−water interface.[26]

3.2. Effect of ILs on the Sizes of Surfactant Aggregates. Dynamic light scattering (DLS) is utilized to further observe the aggregate size and morphology of the aqueous C_{12}mimBr solution above the CMC value with the addition of ILs. The aggregate size and distribution of 20 mM C_{12}mimBr aqueous solution in the presence of varying amounts of different ILs are shown in Figure 3. The obtained hydrodynamic radii (*R*) of the surfactant aggregates at different IL concentrations are summarized in Table 3. Variations of aggregate size are observed when different IL is added.

With the addition of bmimMsa, the hydrodynamic radii (*R*) of the micelles only increase slightly from 1.4 to 1.8 nm. This result indicates that the anions of bmimMsa only slightly adsorbed at the micellar surface, and most of the anions would stay in the bulk solutions and have no effect on the properties of micelles. When bmimBsa is added, the changing trend in the size of the surfactant aggregate is more significant in comparison with bmimMsa. Also, *R* increases from 1.4 nm to 2.1 nm. It can be known from the above results that both the electrostatic attraction and the $\pi-\pi$ stacking interaction between benzene ring and imidazole ring can significantly decrease the electrostatic repulsion between the head groups of C_{12}mimBr in the micelles. As a result, the packing of the C_{12}mimBr molecules in micelles becomes more dense, and in the mean time the micellar aggregation number increases, which is responsible for micellar growth. It is noted that a drastic increase in the hydrodynamic radii *R* of the aggregates can be observed upon the addition of bmimNsa. Two size distributions at 18.6 and 192.2 nm are seen in the presence of 20 mM bmimNsa shown in Figure 3C. Due to the scattered intensity of vesicle peak being much higher than that of the micelles, the number of vesicles is much greater than that of the micelles. Cryo-TEM was employed to confirm that the large aggregates are vesicles as shown in Figure 4. Unilamellar vesicles with diameters from about 100 to 1000 nm could be clearly observed from the micrograph. Also, this result is in agreement with the DLS data above. It can be concluded that the C_{12}mimBr system experiences a phase transition from micelles to vesicles with the addition of bmimNsa. Except for electrostatic attraction, the introduction of the naphthalene ring greatly enhances the hydrophobic effect of the IL and the $\pi-\pi$ stacking interaction between aromatic groups. Therefore, $C_{10}H_7SO_3^-$ anions may penetrate into surfactant aggregate, which is accounted for the phase transition from micelles to vesicles.

3.3. Effect of ILs on Variation of Proton Chemical Shifts. ^{1}H NMR technique was applied to reveal the intermolecular interaction in the IL−C_{12}mimBr aqueous solution. The hydrogen atoms on various carbons of the surfactant molecular are labeled as shown in Scheme 1. ^{1}H NMR spectra of C_{12}mimBr at different concentrations of ILs are shown in Figure 5. The concentration of C_{12}mimBr was chosen to be 20 mM, which is at least twice as large as its CMC values of C_{12}mimBr in all the IL systems. Hence, the protons of the surfactant molecules in the aggregates are mainly reflected by the observed chemical shifts. Figure 6 shows the changes in the chemical shift of protons for C_{12}mimBr as a function of IL concentration in different IL aqueous solution. The chemical shift variations of the C_{12}mimBr molecules in the ^{1}H NMR spectra are different for various ILs.

BmimMsa does not generate remarkable changes of the chemical shift of protons of C_{12}mimBr, indicating that the surfactant aggregates do not have any obvious variations upon the addition of

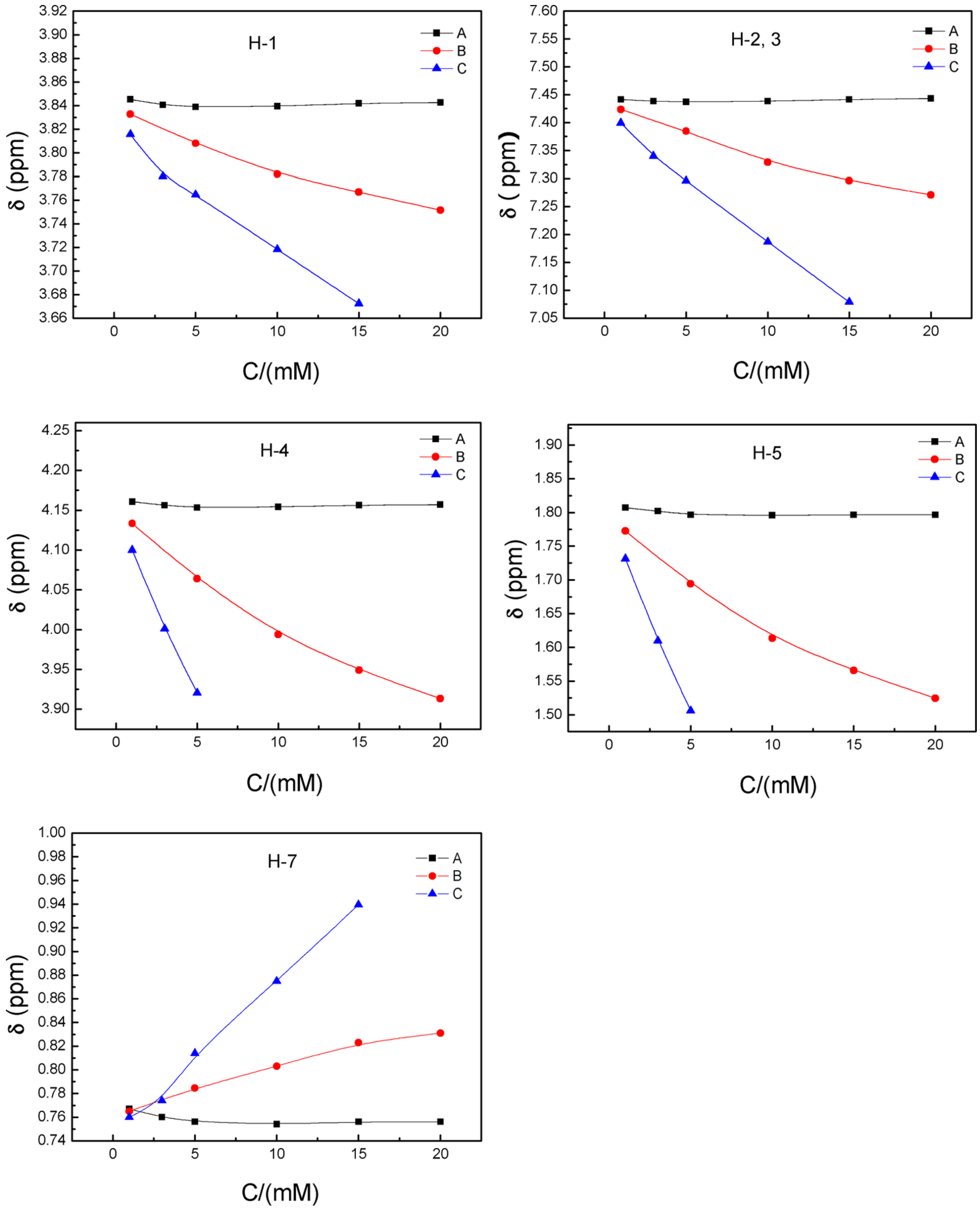


Figure 6. Chemical shifts of protons of C_{12}mimBr against different IL concentrations.

bmimMsa. This result is in good agreement with the conclusion above that the anions of bmimMsa only slightly adsorbed at the micellar surface. However, in the case of bmimBsa, the movement of chemical shift is more significant than that in the presence of bmimMsa, revealing that the interaction between bmimBsa and C_{12}mimBr is much stronger. As can be seen from Figure 6, the chemical shifts of protons around the headgroup (H_1−H_5) move upfield, whereas the protons in the alkyl chain (H_7) show a downfield shift. This is mainly because the addition of bmimBsa generates intermolecular π−π stacking between phenyl and imidazolium ring, and the resulting circular current makes the protons around the headgroup resonate at a higher field due to the shielding effect.[43] Nevertheless, the chemical shift of H_7 moves downfield because the shielding effect is feeble due to the relatively far distance to imidazolium ring.

With the addition of bmimNsa, the chemical shifts of the protons near the headgroup of C_{12}mimBr show an upfield shift with much higher magnitude than those with the other ILs. Meanwhile, the chemical shifts of the protons in the alkyl chain (H_7) move downfield more significantly. The reason for this phenomenon is expected to be similar to that in the presence of bmimBsa. A main difference is that the π−π stacking interaction of aromatic anions with imidazolium ring is stronger due to the introduction of more phenyl rings, which is accounted for the dramatic movements. In particular, all the peaks of protons of C_{12}mimBr gradually become broadened when the bmimNsa concentration reaches 10 mM. Both the peaks of C_{12}mimBr and some peaks of naphthalene sulfonate suddenly disappear when the concentration of bmimNsa increases to 20 mM. This unexpected result indicates that the interaction mode between bmimNsa and C_{12}mimBr has varied. The anions of bmimNsa may strongly bind to C_{12}mimBr headgroup with the aromatic ring penetrating into the hydrophobic cores of the surfactant aggregates which causes the phase transition from micelles to vesicles. The probable reason of the peak broadening and disappearance is that the motion of the molecules is highly restricted in the vesicle phase.[44,45]

3.4. Mechanism of IL Effect on C_{12}mimBr Aggregation. It can be found from the above results that the counterion aromaticity of ILs plays an important role in the aggregation behavior of C_{12}mimBr. For bmimMsa without any phenyl rings, the main interaction is the adsorption of $CH_3SO_3^-$ at the electrical double layer to reduce the electrostatic interaction among the surfactant headgroups, and then the surfactant aggregation is facilitated.

As for bmimBsa, the interaction mode is similar as that in the presence of bmimMsa. The proposed schematic illustration of $C_6H_5SO_3^-$ at the water−micelle interface is shown in Scheme 1. The anions of bmimBsa are first adsorbed at micellar surface in the aqueous solution. Also, the introduction of benzene ring may endow an additional $\pi-\pi$ stacking interaction between $C_6H_5SO_3^-$ and C_{12}mimBr. Both the $\pi-\pi$ stacking interaction and electrostatic attraction can contribute to synergic effect between the surfactant and bmimBsa. Owing to this relatively strong intermolecular interaction, electrostatic repulsion between surfactant headgroups can be screened, and the micellization of C_{12}mimBr is further promoted.

Interestingly, bmimNsa affects the aggregation of the surfactant in different way. Compared with the other two ILs, bmimNsa reduces the CMC of the surfactant much more significantly and induces the micelle-to-vesicle transition. Critical packing parameter (P) is usually employed to explain the phase transition as raised by Israelachvili.[46] P is defined as $P = v/al$, where v is the effective hydrophobic chain volume, a is the effective headgroup area of the surfactant molecules, and l is the surfactant alkyl chain length. Surfactants with P below $^1/_3$ tend to form spherical micelles, while P values between $^1/_3$ and $^1/_2$ prefer to form cylindrical aggregates and P values between $^1/_2$ and 1 prefer to form bilayers. Surfactants with even higher values of P ($P > 1$) favor the formation of reverse structures. It is obvious that $C_{10}H_7SO_3^-$ plays an essential role in the transition process of surfactant solution, which can be attributed to the strong intermolecular interactions between bmimNsa and C_{12}mimBr. The introduction of naphthalene ring can greatly enhance hydrophobicity of the anion and the $\pi-\pi$ stacking interaction between aromatic groups which are accounted for by the penetration of $C_{10}H_7SO_3^-$ anions into the surfactant aggregates with the naphthalene ring located in the hydrophobic microdomain. Benefitting from this penetration, the electrostatic repulsion between surfactant headgroups can be significantly screened. As a consequence, the mean area of surfactant headgroups at the interface of the hydrophobic core in hydrophilic media is decreased, which ultimately increases the molecular packing parameter and induces the transformation from micelles to vesicles. Scheme 1 shows the proposed schematic illustration of the transition from micelles to vesicles.

4. CONCLUSIONS

The anion of IL with more phenyl rings is more efficient to promote the aggregation of C_{12}mimBr in aqueous solution due to the hydrophobic and the $\pi-\pi$ stacking interactions, and the ability to promote the surfactant aggregation is in the order bmimNsa > bmimBsa > bmimMsa. Moreover, the addition of bmimNsa induces a micelle-to-vesicle transition, whereas the other two ILs only slightly increase the micelle sizes. Due to the introduction of naphthalene ring, the hydrophobic effect of $C_{10}H_7SO_3^-$ and the $\pi-\pi$ stacking interaction between aromatic groups can be significantly increased, and this strong intermolecular interaction is accounted for by the penetration of $C_{10}H_7SO_3^-$ into the surfactant aggregates with the naphthalene ring located in the hydrophobic microdomain. As a consequence, the structural transformation from micelles to vesicles occurred. This work is helpful to understand the IL effects on the aggregation behavior of surfactant in aqueous solution and suggests that introducing an aromatic group in ILs can effectively adjust the structure of the surfactant aggregates.

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The authors declare no competing financial interest.

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