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Self-Assembled CTAB Nanostructures in Aqueous/Ionic Liquid Systems: Effects of Hydrogen Bonding

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S Supporting Information

ABSTRACT: Aggregation behavior of a conventional cationic surfactant, *n*-hexadecyl-trimethylammonium bromide (CTAB), in three imidazolium-based ionic liquids, *N*-butyl imidazolium chloride (*N*-BImCl), 1-butyl-3-methyl imidazolium chloride (BMImCl) and 1-hexyl-3-methyl imidazolium bromide (HmImBr)/water systems was investigated by tensiometry, fluorescence, ¹H NMR spectroscopy and dynamic light scattering (DLS). Different physicochemical properties such as the critical micelle concentration (CMC), interfacial properties, aggregate size, and polydispersity were determined. Just like in aqueous medium, micelles formed and CMC values were found to be larger in ionic aqueous/liquids (IL) than in water. The results revealed that the surface activity is much lower in aqueous/IL than in water. The types of anion and alkyl substitutions on the imidazolium ring were shown to be affecting the aggregation behavior. The variation of chemical shifts in the presence of surfactant revealed that the hydrogen bonding is an important factor in defining the solvent properties of ionic liquids since the structure of their hydrogen bond network which depends on their molecular structure has a prominent influence on solubility and the CMC of surfactants. It is demonstrated that HmImBr can be incorporated in CTAB micelles and form mixed micelles, but *N*-BImCl behaves partly as a solvent toward alerting the physicochemical properties of CTAB.

1. INTRODUCTION

Ionic liquids (ILs) are a class of organic compounds with melting points below 100 °C.¹ Their impressive properties such as the ability to dissolve many organic and inorganic compounds, low volatility, nonflammability, and electrochemical and thermal stability have made them very useful green solvents for chemical synthesis and separation.^{2–6} They also can be used as catalysts^{7,8} and electrolytes for batteries, and solar and fuel cells.^{9–11} Their amphiphilic characteristic has recently attracted interest in the investigation of their self-assembly process in water¹² or their effect as additives on self-assembly of amphiphiles in aqueous medium.^{13,14} Moreover, the self-assembly of other amphiphiles like surfactants, lipids, and block copolymers in ionic liquid solvents have been studied widely.¹⁵ Evans et al. investigated the aggregation behavior of alkyltrimethylammonium bromide (C_nTAB), alkylpyridinium bromide (C_nPB), and nonionic Triton X-100 in ethylammonium nitrate (EAN).^{16,17} It was found that the CMC values in EAN are about 5–10 times larger than those obtained in water. The study of aggregation of 1-hexadecyl-3-methylimidazolium chloride (C₁₆MImCl) and 1-hexadecyl-3-methylimidazolium tetrafluoroborate (C₁₆MImBF₄) in EAN showed that the IL/IL mixtures are stable at temperatures up to 250 °C.¹⁸ Zheng et al. investigated the aggregation behavior and micelle formation mechanism of C_nMImBr (*n* = 12, 14, 16) in BMImBF₄ and EAN by surface tension and ¹H NMR.¹⁹ In addition, Zheng's groups studied the micellization of 1-(2,4,6-trimethylphenyl)-3-alkylimidazolium bromide (C_nPIImBr) (*n* = 10, 12, 14) in 1-butyl-3-methylimidazolium tetrafluoroborate (BMImBF₄)²⁰ and *N*-alkyl-*N*-methylpyrrolidinium bromide (C_nMPBr, *n* = 12, 14, and 16) in EAN.²¹ Their results demonstrated that CMC value for C_nMPBr in BMImBF₄ is much higher than that of water due to the weak solvophobic

effect in IL. Thermodynamic analysis revealed that the micelle formation process was enthalpy-driven in the investigated temperature range.

The physical and chemical properties of ionic liquids are highly dependent on their molecular structure.²² For example, in imidazolium-type ionic liquids, the position and length of alkyl chains or type of the inorganic anion affect their CMC value and ability to form hydrogen bonding, and subsequently, their physical and chemical properties.²³ Thus, the investigation of their interactions in a molecular level with various solutes is of great importance to develop new applications. Some common techniques such as NMR,²⁴ tensiometry,¹⁹ conductometry,²⁵ light scattering,¹⁷ and fluorescence spectroscopy²⁶ have been used for this purpose.

Among the various types of ILs, imidazolium-based ILs have been studied more than the others because of their widespread industrial use. Their tendency to form a three-dimensional hydrogen bond network^{27,28} makes them an interesting medium to study the dissolution process of various solutes. Regarding the growing industrial application of surfactants, it is very interesting to investigate the molecular interaction between these substances and ILs.

In this study, the aggregation behavior of a cationic surfactant, *n*-hexadecyl-trimethylammonium bromide (CTAB), in three imidazolium based ionic liquids, *N*-butyl imidazolium chloride (*N*-BImCl), 1-butyl-3-methyl imidazolium chloride (BMImCl) and 1-hexyl-3-methyl imidazolium bromide (HmImBr)/water systems, which differ in alkyl substitution

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and anion, was investigated using tensiometry, dynamic light scattering (DLS), ^1H NMR, and fluorescence spectroscopy. Comparing the aggregation behavior in different IL/water systems, we investigated the effect of anion and alkyl substitutions on the imidazolium ring in micellization of CTAB. We expect that the present study helps to better understand the aggregation mechanism of cationic surfactants in aqueous/IL systems.

2. MATERIALS AND METHODS

2.1. Materials and Sample Preparation. *N*-hexadecyltrimethylammonium bromide (CTAB), 1-bromobutane, 1-bromohexane, 1-methyl imidazole, 1-butylimidazole, and pyrene were purchased from Merck. All three ionic liquids (Figure 1) were synthesized following the processes described

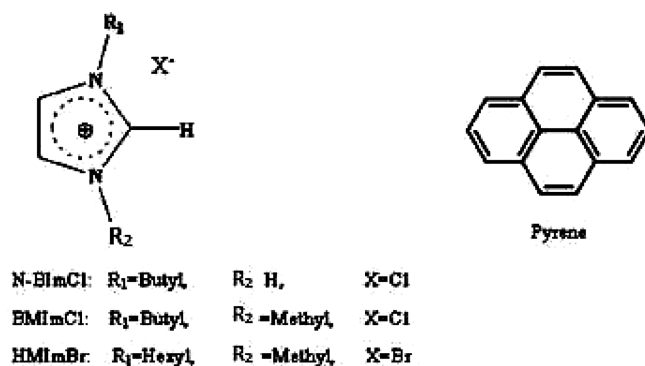


Figure 1. The molecular structure of ILs and pyrene.

in the following sections and identified by ^1H NMR. Pyrene (Figure 1) was purified before use by recrystallization in acetone. Stock solutions of CTAB in aqueous/IL systems were prepared and injected in sample vessels through tensiometric measurements. The water content in all IL solutions was about 17–20 wt %. The saturated water content in ionic liquids is about 17 wt % in the presence of zwitterions.²⁹ The ability to absorb water is expected for imidazolium-based ionic liquids including different alkyl chains as side groups. Water absorption is larger for ionic liquids containing a chloride counterion than for bromide-containing ionic liquids, because the van der Waals volume for a chloride anion is 28 Å,³⁰ whereas for bromide it is 39 Å as determined elsewhere.³¹ This results in a higher charge density for the chloride anion, and it is believed that smaller anions will absorb more water.³⁰ Therefore, the *N*-BMImCl had the highest water uptake values of all the investigated ionic liquids.

Saturated solutions of pyrene in IL/water systems were used to prepare solutions with a desired concentration of CTAB for fluorescence studies. Samples of aqueous/IL systems containing certain concentrations of CTAB were used for ^1H NMR tests. ILs were heated to lower their viscosity through solution preparation. All the experiments were done at 30 ± 0.1 °C.

2.2. Synthesis of Ionic Liquids. **2.2.1. *N*-Butyl Imidazolium Chloride (*N*-BImCl):**³² Hydrochloric acid (0.1 mol) as 37% aqueous solution was added slowly over a period of 30 min to 1-butylimidazole (0.1 mol) at 0 °C under stirring. The reaction mixture was stirred for an additional period of 2 h at the same temperature. Water was removed from the reaction mixture by subjecting it to evaporation for 4 h at 80 °C under reduced pressure (10 mmHg) to give the product (*N*-BImCl) as viscous oil. The ^1H NMR spectrum is shown in Figure 4a.

2.2.2. 1-Hexyl-3-methyl Imidazolium Bromide (HMImBr):

³³ For the synthesis, in a 250 mL flask, equipped with a condenser on a magnetic stirrer, 1-methylimidazolium (0.4 mol) and 1-bromohexane (0.5 mol) were mixed. The reaction mixture was stirred at 50 °C for 3 h. 1-Bromohexane was removed by extraction with hexane, ethyl acetate, and diethyl ether. The product was dried in vacuum as a light yellow, viscous liquid. The corresponding ^1H NMR spectrum is shown in Figure 4b.

2.2.3. 1-Butyl-3-methyl Imidazolium Chloride (BMImCl):

³⁴ To a dry round-bottomed flask under nitrogen atmosphere, 40 mL (0.49 mol) of 1-methylimidazole and 51 mL (0.49 mol) of *n*-butylchloride were added. The reaction mixture was stirred at 75–85 °C for 72 h. The resulting pale yellow, viscous liquid was washed with ethyl acetate. The remaining ethyl acetate was removed by drying on a vacuum line overnight to afford 1-butyl-3-methyl imidazolium chloride. ^1H NMR (300 MHz, CDCl_3) δ : 0.80 (t, 3 H, $^3\text{JHH} = 7.3$), 1.23 (m, 2 H), 1.75 (m, 2 H), 3.98 (s, 3 H), 4.19 (t, 2 H, $^3\text{JHH} = 7.4$), 7.46 (s, 1 H), 7.63 (s, 1 H), 9.55 (s, 1 H). ^{13}C NMR (75 MHz, CDCl_3) δ : 13.6, 19.6, 32.3, 36.6, 49.8, 122.3, 124.0, 137.8.

2.3. Apparatus. Surface tension measurements were made with KRÜSS K12 tensiometer, employing the Du-Nöuy ring method under atmospheric pressure. First, the glass container was rinsed sequentially until the surface tension of distilled water was measured to get 70–72 mN/m. The platinum ring was thoroughly cleaned by acetone and distilled water and flamed until glowing temperature before each measurement. In all cases, more than three successive measurements were carried out, and the standard deviation did not exceed 0.05 mN/m. The uncertainty of the measurements was ± 0.1 mN/m. Fluorescence spectra were recorded on a Shimadzu RF500 spectrofluorometer using 1 cm² path length quartz cuvettes and the I_1/I_3 ratio for pyrene's vibrational peaks were obtained. ^1H NMR spectra were acquired on a Bruker DRX 500 Avance NMR spectrometer. Nano (Malvern, MRK825-02, UK) was used for DLS measurements. The viscosities of the surfactant solutions were measured using semimicro-Cannon Ubbelohde capillary viscometers immersed in a water bath of temperature 30 ± 0.1 °C. The time for a surfactant solution to flow through the capillary was measured with an accuracy of ± 0.01 s. The viscosity of each sample was measured at least five times. Standard deviation in these measurements was less than 1.5% and relative standard deviation or coefficient of variation was less than 0.5.

3. RESULTS AND DISCUSSION

3.1. Determination of CMC Values. Surface tension measurements were performed to investigate the surface activities of CTAB at water and aqueous/IL systems. Surface tension of aqueous/IL systems is lower than that of water because of their hydrophobe alkyl substitution, as it is obvious from Figure 2. The CMC value of CTAB in water was measured 1.0 mM which is consistent with previous reports.³⁵ Surface tension reduction by the addition of CTAB to ILs shows the tendency of surfactant molecules to the solution surface albeit the more nonpolar nature of aqueous/IL systems compared to water. The observed break points for CTAB/water/IL systems (at 4.6 mM in *N*-BImCl and 6.1 mM in BMImCl) can also be considered as surfactant CMCs since the formation of micelles have been reported for similar systems, previously.³⁶ These values confirm the findings of Evans who claimed the CMC of surfactants are 5–10 times higher in ILs than in water.¹⁶ Another break point appeared for the CTAB/

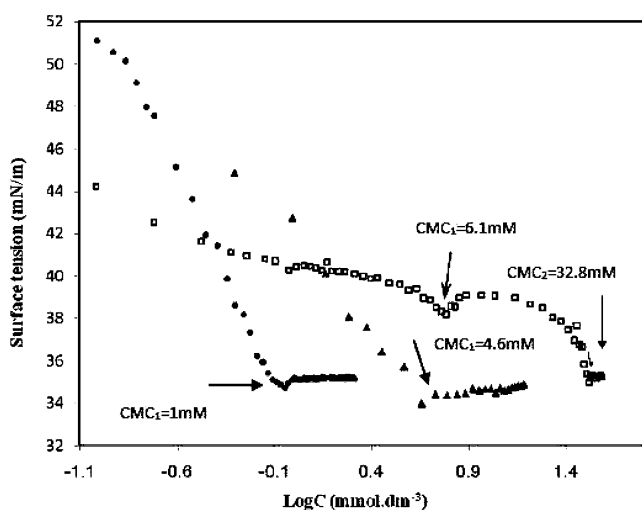


Figure 2. Tensiometry plots for CTAB in water (●); N-BImCl/water (▲); and BMImCl/water (□) mixtures at 30 °C.

BMImCl/water system at $CMC_2 = 32.8$ mM and is probably related to a micellar phase change. The first CMC corresponds to the formation of small spherical micellar aggregates by the association of surfactant monomers at a critical concentration, whereas the second state of aggregation represented by the second CMC is due to structural transformations at surfactant concentrations well above the first CMC. It is insisted that the structure changes in the bulk solution accompany the change of the interfacial tensions at the aqueous solution–air systems.³⁷ The presence of a second CMC was suggested for polyoxyethylene(20) sorbitan monolaurate (Tween 20) in 1-butyl-3-methyl imidazolium tetrafluoroborate (BMImBF₄) and hexafluorophosphate (BMImPF₆).³⁸ It was demonstrated that the aggregates formed at CMC_1 are nanodroplets of Tween 20 segregated from the solution phase, while those formed at

CMC_2 are similar to the usual surfactant micelles formed in aqueous. Moreover, such micellar transitions for cationic surfactant systems in aqueous solutions have been reported by our group^{39–41} and other researchers.^{42,43} A longer alkyl chain of HMImBr makes its surface tension even lower so that its change with surfactant concentration is not noticeable enough to determine the CMCs. Thus, fluorescence spectroscopy was applied to investigate the aggregation behavior of CTAB in HMImBr/water.

The intensity ratio of first to third vibrational peaks of pyrene (I_1/I_3) is highly dependent on the polarity of its medium (spectrum can be found as Supporting Information) and as the solvent polarity decreases, the I_1/I_3 ratio also decreases.⁴⁴ For example, I_1/I_3 has a value of about 1.8 in water,⁴⁵ about 1.1 in ethanol,⁴⁵ and about 0.6 in hydrocarbon solvents.⁴⁵ This characteristic of pyrene makes it a suitable probe to determine the CMC of surfactants in various solvents since the microenvironment polarity of the micellar core generally differs from that of solvents.⁴⁶ Although an initial value of 1.15 for I_1/I_3 tells about the polar medium for pyrene in HMImBr/water (Figure 3), the polarity is still lower compared to water medium because of the alkyl substitution of IL. As the CTAB micelles form at $CMC_1 = 12$ mM, some pyrene molecules, which are completely nonpolar, participate in their hydrophobic core giving rise to a decrease of I_1/I_3 ratio to about 1. Further increase in CTAB concentration causes no change in the I_1/I_3 ratio showing that most of Pyrenes have settled inside the micelles. A ratio value of 1, in this case, shows that the micellar core is not completely nonpolar. This may be caused by the IL molecules existing inside the micellar core under the influence of their chain–chain hydrophobic interactions with alkyl tail of CTAB. As the concentration reaches $CMC_2 = 37$ mM, the I_1/I_3 ratio decreases again to a value about 0.8 which is indicative of a much less polar medium. We propose that this originated from an increase in aggregation number and thereby in nonpolarity

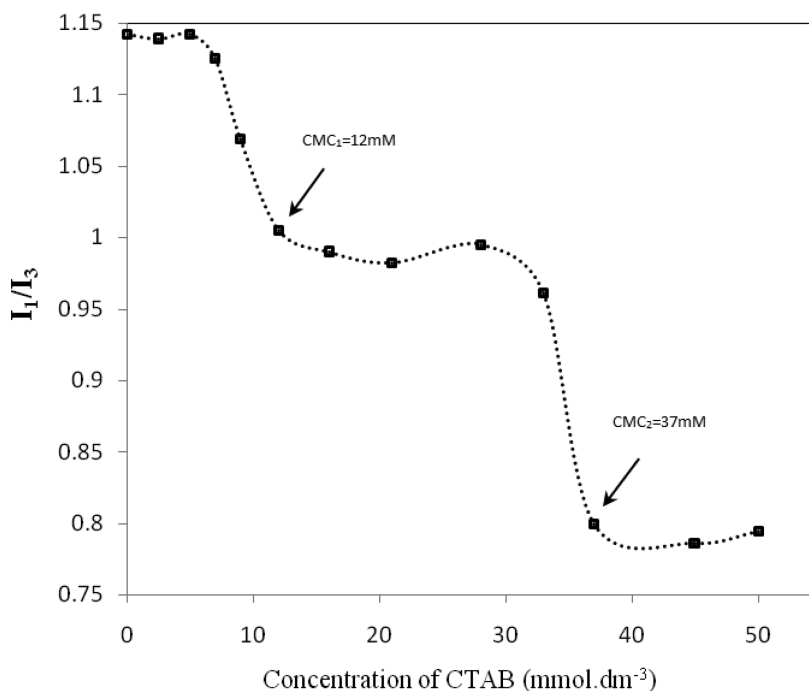


Figure 3. Pyrene I_1/I_3 versus concentration of CTAB in HMImBr/water mixture at 30 °C.

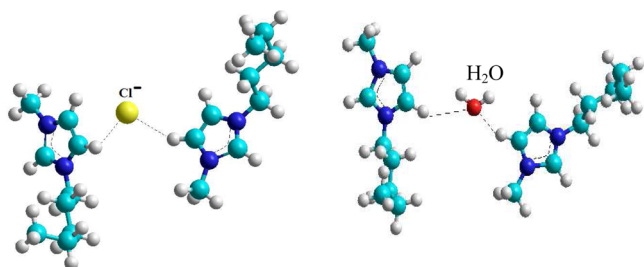
Table 1. Critical Micelle Concentration (CMC), Surface Excess Concentration (Γ_{\max}), Minimum Area (A_{\min}), Surface Tension (γ), Surface Pressure (Π_{CMC}), and Standard Free Energy of Micelle Formation ($\Delta G_{\text{mic}}^{\circ}$) for CTAB in Water and Ionic Liquid/Water Mixtures at 30 °C

solvent	CMC ₁ (mM)	CMC ₂ (mM)	$\Gamma_{\max} \times 10^6$ (mol m ⁻²)	A_{\min} (nm ² /molecule)	γ_0 (mN/m)	γ_{CMC} (mN/m)	π_{CMC} (mN/m)	$\Delta G_{\text{mic}}^{\circ}$ (kJ/mol)
water	1.0 ^a , 1.2 ^b		3.42	0.69	69.11	34.9	34.24	-47.34 ^d
N-BImCl/water	4.6 ^a , 5.0 ^c , 3.9 ^b		1.72	1.67	47.17	34	13.17	-20.55
BMImCl/water	6.1 ^a , 7.2 ^b	32.8 ^a , 32.0 ^b	0.88	5.63	46.14	37.8	9.6	-19.84, -15.66 ^e
HMImBr/water	12.0 ^b , 10.1 ^c	37 ^b			45.28			-15.19, -15.28 ^e

^aTensiometry method. ^bFluorescence method. ^cNMR method. ^dThe α values were taken from literature.⁴¹ ^eThe $\Delta G_{\text{mic}}^{\circ}$ were calculated using CMC₂ values.

of micellar core through a micellar phase change that also occurs for CTAB/BMImCl/water system, as mentioned above.

A comparison of the CMC values (Table 1) reveals that CTAB shows less tendency to aggregate in aqueous/IL systems than in aqueous medium. The nonpolar interaction between alkyl chains of surfactant and ILs increases the solubility and stability, and hence, the CMC of surfactant monomers in ILs. This chain–chain interaction is also responsible for the higher CMC in HMImBr compared to BMImCl which is stronger for the former because of its longer alkyl substitution, hexyl. Besides, hydrogen bonding for CH...Cl⁻ (the C–H group on the imidazolium ring) in comparison with CH...Br⁻ (charge density of Cl⁻ is larger than that of Br⁻) can supply a more rigid hydrogen bond network for BMImCl in which is harder for CTAB molecules to disturb and be dissolved (Scheme 1).

Scheme 1. Schematic Showing the Hydrogen Bonding between Water or Cl⁻ and BMIm⁺

The hydrogen bonding interaction between the C–H group on the imidazolium ring and Cl⁻ anion in BMImCl and 1-ethyl-3-methylimidazolium chloride have been previously reported by Skarmoutsos and et al.,⁴⁷ as was the hydrogen bond formed between H₂O and the CH group on the imidazolium ring. This effect should lead to a decrease in the CMC in ionic liquid–water solutions compared with the pure ionic liquid. The importance of hydrogen bonding gets clearer when the CMC is seen to be larger for CTAB/BMImCl (6.1 mM) than CTAB/N-BImCl system (4.6 mM). The only structural difference between the two ILs is a methyl substitution on the nitrogen atom of the ring (Figure 1). Although the hydrogen atoms of the methyl group have been shown to be capable of forming hydrogen bonds,⁴⁸ the hydrogen atoms on the imidazolium ring are more favorable sites for hydrogen bonding than the methyl C–H groups in pure ionic liquid.²⁸ Thus, the hydrogen bonds of N-BImCl are expected to be stronger than those of BMImCl. This, in turn, originates a less supple hydrogen bond network for N-BImCl which encourages CTAB molecules to aggregate at lower concentrations. Hydrogen bonding can affect the charge distribution on hydrogen atoms; therefore, investigation of the chemical shifts variation through surfactant

addition is a worthwhile approach to gather information at the molecular level about the aggregation process (section 3.3).

The corresponding thermodynamic parameters of micellization have been obtained using the CMC values. According to the mass action or phase separation model, the standard free energy of micelle formation per mole of monomer, $\Delta G_{\text{mic}}^{\circ}$ ionic surfactants in water and ILs are obtained using eq 1, and eq 2, respectively^{20,49}

$$\Delta G_{\text{mic}}^{\circ} = (2 - \alpha)RT \ln X_{\text{CMC}} \quad (1)$$

$$\Delta G_{\text{mic}}^{\circ} = RT \ln X_{\text{CMC}} \quad (2)$$

Where X_{CMC} and α represent the CMC values on the mole fraction scale and degree of counterion dissociation, respectively. α equals 1 because the counterions dissociate very efficiently in ionic liquids, and therefore α is more likely closer to 1 in their systems.⁵⁰ As shown in Table 1, the free energy of micellization is negative and becomes less negative in IL/water systems in comparison with water, indicating that the formation of micelles becomes less spontaneous in IL/water systems due to more solubility in those solvents.

3.2. Interfacial Properties. An effective measure of the adsorption of surfactant in the air–liquid interface is usually obtained by the surface excess concentration, Γ_{\max} , which can be determined by the Gibbs equation for dilute solutions.⁵¹

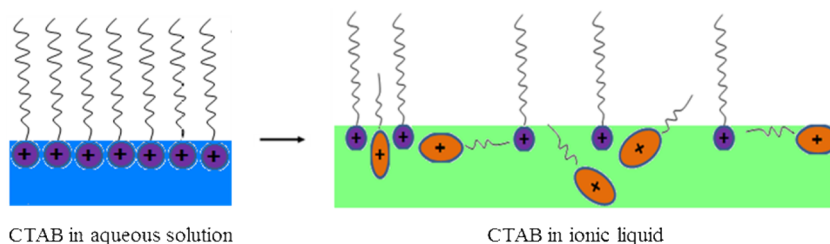
$$\Gamma_{\max} = \frac{-1}{2.303nRT} \left[\frac{d\gamma}{d \log C} \right]_{T,P} \quad (3)$$

Where R and T are gas constant and temperature, respectively, γ is the surface tension, C is the concentration of surfactant, and n is the number of species formed in solution considering the dissociation per monomer. The minimum area per headgroup (A_{\min}) of surfactant molecules at CMC at the saturated interface was obtained by the following equation:⁵¹

$$A_{\min} = \frac{10^{18}}{N_A \Gamma_{\max}} \quad (\text{nm}^2/\text{molecule}) \quad (4)$$

where N_A is Avogadro's number. The Γ_{\max} has been calculated by using curve fitting plot of γ versus $\log C$ to a polynomial equation (PE) of formula $y = ax^2 + bx + C$ and then calculating the slope of the tangent at the CMC.⁵² The R^2 (regression coefficient) value of the fit was between 0.9 and 0.99. According to Figure 2, CTAB produced significantly lower Γ_{\max} values and correspondingly higher A_{\min} values in BMImCl/water and N-BImCl/water than that of water. However, both the limiting surface tensions γ_{cmc} and the pre-cmc portions of the curves differ significantly, with a radical change in the slope resulting in large discrepancies in between the effective areas per molecule A_{\min} .⁵³ This finding is consistent with previous findings,

Scheme 2. Schematic Showing the Effective Area Per Molecule in Water and in Ionic Liquids



showing that the Gibbs equation successfully predicts the value of Γ_{\max} or A_{\min} for CTAB in these solutions. The Γ_{\max} value of CTAB in 1-butyl-3-methylimidazolium tetrafluoroborate, [BMIM][BF₄] has been reported to be $(0.66 \times 10^{-6} \text{ mol/m}^2)$.⁵⁴ This is the expected decrease in the values of Γ_{\max} attributed to several factors such as, (1) the interaction between the IL and the surfactant, and (2) the presence of the IL at the interface.¹⁵ As expected, A_{\min} demonstrates an inverse trend with respect to Γ_{\max} . The A_{\min} values increased in the IL/water system, despite the high ionic strength of the ILs, which could be attributed to a reduction in the bulkiness of the hydrophilic headgroups of ionic surfactant due to the compression of the electrical double layer surrounding the ionic surfactant in ILs compared with water.^{55–57} Furthermore, the low value of A_{\min} in pure water suggests that the air/liquid interface is closely packed and therefore the surfactant molecules at the interface are oriented almost perpendicular to the interface (Scheme 1). The suggested explanation for the high value of A_{\min} in the IL/water systems was justified because the IL was present on the surface (Scheme 2). Hydrogen bonding can affect Γ_{\max} and cause the values of Γ_{\max} to be higher in *N*-BImCl than BMImCl.

The effectiveness of surfactant molecule is measured by the surface pressure at the CMC, Π_{CMC} , which can be obtained from the equation

$$\Pi_{\text{CMC}} = \gamma_0 - \gamma_{\text{CMC}} \quad (5)$$

Here, γ and γ_{CMC} are the surface tension of pure solvent and micellar solution at the CMC, respectively. A priori, an increase in the adsorption of the surfactant should produce a decrease in the surface tension and, therefore, an increase in the surface pressure (Π_{CMC}) (Table 1). However, in this case, the reduction rate in γ_0 is greater than in γ_{CMC} resulting in a decrease of Π_{CMC} , as shown in Table 1. This result indicates that the surface activity of CTAB in IL/water systems is much lower than that in water.

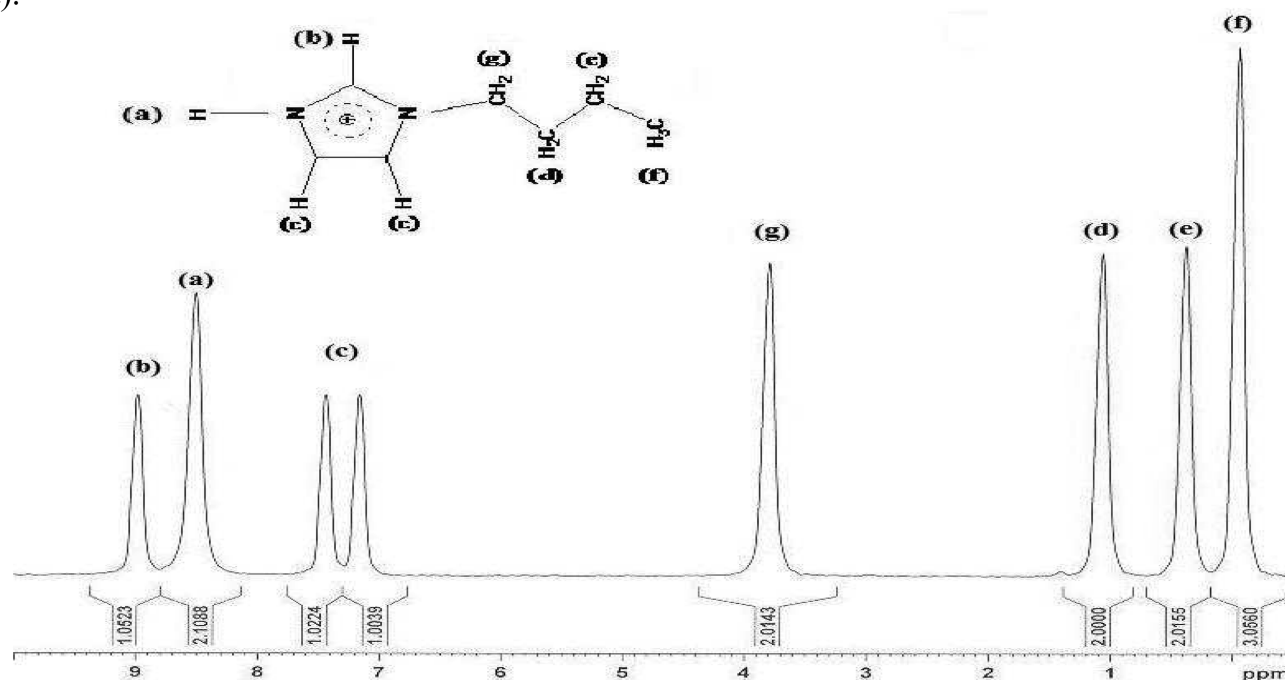
3.3. Characterization of the Effect of ILs' Hydrogen Bonding on Micellization Based on NMR Results. NMR is a useful tool to obtain information about solute–solvent interactions at the molecular level. ¹H NMR measurements were carried out for CTAB in HMImBr/water and *N*-BImCl/water at 30 °C as a function of the surfactant concentration. The spectrum obtained for HMImBr and *N*-BImCl and its peak assignment is shown in Figure 4. When CTAB was added to HMImBr or *N*-BImCl, the chemical shift of the HMIm⁺ or *N*-BIm⁺ protons changed with concentration. Figure 5 shows the plot of the chemical shifts, δ , for different protons in the HMIm⁺ or *N*-BIm⁺ against the surfactant concentration. Since the protons on the imidazolium ring are not so acidic, hydrogen bonding promotes the charge separation on covalent bonds resulting in a shift toward lower magnetic fields. As it is obvious from Figure 5, the chemical shift for the hydrogen atom of *N*-H bond in *N*-BImCl is higher than the chemical shift of methyl

hydrogens in HMImBr. Once again, this confirms that the hydrogen bond in *N*-BImCl is stronger than that of HMImBr. The other three hydrogen atoms on the imidazolium ring have almost the same chemical shifts in both ILs which means there is no significant difference in the strength of their hydrogen bonds in two ILs.

For both ILs, the addition of CTAB causes a shift toward higher magnetic fields (Figure 5). We propose that the entrance of CTAB molecules into the hydrogen bond network of ILs disrupts some of the hydrogen bondings so that the observed mean value of chemical shifts goes toward higher fields. This disruption and the resulting decrease in chemical shifts of H_a , H_b , H_c , and H_f are more obvious for HMImBr than for *N*-BImCl (about 0.7 ppm for HMImBr compared to 0.05 ppm for *N*-BImCl) since its weaker hydrogen bonds are broken more and easier to accept surfactant molecules. This phenomenon is also reflected as a higher CMC value for HMImBr (5 mM for *N*-BImCl and 10 mM for HMImBr) showing its higher solubilization ability for CTAB molecules. On the other hand, the change in chemical shift of the butyl or hexyl protons reflects the interactions between *N*-BIm⁺ or HMIm⁺ and hydrocarbon chain in CTAB, because the butyl or hexyl group would contact the hydrocarbon chain due to solvophobic solvation. By reaching the concentration to the CMC, surfactant monomers aggregate to form micelles. Therefore, IL molecules release CTAB monomers and rearrange their hydrogen bonds giving rise to an increase in chemical shifts. The slope of chemical shift increase is higher for *N*-BImCl showing its higher tendency to reform the hydrogen bond network. For H_a , H_b , H_c , and H_f of HIMm⁺ (the protons attached to the carbon atom of the imidazolium ring, the methyl protons attached to the imidazolium ring, and the protons attached to the hexyl group, respectively), chemical shift remains approximately constant after CMC. This behavior likely corresponded to the presence of HMIm⁺ in micelle and forming mixed micelles with CTAB. At surfactant concentrations greater than CMC₂, the solution contains two types of micelles and there is a dynamic equilibrium between these two types of micelles. This result means that either or both of the following is true: (a) if the exchange rate is fast, then only one peak for each proton of IL will be observed; and/or (b) if the exchange is slow, then in theory, two separate peaks should be observed. In practice it is very likely that the exchange of HIMm⁺ between two types of micelles is fast enough and consequently only one peak for each proton of HIMm⁺ has been observed experimentally. It is likely that the hydrophobic environment of two types of micelles is close to each other, and that the chemical shift remains approximately constant after CMC₁. There is also a good accordance between CMC values obtained by ¹H NMR and two other techniques (Table 1).

3.4. Sizes of the Aggregates. Dynamic light scattering (DLS) was used to obtain the average size of the aggregates

(a).



(b).

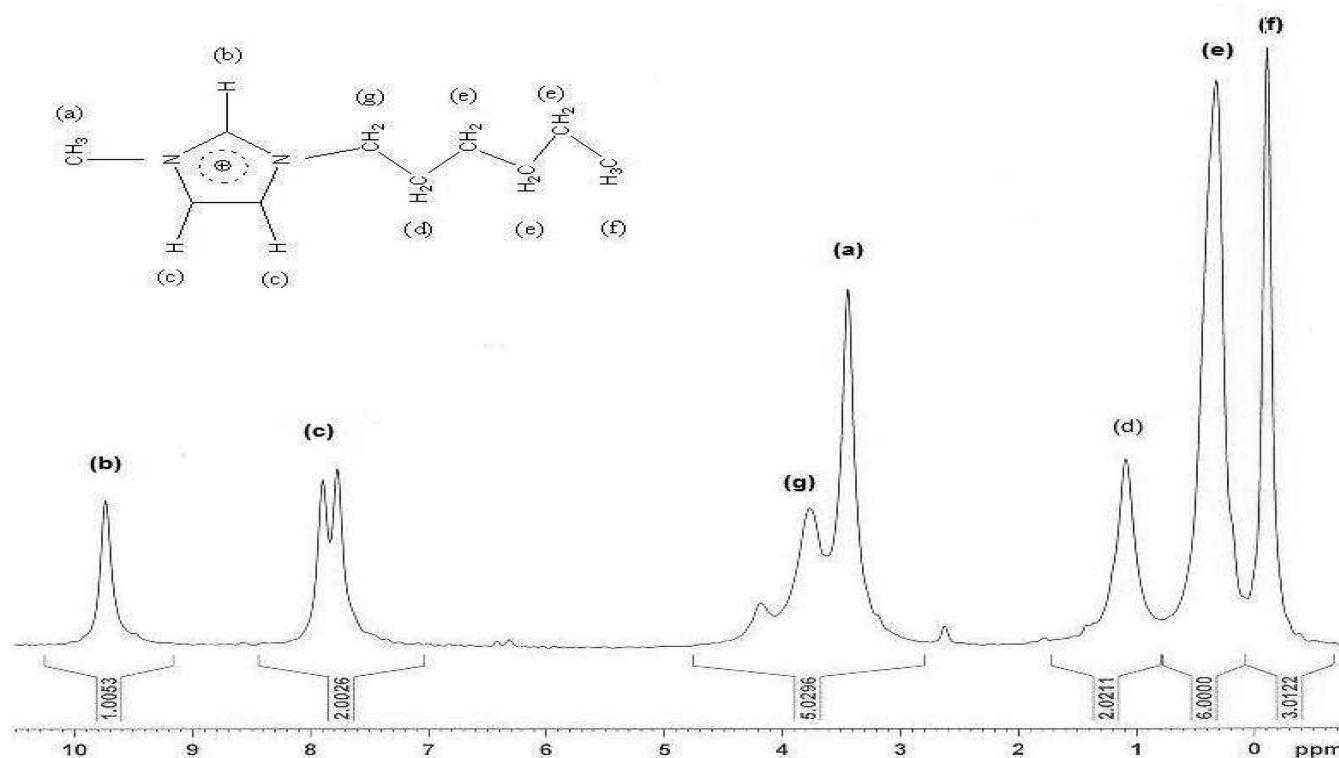


Figure 4. ^1H NMR spectrum for (a) *N*-BImCl and (b) HMImBr.

within CTAB in water and the water/IL system (Figure 6). Monomodal distribution was observed at water, BMImCl/water, and HMImBr/water. Table 2 lists the obtained sizes of the aggregates formed in the examined systems. It is clear from the DLS data that the average aggregate size appears to increase in IL/water systems in comparison with water. The results

showed that CTAB micelles in HMImBr/water, BMImCl/water, and water have an average diameter of 580, 60–100, and 0.72 nm, respectively. It is noteworthy that the obtained size value for CTAB in water is excellent compared with the previous findings.³¹ The size of micelles formed by ($\text{C}_{14}\text{mimBr}$), ($\text{C}_{10}\text{pimBr}$), and ($\text{C}_{14}\text{pimBr}$) in (BMImBF₄)

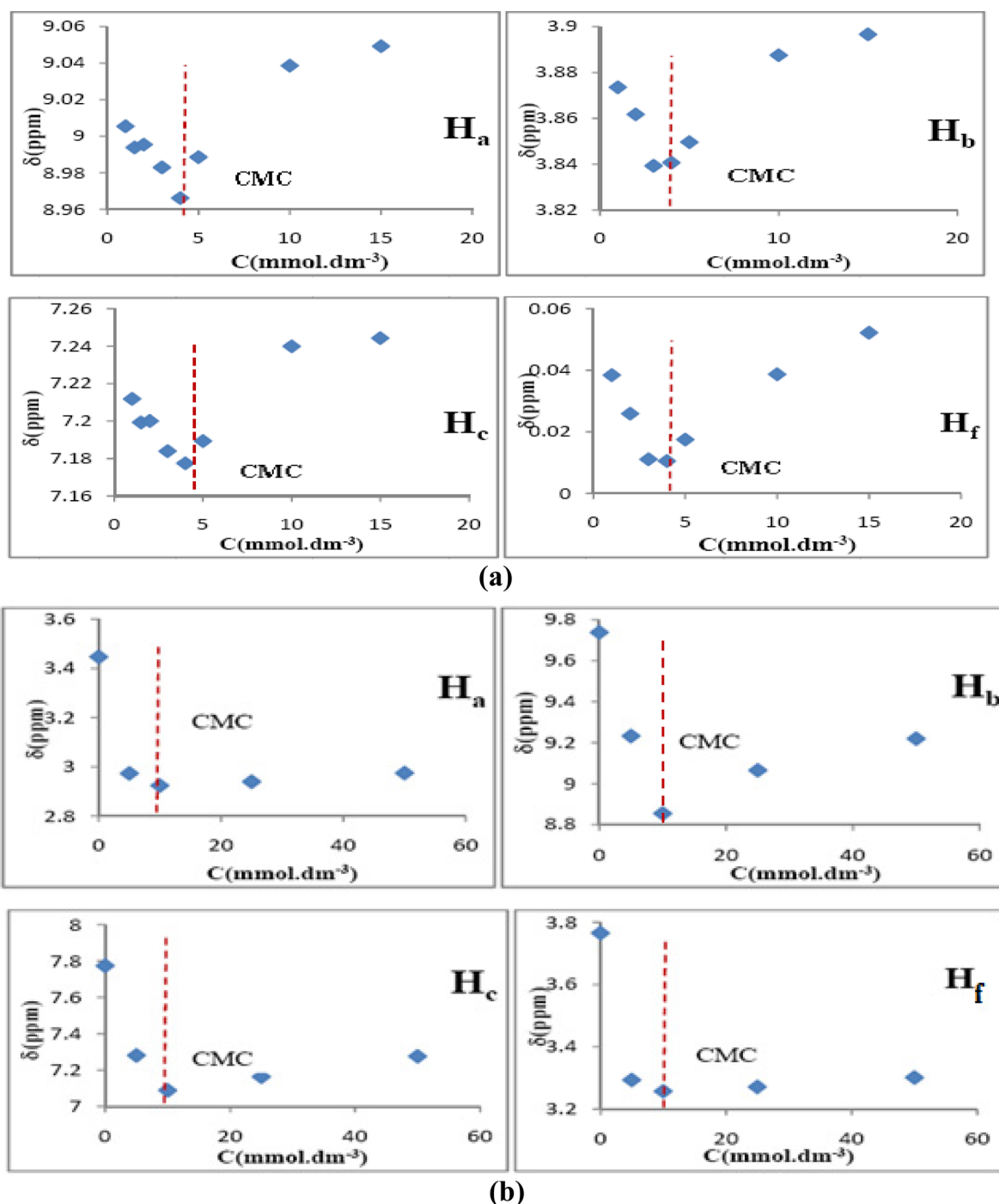


Figure 5. ^1H NMR chemical shifts versus concentration of CTAB in (a) N -BImCl/water and (b) HMIImBr/water mixtures.

was reported to be 76.9,⁵⁸ 21.6, and 45.1 nm,²⁰ respectively. However, the earlier studies demonstrated small aggregates for CTAB formed in EAN.^{17,50} These results confirmed that the interactions involving IL ions and the surfactant are very different for various type of ILs. A more dramatic increase in the aggregate size is observed in HMIImBr/water as compared to BImCl/water. In the case of the HMIImBr/water system, the presence of a hexyl chain on the HMIIm⁺ allows it to align with the tail part of CTAB and form mixed aggregates, whereas, in the case of BImCl, the butyl chain in the BIm⁺ is apparently unable to align with the tail part of CTAB. Therefore, this difference in the alkyl chain of HMIImBr and BImCl is responsible for the different size changes and

different behaviors of the two ILs. The large size of the aggregates observed in CTAB/HMIImBr/water systems indicates that organized structures forms vesicles or worm-like micelles. In addition, polydispersity in the water/IL systems is considerably more than that of water (Table 2).

4. CONCLUSION

We examined the aggregation behavior of CTAB in water and three types of IL/water system: N -BImCl, BImCl, and HMIImBr, analyzing the role of the alkyl chain of solvent. The results demonstrated that in aqueous/IL solutions, the longer the solvent alkyl chain, the less favorable the micellization due

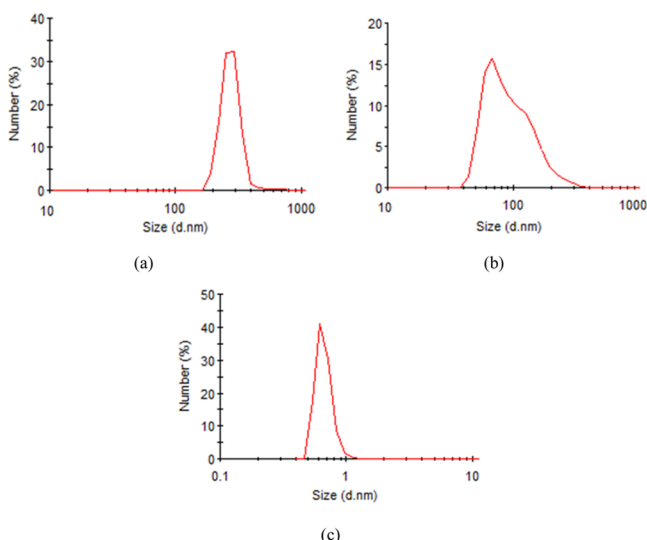


Figure 6. Size distribution of (a) CTAB in HMIImBr/water, (b) CTAB in BMImCl/water, (c) CTAB in water.

Table 2. The Size and Width Obtained for CTAB in Water and Different Ionic Liquids at 30 °C

	water	BMImCl	HMIImBr
size (nm)	0.72	75	280
width (nm)	0.17	85	100
η^a (cp)	1.2	405	242

^aViscosity of solution.

to decrease in solvophobicity; therefore, the greater CMC values were found. Moreover, the micellization of CTAB is more favorable in *N*-BImCl/water than that of BMImCl/water, which suggests the former is more capable of forming hydrogen bonds than the latter. Using DLS technique, we obtained the larger aggregates as the solvophobicity of the solvent decreased. In comparing HMIImBr/water and BMImCl/water, it is acceptable that the HMIIm⁺ ions act as a cosurfactant and incorporate in the micelles and affect such characteristics of the micelle like size and morphology, whereas, *N*-BImCl and BMImCl are not able to incorporate into the micelle, and remain more in the interface. This finding in agreement with previous reports.⁵⁴

We recognize that the difference in the structure of ILs plays an important role in the self-assembly of surfactants. The ability of imidazolium-based ionic liquids to form a hydrogen bond network determine their solvent behavior. The strength of hydrogen bonds, regardless of physical conditions like temperature, concentration, etc., is dependent on molecular structural features. Some factors such as the type of anion, position, and the length of alkyl substitution can determine the strength of hydrogen bonding and this, in turn, defines the nature of solvent–solute interactions. Thus, anything that affects the hydrogen bond network of ionic liquids, also affects both their solvent properties and the solutes' behavior such as aggregation. This can be considered as a key point in the modification of ionic liquids as a solvent for special industrial applications.

■ ASSOCIATED CONTENT

Supporting Information

The fluorescence spectrum of pyrene in HMIImBr/water in the presence of CTAB and pyrene I_1/I_3 versus concentration of

CTAB in water, BMImCl/water, and *N*-BImCl/water. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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Notes

The authors declare no competing financial interest.

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