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Thermodynamic and aggregation properties of aqueous dodecyltrimethylammonium bromide in the presence of hydrophilic ionic liquid 1,2-dimethyl-3-octylimidazolium chloride

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ABSTRACT

The effect of a trisubstituted imidazolium based hydrophilic ionic liquid (IL), 1,2-dimethyl-3-octylimidazolium chloride [odmim][CI] on the thermodynamic and aggregation properties of dodecyltrimethylammonium bromide (DTAB) at temperatures 298.15–318.15 K has been studied by conductivity measurements in aqueous media. From the temperature dependence of critical micelle concentration (cmc), various thermodynamic parameters of micellization viz. standard free energy change (ΔG_m), standard enthalpy change (ΔH_m) and standard entropy change (ΔS_m) have been evaluated. Further fluorescence probe analysis has been utilized to obtain cmc value in order to validate the cmc values obtained from conductivity measurements. The micelles formed just like in aqueous medium and cmc values were found to be changing at different wt% of IL than in water. The cmc value of aqueous DTAB solution decreases until 2.0 wt% of IL in the medium. The properties of auguos DTAB solution change in a different way at higher concentration of IL. The variation in chemical shifts of surfactant protons in the presence of IL revealed that the electrostatic interactions have a prominent influence on the DTAB micellization in IL/water systems. It is shown that the modification in aggregation properties of DTAB is related to the lipophilicity of interacting ions.

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1. Introduction

ILs comprise a class of compounds which is composed of bulky organic cations and appropriate organic or inorganic anions, usually present in molten state below 373 K. These have a wide spectrum of applications in the field of chemical synthesis, separation science, catalysis, electrochemistry and many more [1–4]. The unusual and interesting properties of ILs such as negligible vapour pressure, non-flammability, high thermal and mechanical stability, low toxicity, wide electrochemical window, easy recyclability and excellent capacity to dissolve organic and inorganic solutes makes these the central spot of many research applications [5–9]. The physicochemical properties of ILs can be easily modified by changing the N-alkyl substituents and/or anions [10]. The term "task specific ILs" is used when certain functional groups are introduced in their structure to impart a specific characteristic. Such as the primary amine-functionalized IL shows superior ability for carbon dioxide capture if compared to other conventional ILs [11]. Different types of ILs are also utilized to induce favourable alterations in properties of various surfactant systems.

The self-assembly of surfactant molecules into a large number of aggregate structures is a topic of basic and fundamental research.

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http://dx.doi.org/10.1016/j.molliq.2015.10.042 0167-7322/© 2015 Elsevier B.V. All rights reserved. Surfactants play a significant role in many applications such as nanomaterial synthesis, drug delivery, chemical separations, pharmaceutical formulations and other dispersant technologies [12–15]. The surface and thermodynamic properties of surfactants in different solvent systems are routinely probed by researchers, both in the absence and presence of additives. This helps to understand the various solute–solute and solute–solvent interactions of surfactants in solution of different additives [16]. The related balance of solvophobic and solvophilic interactions governs the aggregation properties of surfactant solution in presence of different additives. These properties can also be modified by variation in temperature and pressure.

Reddy's group first showed the effect of ILs of different chain lengths on the aggregation properties of aqueous sodium dodecyl sulphate (SDS) [17]. Then Pandey et al. highly explored the effect of hydrophilic and hydrophobic ILs on the aggregation behaviour of different surfactants [18–22]. Inoue's group specifically studied the effect of ILs on polyoxyethylene (POE)-type non-ionic surfactants [23–25]. Sarkar and coworkers have studied the effect of a mixture of two different kinds of ILs on the aggregation behaviour of non-ionic surfactant Triton X-100 [26]. Our own group has also studied the effect of different anions of IL on the micellization properties of SDS [27,28]. Most of this work is limited to the use of 1,3-dialkyl substituted imidazolium based ILs. In our previous work, we have effectively demonstrated the effect of using trisubstituted imidazolium based IL, 1-butyl-2,3-dimethylimidazolium chloride, [bdmim][Cl] in altering the micellization properties of SDS [29] and dodecyltrimethylammonium bromide (DTAB) [30] in aqueous media. Therein we have shown the difference in the modulating effect of IL [bdmim][Cl] on surfactant properties when the charge on the head group of surfactant under study is different.

Further it will be interesting to study the effect of change of alkyl chain length of these ILs on a surfactant. Therefore, as extension to our previous work, herein we are reporting the modulations in the aggregation properties of aqueous DTAB (Scheme 1) solutions upon the addition of IL 1,2-dimethyl-3-octylimidazolium chloride [odmim][Cl] (Scheme 1). Conductivity and fluorescence measurements have been used to obtain the cmc value for different surfactant-IL solutions. The thermodynamic parameters have been analysed to understand the driving force of micellization. It was possible to obtain the cmc values from both conductometry and fluoremetry up to 1.0 wt% of added IL, after that cmc determination has been done through fluorescence only. The aggregation number has been determined through a fluorescence quenching method. ¹H NMR measurements have been done to understand the preferential site of interactions between IL and surfactant molecules. Here due to the addition of IL [odmim][Cl], highly unpredictable results have been obtained from our previous investigation on DTAB [30]. The dependency of cmc and other properties of DTAB solution on the alkyl chain of investigated ILs have been observed. The aim of this manuscript is to offer a comparative study and establish the role of the alkyl chain length of the cation of the imidazolium IL on the physicochemical properties of aqueous DTAB solution.

2. Experimental

2.1. Materials

DTAB (99%, AR) was obtained from Acros Organics and 1,2dimethylimidazole (98%) and pyrene (99.9%) were procured from Sigma-Aldrich. Cetylpyridinium chloride (99%) was purchased from Loba Chemie and methanol (99%) from Rankem. Deuterium oxide having isotopic purity (\geq 99.9%) and 1-chlorooctane (>98%) was obtained from SD Fine Chemicals. IL 1,2-dimethyl-3-octylimidazolium chloride [odmim][Cl] used in the present study is synthesized using the same procedure as described in our earlier study [29].

2.2. Synthesis of 1,2-dimethyl-3-octylimidazolium chloride [odmim][Cl]

For the synthesis of 1,2-dimethyl-3-octylimidazolium chloride [odmim][Cl], initially a slight excess of 1-chlorooctane (16.1 g, 108 mmol) was added drop wise to 1,2-dimethylimidazole (10 g, 104 mmol) in a round bottom flask followed by refluxing the solution at about 60–70 °C for 24 h under N₂ atmosphere and then cooled to room temperature for 12 h. The resultant compound was washed with



Scheme 1. Chemical structures of IL 1,2-dimethyl-3-octylimidazolium chloride [odmim][Cl] and cationic surfactant dodecyltrimethylammonium bromide (DTAB).

ether several times to get a solid, which was dried in vacuum to get 1,2-dimethyl-3-octylimidazolium chloride [odmim][Cl], with 85% yield. Karl–Fisher examination of the IL indicated that the water content reduced to less than 280 ppm. The product obtained was flushed with N_2 and stored in a dry place before use.

¹H NMR (400 MHz, CDCl₃, δ-ppm): 0.762(t, 3 H), 1.1745(m, 10 H), 1.696(m, 2 H), 2.476(s, 3 H), 3.659(s, 3 H), 3.997(t, 2 H), 7.206(d, 1 H), 7.235(d, 1 H).

2.3. Experimental procedure

Required amounts of materials were weighed using an A&D Co. Ltd. electronic balance (Japan, model GR-202) with a precision of ± 0.1 mg. All the experiments have been carried out in doubly distilled de-ionized water obtained from a Millipore, Milli-Q Academic water purification system having conductivity $\leq 5 \ \mu$ S cm⁻¹. All experiments were performed in triplicate and obtained values were averaged.

The conductivity measurements were taken with a digital conductivity meter CM-183 microprocessor based EC-TDS analyser having ATC probe and conductivity cell with platinized platinum electrodes purchased from Elico Ltd., India having cell constant 1.0021 cm⁻¹. The cell was calibrated with the standard aqueous potassium chloride solutions in the concentration range of 0.01–1.0 mol kg⁻¹ of known specific conductance. The electrical conductivities were measured at different temperatures with an uncertainty of \pm 0.01 K in a water jacketed flow dilution cell. This instrument works on the power supply of 90–260 V alternating current and at frequency of 50–60 Hz. The surfactant conductance was measured after thoroughly mixing the solution and temperature equilibration. The small conductance due to water was subtracted from the measured data. The uncertainty of the measurements was found to be less than 4%.

The fluorescence spectra were recorded using a Shimadzu (model RF-5301PC) spectrofluorimeter. It is provided with blazed holographic grating excitation and emission monochromators fitted with a 150 W Xenon lamp. Pyrene and cetylpyridinium chloride (CPC) were used as fluorescence probe and quencher, respectively. Stock solution of pyrene and CPC were prepared in methanol and water, respectively. The solution of DTAB and IL/water at various concentrations had been freshly prepared in doubly distilled de-ionized degassed water. After stirring the solutions for 12 h, these solutions were allowed to stabilize for half an hour to record the spectra. The excitation wavelength was kept at 334 nm and the emission was recorded in the wavelength region 350–600 nm. The excitation and emission slits were kept at (3 and 1.5) nm, respectively. The ' I_1/I_{III} ' ratio has been obtained from fluorescence intensities of the first and third vibronic peaks of pyrene for data analysis.

The NMR chemical shifts for various protons were observed with a Brüker Avance III spectrometer operating at 400 MHz. In order to determine chemical shift δ for DTAB + [odmim][Cl] solution in water, deuterium oxide (D₂O) was used as a solvent for all the NMR measurements. The chemical shifts are reported as δ units (ppm). The chemical shift values of peaks of interest were obtained using peak pick facility.

3. Results and discussion

3.1. Conductivity measurements

3.1.1. Effect of IL [odmim][Cl] on the cmc of DTAB

The conductivity, κ , values were obtained as a function of [DTAB] concentration on the addition of different wt% of IL [odmim][Cl] in the solutions at temperature range of 298.15–318.15 K with an interval of 10 K. The conductivity vs concentration plots of DTAB in the absence and presence of different wt% of IL at 298.15 K are shown in Fig. 1. Two linear regimes were observed in the conductivity graph for each studied wt% of IL corresponding to the pre- and post-micellar regions. The x-intersection of these two regions is identified as cmc. The slope



Fig. 1. (a) The conductivity, (κ) of aqueous DTAB solutions in the absence and presence of different wt% of IL [odmim][Cl] at 298.15 K. (b) The κ versus [DTAB] plots at 0 (black symbols) and 0.5 (red symbols) wt% of IL at temperatures (□) 298.15 K, (○) 308.15 K and (△) 318.15 K in aqueous media. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

ratio of post- to pre-micellar region provides the information about degree of dissociation (α) of counter-ions from the micellar surface. We have measured conductivity up to 1.0 wt% of added IL above this wt% it was difficult to draw any meaningful conclusion from conductivity data owing to very high conductivity of IL itself.

The cmc value for aqueous DTAB solution obtained from our data is in good agreement with literature which is 15.7 mmol kg⁻¹ [31]. It can be clearly seen from Fig. 1 that the value of cmc gradually decreases with the addition of IL [odmim][Cl] in the DTAB solution. The higher the wt% of IL in the solution the lower the cmc value observed. The cmc values obtained at different temperatures are reported in Table 1. The IL [odmim][Cl] is constituted of two parts, bulky imidazolium cation, [odmim]⁺ and small anion, [Cl]⁻. The surfactant DTAB also has a cationic head group with long dodecyl chain and bromide counter ion. During micellization the interaction between the [DTA]⁺ ion of surfactant and [odmim]⁺ ion of IL is restricted due to presence of similar charge on these species, although the possibility of interaction between alkyl chains cannot be ruled out. If one look at the anion of IL i.e. Cl⁻ ion, this can easily interact with the [DTA]⁺ ion of the surfactant. The electrostatic interactions between IL anions and surfactant cations lead to a decrease in repulsions among surfactant head groups. This allows surfactant monomers to undergo micellization at a lower concentration and the cmc value of surfactant solution decreases in the presence of IL.

Although this was also observed in case of our previous study with $DTAB + [bdmim][Cl]/H_2O$, but the decrease in cmc here is lesser as compared to what is observed there. In that study lowering in cmc took place to a greater extent [30]. There can be two probable reasons for this observation. First, due to longer alkyl chain in IL [odmim][Cl] than [bdmim][Cl] it will be less dissociated in the solution, so Cl⁻ ions will be available to lesser extent for interaction with surfactant head groups. This fact is also supported by the low conductivity values of DTAB/ [odmim][Cl] systems than DTAB/[bdmim][Cl] systems at a fixed wt% of IL (Fig. S1). Secondly due to the presence of octyl chain in [odmim][Cl], and the support of the presence of octyl chain in [odmim][Cl], the presence of octyl chain in [odmim]

it can provide stabilizing hydrophobic interactions to DTAB molecules than the butyl chain of IL [bdmim][Cl]. Thus [odmim][Cl] will solubilize surfactant monomers to certain extent and decreases the solvophobicity of surfactant molecules. This leads to a slight delay in the micellization process. Consequently the cmc value decreases on the addition of [odmim][Cl] but not as effectively as in the case of [bdmim][Cl]. Here

Table 1

The critical micelle concentration (cmc) of the aqueous DTAB solutions in different wt% of IL and the corresponding values of various thermodynamic parameters of micellization obtained from Eqs. (1)–(3) at temperatures 298.15–318.15 K.

T (K)	cmc (mmol kg ⁻¹)	α	ΔG_m° (kJ mol ⁻¹)	ΔH_m° (kJ mol ⁻¹)	$\frac{-T\Delta S_m^\circ}{(\mathrm{JK}^{-1} \mathrm{mol}^{-1})}$		
DTAB + [odmim][Cl] (0 wt%)							
298.15	15.8	0.268	-35.05	-8.48	-26.57		
308.15	16.4	0.274	-35.94	-8.83	-27.10		
318.15	17.0	0.280	-36.81	-9.19	-27.61		
DTAB + [odmim][Cl] (0.05 wt%)							
298.15	15.5	0.276	-34.97	-8.56	-26.41		
308.15	16.1	0.282	-35.85	-8.91	-26.94		
318.15	16.7	0.288	-36.72	-9.27	-27.45		
DTAB + [odmim][Cl] (0.1 wt%)							
298.15	15.3	0.284	-34.87	-8.99	-25.88		
308.15	15.8	0.292	- 35.73	-9.63	-26.10		
318.15	16.4	0.299	- 36.57	-10.27	-26.30		
DTAB + [odmim][Cl] (0.5 wt%)							
298.15	13.5	0.317	-34.72	-10.14	-24.58		
308.15	14.2	0.323	-35.54	-11.19	-24.35		
318.15	14.7	0.333	-36.32	-11.27	-25.05		
DTAB + [odmim][Cl] (1.0 wt%)							
298.15	11.6	0.355	-34.55	-10.67	-23.88		
308.15	12.2	0.362	- 35.35	-12.07	-23.28		
318.15	12.9	0.369	-36.10	- 12.55	-23.55		

the possibility of repulsions between [odmim]⁺ and [DTA]⁺ ions are less than those between [bdmim]⁺ and [DTA]⁺ ions. The greater extent of electrostatic interactions than hydrophobic interactions between the additive and surfactant moieties lead to lowering in cmc of the system studied here.

3.1.2. Effect of temperature on the cmc of DTAB

It is observed that for the studied temperature range the value of cmc increases with an increase in temperature. It is well known in literature that ionic surfactants have minima in cmc values when studied from low to high temperatures [32]. For DTAB + [odmim][Cl]/H₂O systems as we studied from 298.15 K to 318.15 K, a continuous increase is observed. The variation in cmc with temperature is usually analysed by considering two opposite factors. First, with the increase in temperature the degree of hydration of hydrophilic group of surfactant decreases, this favours the micellization process. Secondly the increase in temperature causes the disruption of water structure; this leads to the increase in solubilisation of surfactant monomers and disfavours the micellization. The cmc of DTAB solution has been found to increase with temperature at all the studied wt% of IL. It indicates that the disruption of water structure occurs to greater extent due to thermal agitation of molecules in the system so cmc increases with temperature.

3.1.3. Effect of IL and temperature on the thermodynamic parameters of micellization of DTAB

To understand the driving force of micellization process various thermodynamic parameters of micellization such as standard free energy change, ΔG_m° , the standard enthalpic change, ΔH_m° and the standard entropy change, ΔS_m° , in DTAB solutions have been obtained by using the following equations [33]:

$$\Delta G_m^o = (2 - \alpha) RT \ln X_{cmc} \tag{1}$$

$$\Delta H_m^o = -RT^2 \left[(2-\alpha) \frac{d \ln X_{cmc}}{dT} + \ln X_{cmc} \frac{d(1-\alpha)}{dT} \right]$$
(2)

$$\Delta S_m^o = \frac{\Delta H_m^o - \Delta G_m^o}{T} \tag{3}$$

where α is the degree of dissociation, *R* is gas constant, *T* is temperature and X_{cmc} is the cmc expressed in terms of mole fraction. The calculated values of these parameters for all the studied systems at different temperatures have been presented in Table 1. If one analyses the trend observed for α with the increase in temperature and wt% of IL, it is found to increase in both the cases. The increase in α with temperature is due to greater dissociation of counter ions from micellar surface as a consequence of high thermal agitation in the system. While the increase in α with high wt% of IL is due to interaction of [CI]⁻ ions of IL near micelle surface which interacts with $-N^+(CH_3)_3$ head groups. It causes some of the [Br]⁻ ions of surfactant to dissociate from micellar aggregate. With the increase in concentration of IL the number of interacting [CI]⁻ ions also increases.

A perusal of data from Table 1 reveals that the negative values of ΔG_m° and ΔH_m° are observed at all the studied temperatures. This indicates the spontaneous and exothermic nature of micellization process. The negative values of ΔG_m° have been found to be slightly dependent of temperature and the wt% of IL added. The value of ΔG_m° itself is obtained by the contribution of two terms, enthalpic (ΔH_m°) and entropic ($-T\Delta S_m^{\circ}$). It is observed that the entropy change for micellization process, ΔS_m° is large and positive for all the studied systems. This contributes to greater extent to ΔG_m° values at lower wt% of IL. At higher wt% of IL the enthalpic contribution increases towards ΔG_m° , as depicted in Table 1. If compared to DTAB + [bdmim][Cl]/H₂O system [30], there enthalpic contribution increases more significantly with higher wt% of IL. Here the lesser interaction of IL anions near micellar surface as discussed earlier leads to a less exothermic micellization process in

comparison to the previous study [30]. The value of entropy decreases at higher wt% of IL. With the increase in temperature the value of enthalpy increases while that of entropy decreases. At high temperature it is easy to break the three-dimensional water structure due to thermal agitation so a high value of ΔH_m^* is obtained. So the micellization process starts shifting from entropy-driven to enthalpy-driven with the increase in temperature and wt% of added IL. This kind of behaviour is also known for conventional ionic surfactants [34,35].

3.2. Fluorescence measurements

3.2.1. Determination of cmc

The fluorescence behaviour of fluorescent probes is highly used to study the micellization behaviour of surfactants in different medium [36,37]. We have studied the aggregation properties of DTAB +[odmim][Cl]/H₂O systems using the most common and popular probe pyrene. The intensity ratio of first to third vibronic peak of pyrene is highly sensitive towards the polarity of its microenvironment. This ratio has a high value in a polar medium and vice-versa [38]. The polarity sensed by pyrene molecules in a pre-micellar solution is high while in a post-micellar solution pyrene molecules partition themselves near the palisade layer of micelles. The environment inside micelles is a hydrocarbon like solvent so I_l/I_{lll} ratio decreases. This drop in I_l/I_{lll} ratio marks the onset of micellization. Fig. 2 represents the pyrene I_l/I_{lll} versus log₁₀[DTAB] in the presence of different amount of IL [odmim][Cl]. The data were fitted to simplistic sigmoidal expression. The cmc values of aqueous DTAB in the presence of different amounts of IL are reported in Table 2. These have been found in good relevance to those obtained from conductance measurements.

The cmc of aqueous DTAB solution decreases from 15.9 mmol kg^{-1} to 10.5 mmol kg⁻¹ with the addition of 2 wt% [odmim][Cl], but the further increase in concentration of IL up to 10 wt% causes the increase in cmc up to 38.5 mmol kg $^{-1}$. The cmc value at 5 wt% of IL increases but remains lower than the value of DTAB in pure water. So the titled IL is able to enhance the surface activity of DTAB upon addition of up to 5 wt% of IL after this it highly decreases the surface activity as the cmc value gets almost doubled at 10 wt% of IL. Interestingly, in the case of [bdmim][Cl], only the decrease in cmc takes place upon the addition of 10 wt% of IL [30]. The inset in Fig. 2 clearly indicates the more effectiveness of [bdmim][Cl] in lowering the cmc of DTAB. So the dissimilar effect of the two ILs, [odmim][Cl] and [bdmim][Cl] is noticeably observed by the variation in cmc of DTAB on the addition of ILs. Our results clearly demonstrate that the two ILs [bdmim][Cl] and [odmim][Cl] produce different effects on the aggregation properties of aqueous DTAB solutions. At a lower concentration (i.e., $\leq 2 \text{ wt\%}$) both ILs show the same trend in modifying properties of aqueous DTAB solution although to different extent. But at the higher concentration of ILs, the properties of aqueous DTAB solutions start changing in other way.

To account for these differences we need to understand the structural difference between the two ILs. Due to the long octyl chain, [odmim][Cl] can interact like a co-surfactant and penetrate in the micelle of DTAB, whereas [bdmim][Cl] will be unable to properly act like a co-surfactant. IL [bdmim][Cl] has more tendencies to behave like an electrolyte. It was expected that IL [odmim][Cl] can show mixed micellization with DTAB. So, we studied the aggregation behaviour of pure IL [odmim][Cl] in aqueous media, it has two distinct break points in conductivity graph corresponding to critical aggregation concentration (cac) at 24.4 mmol kg⁻¹ and the cmc value at 230.7 mmol kg⁻¹ (Fig. S2). It is reported in literature [39] that surfactant molecular interaction parameter, β has a value near to zero if the two ionic surfactants have similar charge on head groups as in our study (DTAB + [odmim][Cl]). This is due to the negligible change in the magnitude of self-repulsion before mixing and mutual repulsion after mixing with each other. The addition of IL increases the ionic strength of surfactant solution this decreases the electrostatic self-repulsion. Here at low wt% [odmim][Cl] decreases the cmc of aqueous DTAB solution. This



Fig. 2. Pyrene $I_{//I_{III}}$ versus \log_{10} [DTAB] in the absence and presence of different wt% of IL [odmim][CI] in the aqueous media. Inset shows the variation in cmc of DTAB in presence of different wt% of ILs, [bdmim][CI] [27] and [odmim][CI].

result reduces the possibility of mixed micellization between DTAB and [odmim][Cl]. As [odmim][Cl] has very high cmc value so the decrease in surfactant cmc value indicates electrolyte behaviour of IL at lower wt%. Only few IL molecules penetrated and interacted inside the micelle while most of them present near outer corona. If the size of the alkyl chain attached to IL is considered octyl chain is longer than butyl chain, stearic repulsion increases with increased bulkiness of the group. It is also known that stearic effect is greater at convex mixed micellar interior than electrostatic effect [33]. In the study of mixed micellization of cationic surfactants among themselves when taken in 1:1 ratio it was seen that the cmc value lies closer to the surfactant cmc which has a lower cmc value [40]. Accordingly, the cmc value should be intermediate of the surfactant cmc values under study. It is interesting that, in our study the cmc value is below pure DTAB cmc, indicating IL effects on DTAB micellization rather doing mixed micellization. As van der Waals interactions will always be positive and depend on length and closeness of packing of hydrophobic groups; so [odmim][Cl] will be interacting more with DTAB due to longer octyl chain. These interactions will substantially increase at higher concentration of IL. At 10 wt% IL [odmim][Cl] solubilizes surfactants molecules due to prominent hydrophobic interaction of alkyl chains, this indicates the co-

Table 2

The cmc values and aggregation number obtained from fluorescence measurements in the aqueous solution of DTAB on the addition of different wt% of IL [odmim][CI] at 298 K.

[odmim][Cl] (wt%)	cmc (mmol kg ⁻¹) fluorescence	Nagg
0	15.9	49
0.05	15.6	52
0.1	15.2	54
0.5	13.8	59
1.0	11.9	62
2.0	10.5	67
5.0	11.4	51
10.0	38.5	42

solvent nature of IL at high concentration. The asymmetric size of IL head group as compared to DTAB will also hinder the micellization process at such high concentration. If we compare the I_I/I_{III} ratio at each wt% studied its value is less for [odmim][Cl] than [bdmim][Cl] [30]. The low value clearly indicates a less polar environment due to interaction of alkyl chains of surfactant and IL. The trend in cmc of aqueous DTAB solution shows that at lower concentration [odmim][Cl] majorly acts like an electrolyte. The anion of IL undergoes coulombic attractive interaction with the cationic head groups of DTAB, lowers the electrostatic repulsion among head groups and decreases the cmc. However at high concentration it acts like a solvent and solubilizes surfactant molecules thus delays the aggregation. At higher wt%, due to the low solvophobicity of the environment surfactant molecules undergo micellization at a higher concentration than cmc. While in the case of [bdmim][Cl], it specifically behaves like an electrolyte even at 10 wt% and lowers the cmc of aqueous DTAB solution. It is noteworthy that at concentrations greater than 10 wt% of IL the fluorescence measurements here become unreliable rendering it impossible to extract any meaningful conclusion.

3.2.2. Determination of micellar aggregation number

The aggregation numbers (N_{agg}) of aqueous DTAB micelle in the presence of different amounts of IL [odmim][CI] is obtained by observing the fluorescence quenching behaviour of pyrene by CPC. The following equation is used for the determination of micellar aggregation number [41–43]:

$$\ln\left(\frac{I_o}{I_Q}\right) = \frac{Q_{micelle}}{[micelle]} = \frac{[CPC]_{micelle}}{[micelle]_{DTAB}} = [CPC]_{micelle} \left[\frac{N_{agg}}{[DTAB] - cmc_{DTAB}}\right] \quad (4)$$

where $I_{\rm O}$ and $I_{\rm Q}$ are fluorescence intensities of pyrene in the absence and presence of quencher CPC, respectively. Q_{micelle} (or [CPC]_{micelle}), [micelle]_{DTAB}, and [DTAB] are the concentrations of quencher CPC within the micellar phase, micelles, and DTAB surfactant, respectively.

Aggregation number is determined from the slope of the $\ln(I_0/I_Q)$ versus [CPC]_{micelle} plot for all the systems. The plots of $\ln(I_0/I_Q)$ versus [CPC] for quenching of pyrene by CPC within IL-added 50 mmol kg⁻¹ aqueous DTAB solution is presented in Fig. 3. It is suggesting a good linear behaviour on the addition of IL. The obtained slope increases up to 2.0 wt% of IL and then starts decreasing from 5.0 wt% of IL. The aggregation number thus obtained for aqueous DTAB micelles in the presence of different amount of IL [odmim][Cl] are listed in Table 2.

Our result of N_{agg} for aqueous DTAB solution is in good agreement with that reported in the literature [44]. The aggregation number of DTAB increases from 49 to 67 with the addition of 2 wt% of IL, but the further increase in concentration of IL up to 10 wt% causes a decrease of aggregation number to 42. It is well known in literature that the aggregation number increases with the decrease in cmc and vice-versa. The increase in aggregation number is due to the lesser head group repulsions among surfactant monomers which allow greater a number of surfactant molecules to form the micellar aggregate. The decrease in aggregation number at higher concentration of IL evidences the co-solvent nature of IL. The asymmetric head group of [odmim][CI] will prevent a greater number of surfactant monomers to assemble for the micellar aggregate. As co-solvents like glycerol [45] and ethylene glycol [46] also decrease the aggregation number of cationic surfactants when present in high concentration.

3.3. ¹H NMR measurements

The ¹H NMR technique was applied to reveal the intermolecular interaction in the IL-DTAB aqueous solutions. The hydrogen atoms on various carbons of surfactant are labelled as shown in Scheme 1. The observed chemical shifts reflect the changes in surrounding environment of surfactant protons in the micelles upon the addition of IL. The chemical shift, δ of protons of DTAB (50 mmol kg⁻¹) aqueous systems, upon the addition of different IL concentration up to 1.0 wt% of IL are presented in Table S1. The ¹H NMR spectrum of DTAB (50 mmol kg⁻¹) shows five characteristic peaks corresponding to the terminal - CH₃ (a) protons of the dodecyl chain at 0.8006 ppm, bulk $-CH_2$ (b) protons at 1.2767 ppm, β -CH₂ (c) protons at 1.6868 ppm, α -CH₂ (d) at 3.253 and $-CH_3$ (e) protons attached to ammonium group resonates at 3.0408 ppm (Scheme 1). The chemical shift of the protons (a and b) of tail the region of DTAB varies to small extent while that of the head region (c, d and e) varies more at high concentration of IL. The overall trend is a downfield shift for all the protons but more prominent for protons near head group. This result is in good agreement with



Fig. 3. Pyrene fluorescence quenching by CPC in aqueous DTAB in the absence and presence of different wt% of [odmim][Cl]. Solid lines represent the results of linear regression analysis.



Fig. 4. The change in chemical shifts, $\Delta \delta$ for the protons of DTAB against different wt% of IL in aqueous media.

the conclusion derived earlier that interaction of IL anions occurs at the micellar surface. The greater dissociation of counter-ions from micellar surface leads to slight deshielding of surfactant protons so the δ values shifts downfield as shown in Fig. 4. At wt% of IL ^{*} 1.0, the peaks of surfactant protons get diminished and unaccountable, so NMR study has been done up to 1.0 wt% of IL.

4. Conclusions

In conclusion, we can say that trisubstituted imidazolium based ionic liquids of varying N-alkyl chain length can be used to modify the thermodynamic and aggregation properties of cationic surfactants in a controlled fashion. Here the anion of IL acts as oppositely charged counterion for cationic DTAB micelles and supports the micellization process at low wt% of IL. Nevertheless, a clear change is observed in the physicochemical behaviour of aqueous solution of DTAB at high concentration of [odmim][Cl] and [bdmim][Cl] [27]. The longer alkyl chain that is present on the [odmim][Cl] allows it to participate with micelle at lower concentration and as a co-solvent at high wt% of IL. This decreases the solvophobicity of DTAB monomers and micellization gets delayed. While [bdmim][Cl] mainly behaves like an electrolyte even at a concentration as high as 10 wt%. These surfactant-IL mixed systems may have enormous future applications in conducting interfacial reactions and micellar catalysis. The micellization of DTAB in the presence and absence of IL [odmim][Cl] was found to be entropy driven at low temperatures and low wt% of IL while enthalpy driven at high temperatures and high wt% of IL. The results obtained from conductivity measurements are well-supported by fluorescence and NMR techniques.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at http://dx. doi.org/10.1016/j.molliq.2015.10.042.

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