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Influence of tetra ethyl ammonium bromide $(C_2H_5)_4$ NBr on the aggregation behavior of surface active ionic liquid 1-tetradecyl-3-methylimidazolium bromide $[C_{14}mim][Br]$

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ABSTRACT

In this work, we tend to explore the effect of organic electrolyte i.e. tetra ethyl ammonium bromide $(C_2H_5)_4$ NBr on the aggregation behavior of 1-tetradecyl-3-methylimidazolium bromide [C₁₄mim][Br] by utilizing electrical conductivity measurement, refractive index measurement, UV-Visible spectroscopy as well as FT-IR spectroscopic study. First of all, the synthesis of [C14mim][Br] is carried out in the laboratory, then the critical micelle concentration (CMC) of [C14mim][Br] is determined using conductivity measurements at temperatures 298.15 K, 308.15 K and 318.15 K in the absence and presence of $(C_2H_5)_4$ NBr at different concentrations 1 mM, 2 mM and 5 mM. The reduction in value of CMC is observed with respect to increasing concentration of $(C_2H_5)_4$ NBr and with the increase in temperature, the value of CMC also increases. These results are observed due to the establishment of reinforced hydrophobic interactions between the hydrophobic parts of surface active ionic liquid and the electrolytes. Then we reflected different thermodynamic parameters such as, standard free energy of micellization (ΔG_m^0), standard enthalpy of micellization (ΔH_m^0), and standard entropy of micellization (ΔS_m^0) in the temperature range 298.15 K-318.15 K, utilizing the value of CMC obtained from conductivity measurements. A graphical contrast of these thermodynamic parameters has been made. Further refractive index measurement and UVvisible spectroscopic study have been employed to verify the CMC obtained using conductivity measurement, which is found to be very close to that obtained via conductivity study. The alterations produced in the respective system have been confirmed via FT-IR spectroscopic study, which signify the variations produced by electrolyte on the aggregation of surface active ionic liquid in aqueous media.

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1. Introduction

lonic liquids are a class of molten electrolytes having specific properties such as excellent dissolution capacity, no vapor pressures, high ion conductivity, outstanding catalytic properties, no flammability etc. which make them potential candidates in many fields including preparation of novel nanomaterials, organic synthesis, homogeneous catalysis, and electrochemistry [1–4]. In addition, the ionic liquids containing a long hydrophobic alkyl chain are termed as surface active ionic liquids (SAILs) that possess surface active properties similar to conventional surfactants. Due to their structure, inherent charge and surface active nature, these SAILs can self-assemble in aqueous solution to form different types of aggregates such as micelles, vesicles and lyotropic liquid crystals etc. [5–11]. The length of alkyl chain, type of head group as well as nature of counterions effect the self-aggregation of surface active ionic liquids [12–14]. Understanding the influence of specific salt on the micellization behavior of imidazolium based ionic

* Corresponding author. *E-mail address:* manchandah@nitj.ac.in (H. Kumar). liquids helps us to know how these components participate in various applications because ILs based on the imidazolium ring are also biologically active due to the imidazolium ring [15]. The organic or inorganic salts interact with amphiphiles by salting in and salting out mechanisms depending upon the conditions [16]. CMC as well as other parameters get modified due to the various interactions occurring between SAIL and the electrolyte [15,17–20].Generally CMC of surfactants get reduced upon addition of inorganic electrolytes [21–23].

Rafati et al. investigated the effect of electrolytes on the micellization behavior of ILs where the surface tension and CMC decreases upon addition of salts in the system [24]. Wang et al. reported the modulation in the aggregation behavior of 1-decyl-3-methylimidazolium bromide ($[C_{10}mim]Br$) by addition of sodium electrolytes followed the Hofmeister series which can be explained by considering the hydrophobicity of anions [25]. Dong and his co-workers studied the interfacial and bulk behavior of SAILs such as 1-decyl-3-methylimidazolium bromide, $[C_{10}mim]$ [Br], 1-dodecyl-3-methylimidazolium bromide, $[C_{12}mim]$ [Br], and 1-dodecyl-3-methylimidazolium tetrafluoroborate, $[C_{12}mim]$ [BF] with or without sodium halide at room temperature (298 K) by employing tensiometry and conductometry. A significant decrease in value of CMC and π_{cmc} is observed upon addition of salts [26]. Jiao et al. investigated the effect of three inorganic electrolytes (LiCl, NaCl, and MgCl₂) and four organic electrolytes, viz. tetraalkylammonium bromides ((CH₃)₄NBr, (C₂H₅)₄NBr, (C₃H₇)₄NBr, and (C₄H₉)₄NBr) on the aggregation behavior of the anionic halogenfree surface active ionic liquid, 1-butyl-3-methylimidazolium dodecylsulfate ([C₄mim][C₁₂SO₄]), in aqueous solution and found that for a given electrolyte (i.e., NaCl), critical micelle concentration decreases with increasing electrolyte concentration [27].

However there are very few reports investigating the effect of electrolytes on the aggregation of SAILs. The present investigation has been undertaken with an aim to get clear and detailed information on the effect of temperature and concentration of organic electrolyte $(C_2H_5)_4NBr$ on the aggregation behavior of $[C_{14}mim][Br]$. With this purpose, the CMC values as well as other thermodynamic parameters of micellization have been evaluated by employing conductivity measurement. The refractive index and UV–visible spectroscopy have been employed to confirm the obtained CMC values. FT-IR spectroscopy has been utilized to understand the various interactions prevailing in the system constituting SAIL and organic electrolyte.

2. Experimental section

2.1. Materials

1-Methylimidazole purchased from HIMEDIA Laboratories Pvt. Ltd. was used to synthesize the surface active ionic liquid 1-tetradecyl-3-methylimidazolium bromide $[C_{14}mim][Br]$. 1-Bromotetradecane and hexane used for the synthesis were purchased from TCI Pvt. Ltd. aceto-nitrile and tetraethyl ammonium bromide used in this study was procured from LOBA Chemie Pvt. Ltd. Mumbai India and Spectrochem Pvt. Ltd. Mumbai India respectively. Tetraethyl ammonium bromide was dried under vacuum for 48 h by keeping in vacuum desiccators before use. Table 1 contains the list of all the chemicals used in experimental work along with their source, CAS number, purification method and mass fraction purity.

2.2. Synthesis of ionic liquid

In 500 ml round bottom flask, 1-methylimidazole was taken in acetonitrile. Then 1-bromotetradecane was added in above reaction mixture in the ratio 1:1 dropwise and with continuous stirring. After the complete addition, the reaction mixture was refluxed for 24 h at 80 °C. Thin layer chromatography was used to know about the completion of

Table 1

Specification of chemicals.

reaction. Once the reaction completed, acetonitrile which was taken as solvent was evaporated by employing rota-evaporator. Then the product was washed with hexane in separating funnel to remove unreacted substrate. The resulting product was recrystallized to yield a white solid. At last, product was dried in vacuum for 8 h before use. The structure of obtained SAIL was confirmed by employing ¹H NMR and FT-IR spectroscopic studies.

2.3. Methods

Sartorius CPA 225 D electronic balance was used to accurately weigh the compounds with a precision of ± 0.00001 g to prepare the stock solutions. For sample preparation, doubly distilled deionized water obtained from Millipore, Milli-Q Academic water purification system had been used which was having a conductance<5 μ S cm⁻¹. Three times measurements were made for each experiment, average value of which was considered as final measurement.

2.3.1. Electrical conductivity measurement

A digital conductivity meter Systronics 306 having a cell with cell constant unity had been used to measure the electrical conductivity of samples. Before the measurements, the instrument was calibrated using aqueous KCl solutions having the concentration in the range $0.01-1.0 \text{ mol kg}^{-1}$. To obtain the value of conductivity at constant temperatures i.e. 298.15 K, 308.15 K and 318.15 K, the solution was taken in the double jacketed vessel, whose temperature was maintained with accuracy of ± 0.1 K using refrigerated circulated water thermostat provided by Macro Scientific Works Pvt. Ltd. Delhi. The solution was properly stirred after each addition of SAIL to the cell, only then the value of conductivity is noted. From the plot of conductivity versus concentration of SAIL, the critical micelle concentration of $[C_{14}\text{mim}][Br]$ in aqueous solution of 0 mM, 1 mM, 2 mM and 5 mM (C_2H_5)₄NBr at different temperatures is obtained at the breakpoint of two linear regimes as shown in Fig. 2.

2.3.2. Refractive index measurements

A compact and convenient Abbemat 300 refractometer by Anton Paar was used to determine the refractive index of the samples, which was having a resolution of 0.00001 nD. Very low volume of sample is required for the measurement by using this instrument. The measurement can be made in temperature range of 4 °C to 85 °C with temperature probe accuracy of ± 0.05 °C. Before measurement the instrument was always checked by measuring the refractive index of water. The instrument allows us to take the readings

Chemicals	Sources	CAS no.	Purification method	Mass fraction purity [#]	Structure
1-Methylimadazole	HiMedia Laboratories Pvt. Ltd., India	616-47-7	No further purification	>0.99	
1-Bromotetradecane	TCI Chemicals (India) Pvt. Ltd.	112-71-0	No further purification	>0.97	Br
Hexane	TCI Chemicals (India) Pvt. Ltd.	110-54-3	No further purification	>0.96	$\sim \sim$
Acetonitrile	LOBA Chemie Pvt. Ltd., India	75-05-8	No further purification	>0.995	$H_3C-C\equiv N$
Tetraethylammonium bromide	Spectrochem Pvt. Ltd., India	71-91-0	Vacuum drying	>0.98	$H_3C - CH_3$ $N^+ Br^-$
1-Tetradecyl-3-methylimidazolium bromide [C ₁₄ mim][Br]	Synthesized in the laboratory	471907-87-6	Vacuum drying	>0.99 ^{##}	

As declared by supplier.

As per NMR analysis.

within seconds. The measurement was taken at least 3 times, the mean value of which was considered as the final reading. After each measurement the measuring prism was cleaned.

2.3.3. UV-visible spectroscopy

The critical concentration was determined from a plot of the absorbance at a fixed wavelength versus the sample concentration [28]. The spectra was recorded after each addition of [C₁₄mim][Br] to the cuvette. The absorbance of [C₁₄mim][Br] was measured in the absence and presence of organic electrolyte (C₂H₅)₄NBr at different concentrations i.e. 1 mM, 2 mM and 5 mM at $\lambda_{max} = 264$ nm. All the measurements were made at room temperature 298.15 K by employing Shimadzu UV 3600 UV–Vis spectrophotometer with a quartz cuvette having path length of 1 cm. The concentration corresponding to the point of intersection of two line segments in the plot of absorbance versus concentration of [C₁₄mim][Br] corresponds to the point of CMC as shown in Fig. 6.

2.3.4. FT-IR spectroscopic study

FT-IR spectroscopic studies were employed to analyze various structural alterations taking place in the SAIL/electrolyte system. For this various FT-IR spectra were recorded using Agilent technologies Carry 630 FT-IR Spectrophotometer in the wave number region from 4000 cm⁻¹ to 400 cm⁻¹ for different samples of [C₁₄mim][Br] in aqueous solution of 0 mM, 1 mM, 2 mM and 5 mM (C₂H₅)₄NBr with concentration of [C₁₄mim][Br] corresponding to concentration below CMC, at CMC and above CMC to analyze the variations occurring in the system near the point of critical micelle concentration.

3. Result and discussions

3.1. Characterization of synthesized ionic liquid

To confirm whether the desired ionic liquid $[C_{14}mim][Br]$ has been synthesized or not, the characterization of synthesized ionic liquid is done by utilizing ¹H NMR and FT-IR spectroscopic studies. The results obtained via both the techniques are shown in Fig. 1. ¹H NMR (Bruker 400 MHz) spectrum of $[C_{14}mim][Br]$ in CDCl₃ used as a solvent is as shown: 0.77 (3H, Triplet), 1.22 (22H, Multiplet), 1.81 (2H, Pentet), 4.02 (3H, singlet), 4.22 (2H, Triplet), 7.38 (1H, Singlet), 7.57 (1H, Singlet), 9.98 (1H, Singlet). The characteristic absorption bands in FT-IR spectra of $[C_{14}mim][Br]$ is as shown: $+NR_4$ stretching: 3482 cm^{-1} and 3436 cm^{-1} , aromatic C—H stretch: 3068 cm^{-1} , aliphatic C—H stretch: 2919 cm^{-1} and 2854 cm^{-1} , C=N stretch: 1632 cm^{-1} ; C=C stretch: 1577 cm^{-1} , CH₂ bending: 1472 cm^{-1} , and C—N stretch: 1176 cm^{-1} . The data obtained for the synthesized ionic liquid is quite consistent with the literature data [7,29], which shows that the desired ionic liquid has been synthesized.

3.2. Determination of critical micelle concentration

3.2.1. Electrical conductivity measurement

The self-aggregation of SAIL [C₁₄mim][Br] has been studied by taking the electrical conductivity measurements of [C₁₄mim][Br] in the absence and presence of (C₂H₅)₄NBr in aqueous medium at different temperatures i.e. 298.15 K, 308.15 K and 318.15 K. Table 2 constitutes the



Fig. 1. ¹H NMR spectra and FT-IR spectra of [C₁₄mim][Br].

Conductivity values of [C₁₄mim][Br] solutions in the presence of 0 mM, 1 mM, 2 mM and 5 mM of (C₂H₅)₄N⁺Br⁻ at different temperatures 298.15 K, 308.15 K and 318.15 K in the aqueous media.

[C ₁₄ mim][Br]/mM	M κ (mS/cm)											
	$0 \text{ mM} (C_2H_5)_4 \text{N}^+\text{Br}^-$			1 mM (C ₂ H	$H_5)_4 N^+ Br^-$		2 mM (C ₂ H	$H_5)_4 N^+ Br^-$		$5 \text{ mM} (C_2H_5)_4 \text{N}^+ \text{Br}^-$		
	298.15 K	308.15 K	318.15 K	298.15 K	308.15 K	318.15 K	298.15 K	308.15 K	318.15 K	298.15 K	308.15 K	318.15 K
0.000	0.0046	0.0115	0.0157	0.1151	0.1416	0.1767	0.1976	0.2401	0.2937	0.4172	0.5090	0.6128
0.263	0.0249	0.0401	0.0409	0.1334	0.1646	0.1983	0.2129	0.2638	0.3183	0.4271	0.5297	0.6297
0.519	0.0459	0.0671	0.0708	0.1521	0.1873	0.2235	0.2303	0.2828	0.3448	0.4436	0.5417	0.6484
0.769	0.0650	0.0930	0.1010	0.1697	0.2095	0.2497	0.2492	0.3061	0.3654	0.4594	0.5601	0.6652
1.013	0.0834	0.1104	0.1270	0.1845	0.2312	0.2714	0.2639	0.3253	0.3893	0.4719	0.5805	0.6814
1.250	0.1010	0.1345	0.1541	0.2007	0.2506	0.2936	0.2813	0.3432	0.4159	0.4791	0.5936	0.7046
1.481	0.1186	0.1543	0.1816	0.2156	0.2682	0.3175	0.2950	0.3636	0.4325	0.4901	0.6113	0.7234
1.707	0.1357	0.1725	0.2062	0.2319	0.2861	0.3411	0.3066	0.3805	0.4514	0.4931	0.6178	0.7384
1.928	0.1521	0.1991	0.2317	0.2482	0.3053	0.3625	0.3147	0.3994	0.4721	0.4954	0.6194	0.7485
2.143	0.1670	0.2181	0.2528	0.2609	0.3241	0.3844	0.3183	0.4052	0.4922	0.4941	0.6212	0.7516
2.353	0.1826	0.2375	0.2802	0.2652	0.3331	0.4036	0.3219	0.4091	0.5108	0.4970	0.6223	0.7530
2.558	0.1921	0.2518	0.3026	0.2711	0.3405	0.4197	0.3264	0.4139	0.5182	0.4988	0.6234	0.7557
2.759	0.1992	0.2652	0.3220	0.2744	0.3454	0.4317	0.3294	0.4190	0.5254	0.4996	0.6269	0.7583
2.955	0.2042	0.2732	0.3348	0.2779	0.3502	0.4410	0.3327	0.4234	0.5308	0.5011	0.6298	0.7611
3.146	0.2087	0.2815	0.3455	0.2830	0.3544	0.4486	0.3357	0.4275	0.5337	0.5028	0.6304	0.7632
3.333	0.2134	0.2879	0.3563	0.2862	0.3591	0.4550	0.3381	0.4318	0.5406	0.5048	0.6332	0.7684
3.516	0.2174	0.2938	0.3651	0.2890	0.3636	0.4608	0.3413	0.4352	0.5424	0.5072	0.6359	0.7733
3.696	0.2214	0.3001	0.3719	0.2933	0.3676	0.4670	0.3439	0.4386	0.5483	0.5085	0.6372	0.7774
3.871	0.2251	0.3054	0.3770	0.2958	0.3731	0.4727	0.3464	0.4418	0.5519	0.5108	0.6412	0.7814
4.043	0.2290	0.3109	0.3830	0.2988	0.3751	0.4775	0.3494	0.4453	0.5554	0.5119	0.6459	0.7845
4.211	0.2326	0.3163	0.3893	0.3023	0.3817	0.4822	0.3513	0.4529	0.5612	0.5162	0.6496	0.7862
4.375	0.2361	0.3210	0.3959	0.3040	0.3886	0.4847	0.3535	0.4554	0.5685	0.5192	0.6542	0.7892
4.536	0.2397	0.3256	0.4077	0.3066	0.3911	0.4920	0.3558	0.4578	0.5714	0.5217	0.6579	0.7916
4.694	0.2429	0.3289	0.4140	0.3081	0.3951	0.4960	0.3580	0.4617	0.5728	0.5241	0.6598	0.7958
4.848	0.2464	0.3331	0.4185	0.3125	0.3993	0.5018	0.3603	0.4641	0.5801	0.5262	0.6654	0.8015

Standard uncertainties s are s (T) = ± 0.1 K, s (κ) = ± 0.0001 mS/cm.

data obtained via electrical conductivity measurement in the presence of 0 mM, 1 mM, 2 mM and 5 mM of $(C_2H_5)_4N^+Br^-$ at different temperatures. The specific conductivity increases with increase in concentration of free $[C_{14}mim]^+$ and $[Br]^-$ ions in the solution. At the concentration corresponding to the critical micelle concentration, a break arises in the line. This happens because of the change in slope of line near the CMC. At CMC, micelle formation takes place. The low mobility of micelles as compared to free ions is responsible for the change in slope of line [30]. The concentration corresponding to the point of intersection of two line segments in the graph of specific conductivity versus concentration of [C₁₄mim][Br] corresponds to the CMC value. The value of CMC is firstly obtained in aqueous medium without the addition of organic electrolyte at all the studied temperatures as shown in Fig. 2(a). The CMC values obtained by employing this method for [C₁₄mim][Br] in water has been compared with the previous literature [31–35] as reported in Table 3. The values obtained are found to be very close to each other. Then the same is repeated to find the CMC value of [C₁₄mim][Br] in presence of (C₂H₅)₄NBr at different concentrations as well as temperatures as shown in Fig. 2(b), (c), (d). The obtained values of CMC in the presence of 0 mM, 1 mM, 2 mM and 5 mM of $(C_2H_5)_4N^+Br$ at temperatures 298.15 K, 308.15 K and 318.15 K has been reported in Table 4.

It can be observed from Fig. 3(a) that the value of CMC decreases on the addition of $(C_2H_5)_4$ NBr and increases with the increase in temperature. The decrease in CMC value upon addition of organic electrolyte can be explained by considering the fact that the anion of electrolyte interact with the cationic head group of SAIL leading to decrease in thickness of electrical double layer at interface. This favors the micellization of SAILs by reducing the electrostatic repulsions between the head groups leading to decrease in CMC value upon addition of electrolyte [36]. On the other hand, the increase in value of CMC with the increase in temperature is due to disruption of water structure leading to delay in process of micellization. The electrostatic repulsions between head groups of SAIL monomers are reduced more with the addition of higher concentration of organic electrolyte $(C_2H_5)_4$ NBr in the system. Thus, more reduction in CMC value has been achieved with the increase in electrolyte concentration from 1 mM to 5 mM as observed from Fig. 4 (a). In general, in case of concentration of organic electrolyte (C_2H_5) ₄NBr beyond 5 mM, it is expected that there will be more and more reduction of electrostatic repulsions between head groups, thereby leading to more decrease in value of CMC. In other way, it can also be assumed that due to higher concentration reverse phenomenon will happen and CMC may increase that has been observed and discussed in some cases [37–41]. So in our opinion that makes it different aspect of study at higher temperature and is beyond the scope of this paper and will be studied separately.

3.2.2. Refractive index measurement

Refractive index is very important property of any material, which describes how fast light moves through a specific medium in relation to how fast it moves through vacuum. The speed of light changes when it pass through the interface of two different substances resulting in change of direction of light, which is typically known as "refraction". The determination of CMC using refractive index measurement is based on the principle that the surfactant monomers have lower refractive index as compared to the micelle. The refractive index of solution increases rapidly before CMC and slowly after CMC, leading to clear determination of CMC value at the breakpoint in the graph of refractive index versus concentration of SAIL [42–44]. Table 5 shows the refractive index values of different solutions of [C14mim][Br] in the absence and presence of (C₂H₅)₄NBr at different temperatures in aqueous media. The value of CMC is determined at the breakpoint obtained by plotting refractive index versus concentration of [C14mim][Br] as shown in Fig. 4 and are reported in Table 6.

3.2.3. UV–visible spectroscopy

The interaction of $[C_{14}mim][Br]$ with organic electrolyte (C_2H_5) ₄NBr has been studied using UV–visible spectroscopy. Absorption measurements can be at a single wavelength or over an extended spectral range. The critical micelle concentration was determined from a plot of the absorbance at a fixed wavelength versus the sample concentration [28]. The determination of CMC of imidazolium



Fig. 2. Specific conductance (κ) of [C₁₄mim][Br] solutions in the presence of (a) 0 mM (b) 1 mM (c) 2 mM (d) 5 mM (C₂H₅)₄N⁺Br⁻ at different temperatures 298.15 K, 308.15 K and 318.15 K in the aqueous media.

Comparison of experimentally obtained and literature values of CMC for [C₁₄mim][Br] in aqueous solution by (a) conductivity, (b) refractive index, (c) UV–Visible spectroscopy, (d) surface tension and (e) fluorescence (f) isothermal titration microcalorimetry at different temperatures.

Temperatures	CMC (mM) for $[C_{14}min][Br]$									
	Expt. CMC	Literature [31]	Literature [32]	Literature [33]	Literature [34]	Literature [35]				
298.15 К 308.15 К 318.15 К	2.558 ^a 2.516 ^b 2.498 ^c 2.756 ^a 2.703 ^b 2.975 ^a 2.912 ^b	2.50 ^a 2.30 ^d - -	2.53 ^a 2.39 ^d - -	2.60 ^a 2.80 ^d 2.90 ^e -	2.69 ^d 2.52 ^f 2.74 ^d 2.82 ^d	2.53 ^a 2.76 ^d				

based ionic liquid do not need the involvement of any probe for absorption of light because imidazolium ring present in these SAILs can itself absorb in the entire UV-region [45–48]. The absorbance values have been taken at 264 nm wavelength for various solutions of [C_{14} mim][Br] in the absence and presence of (C_2H_5)₄NBr which is presented in Table S1. All the measurements were made at room temperature i.e. 298.15 K. The plot of absorbance versus concentration of [C_{14} mim][Br] has been shown in Fig. 5. It is observed from the Fig. 5(a) that the value of absorbance show increment upon

the addition of $[C_{14}mim][Br]$ in aqueous medium in the absence of organic electrolyte. But the rate of increase in absorbance value above CMC is less than that of the rate below CMC. This gives the clear indication of point of CMC in the graph. [49]. On the other hand, the absorbance value at $\lambda_{max} = 264$ nm starts decreasing upon the addition of organic electrolyte in aqueous media [50]. But the rate of decrease below CMC was different from the rate above CMC, leading to recognize the CMC value as shown in Fig. 5 (b), (c), (d). The CMC value obtained using this method has been

6

Critical micelle concentration (CMC), degree of counterion dissociation (α), free energy of micellization (ΔG_m^0), enthalpy of micellization (ΔH_m^0), and entropy of micellization (ΔS_m^0) of [C₁₄mim][Br] solutions in the presence of 0 mM, 1 mM, 2 mM and 5 mM of (C₂H₅) $_4$ N⁺Br⁻ at different temperatures 298.15 K, 308.15 K and 318.15 K in the aqueous media.

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	$(C_{2}H_{5})_{4}N^{+}Br^{-}/mM$	CMC (mM)	α	ΔG_m^0 (kJ·mol ⁻¹)	ΔH_m^0 (kJ·mol ⁻¹)	$\Delta S_m^0 (J \cdot mol^{-1} \cdot K^{-1})$
	T = 298.15 K					
	0 mM	2.6	0.300	-42.08	-9.49	109.32
	1 mM	2.2	0.269	-43.58	-12.24	105.13
	2 mM	1.8	0.236	-45.12	-15.07	100.79
	5 mM	1.4	0.1969	-47.29	-18.02	98.15
	T = 308.15 K 0 mM 1 mM 2 mM 5 mM	2.8 2.2 1.9 1.6	0.340 0.308 0.269 0.218	-42.16 -43.87 -45.51 -47.66	-9.90 -12.78 -15.79 -19.03	104.71 100.88 96.42 92.92
	T = 31815 K					
	0 mM	2.9	0.377	-42.23	-10.32	100.32
	1 mM	2.6	0.330	-44.02	-13.44	96.10
	2 mM	2.3	0.286	-45.74	-16.67	91.36
	5 mM	1.9	0.244	-47.88	-19.98	87.68
-						

Standard uncertainties s are s (T) = ± 0.1 K, s (CMC) = ± 0.001 mM, s (ΔG_m^0) = ± 0.03 kJ·mol⁻¹, s (ΔH_m^0) = ± 0.02 kJ·mol⁻¹, s (ΔS_m^0) = ± 0.02 J·mol⁻¹·K⁻¹.

compared with that obtained using electrical conductivity and refractive index measurements, which are found to be very close to each other as reported in Table 6.

3.3. Determination of degree of counterion dissociation (α)

The degree of counterion dissociation (α) is determined by evaluating the ratio between the slopes of post-micellar region to premicellar region as obtained in the electrical conductivity measurements. The obtained values of degree of counterion dissociation (α) have been reported in Table 4. The variation of degree of counterion dissociation (α) with the concentration of organic electrolyte and temperature of system has been presented graphically in Fig. 3 (b). It can be observed from the Table that the value of degree of counterion dissociation (α) decreases with the addition of organic electrolyte, whereas it increases with the increase in temperature. It means that the degree of counterion binding ($\beta = 1 - \alpha$) increases on the addition of electrolyte leading to formation of better packed aggregates in the system. This leads to increase in charge density of the stern layer of the micelles formed. Hence the number of bromide ions bound to the micelles also increase [51]. But with the increase in temperature of the system, the degree of counterion dissociation (α) increases indicating high thermal agitation in the system causes more dissociation of counterions at the surface of micelle [52-55].

3.4. Determination of thermodynamic parameters of micellization

The values of CMC obtained from electrical conductivity measurements have been considered to obtain various thermodynamic parameters of micellization, which are important to understand



Fig. 3. Plot of (a) critical micelle concentration (b) degree of counter ion dissociation α of [C₁₄mim][Br] solutions in the presence of 0 mM, 1 mM, 2 mM and 5 mM of (C₂H₅)₄N⁺Br⁻ at different temperatures 298.15 K, 308.15 K and 318.15 K in the aqueous media from conductivity measurements.



Fig. 4. Plot of refractive index (n) of [C₁₄mim][Br] solutions in the presence of 0 mM, 1 mM, 2 mM and 5 mM of (C₂H₅)₄N⁺Br⁻ at temperatures (a) 298.15 K (b) 308.15 K and (c) 318.15 K.

Refractive index values of $[C_{14}mim][Br]$ solutions in the presence of 0 mM, 1 mM, 2 mM and 5 mM of $(C_2H_5)_4N^+Br^-$ at different temperatures 298.15 K, 308.15 K and 318.15 K in the aqueous media.

[C ₁₄ mim][Br]/mM	n][Br]/mM Refractive index (n)											
	0 mM (C ₂ H	$I_5)_4 N^+ Br^-$		1 mM (C ₂ H	$1 \text{ mM} (C_2H_5)_4N^+Br^-$		$2 \text{ mM} (C_2H_5)_4 \text{N}^+\text{Br}^-$			$5 \text{ mM} (C_2H_5)_4 \text{N}^+\text{Br}^-$		
	298.15 K	308.15 K	318.15 K	298.15 K	308.15 K	318.15 K	298.15 K	308.15 K	318.15 K	298.15 K	308.15 K	318.15 K
0	1.33250	1.33127	1.32978	1.33252	1.33129	1.32979	1.33256	1.33131	1.32981	1.33265	1.33140	1.32989
0.26316	1.33252	1.33129	1.3298	1.33256	1.33131	1.32981	1.33258	1.33133	1.32983	1.33268	1.33143	1.32992
0.52632	1.33254	1.33132	1.32982	1.33257	1.33133	1.32983	1.33259	1.33134	1.32984	1.33270	1.33145	1.32994
0.78947	1.33256	1.33133	1.32983	1.33260	1.33135	1.32985	1.33262	1.33137	1.32987	1.33272	1.33147	1.32996
1.05263	1.33258	1.33135	1.32985	1.33262	1.33137	1.32987	1.33264	1.33139	1.32989	1.33274	1.33149	1.32998
1.31579	1.33260	1.33137	1.32987	1.33265	1.33140	1.32990	1.33267	1.33142	1.32992	1.33276	1.33152	1.33000
1.57895	1.33262	1.33139	1.32989	1.33268	1.33143	1.32993	1.33270	1.33145	1.32995	1.33277	1.33154	1.33002
1.84211	1.33264	1.33140	1.32990	1.33269	1.33144	1.32994	1.33272	1.33147	1.32997	1.33278	1.33155	1.33004
2.10526	1.33266	1.33142	1.32992	1.33271	1.33146	1.32996	1.33273	1.33149	1.32999	1.33279	1.33156	1.33005
2.36842	1.33268	1.33144	1.32994	1.33272	1.33148	1.32998	1.33274	1.33150	1.33001	1.33280	1.33157	1.33006
2.63158	1.33270	1.33146	1.32996	1.33273	1.33149	1.33000	1.33275	1.33151	1.33002	1.33281	1.33158	1.33007
2.89474	1.33271	1.33148	1.32998	1.33274	1.33150	1.33001	1.33276	1.33152	1.33003	1.33282	1.33159	1.33008
3.15789	1.33272	1.33149	1.32999	1.33275	1.33151	1.33002	1.33277	1.33153	1.33004	1.33284	1.33160	1.33009
3.42105	1.33273	1.33150	1.33000	1.33276	1.33152	1.33003	1.33278	1.33154	1.33005	1.33285	1.33161	1.33010
3.68421	1.33274	1.33152	1.33001	1.33277	1.33153	1.33004	1.33279	1.33155	1.33006	1.33286	1.33162	1.33011
3.94737	1.33275	1.33153	1.33003	1.33278	1.33154	1.33005	1.3328	1.33156	1.33007	1.33287	1.33163	1.33012
4.21053	1.33276	1.33154	1.33005	1.33279	1.33155	1.33006	1.33281	1.33157	1.33008	1.33288	1.33164	1.33013
4.47368	1.33278	1.33155	1.33006	1.33281	1.33156	1.33007	1.33282	1.33158	1.33009	1.33289	1.33165	1.33014

Standard uncertainties s are s (T) = ± 0.05 K, s (n) = ± 0.00001 .

CMC values of $[C_{14}mim][Br]$ solutions in the presence of 0 mM, 1 mM, 2 mM and 5 mM of $(C_{2}H_{5})_{4}N^{+}Br^{-}$ at different temperatures in the aqueous media obtained using conductivity measurement, refractive index measurement and UV-visible spectroscopy.

CMC (mM)									
Conductivity n	neasurement		Refractive inde	ex measurement	UV-visible spectroscopy				
298.15 K	308.15 K	318.15 K	298.15 K	308.15 K	318.15 K	298.15 K			
2.558	2.756	2.975	2.516	2.703	2.912	2.498			
2.158	2.245	2.613	2.116	2.244	2.591	2.136			
1.834	1.939	2.311	1.821	1.911	2.281	1.791			
1.416	1.628	1.856	1.363	1.536	1.845	1.411			
	CMC (mM) Conductivity m 298.15 K 2.558 2.158 1.834 1.416	CMC (mM) Conductivity measurement 298.15 K 308.15 K 2.558 2.756 2.158 2.245 1.834 1.939 1.416 1.628	CMC (mM) Conductivity measurement 298.15 K 308.15 K 318.15 K 2.558 2.756 2.975 2.158 2.245 2.613 1.834 1.939 2.311 1.416 1.628 1.856	CMC (mM) Refractive index 298,15 K 308.15 K 318.15 K 298.15 K 298,15 K 308.15 K 298.15 K 298.15 K 2.558 2.756 2.975 2.516 2.158 2.245 2.613 2.116 1.834 1.939 2.311 1.821 1.416 1.628 1.856 1.363	CMC (mM) Refractive index measurement 298.15 K 308.15 K 318.15 K 298.15 K 308.15 K 2.558 2.756 2.975 2.516 2.703 2.158 2.245 2.613 2.116 2.244 1.834 1.939 2.311 1.821 1.911 1.416 1.628 1.856 1.363 1.536	CMC (mM) Conductivity measurement Refractive index measurement 298.15 K 308.15 K 318.15 K 298.15 K 308.15 K 318.15 K 308.15 K 2.558 2.756 2.975 2.516 2.703 2.912 2.158 2.245 2.613 2.116 2.244 2.591 1.834 1.939 2.311 1.821 1.911 2.281 1.416 1.628 1.856 1.363 1.536 1.845			

Standard uncertainties s are s (T) = ± 0.1 K, s (CMC) = ± 0.001 mM.



Fig. 5. Variation of absorbance of $[C_{14}mim][Br]$ solutions in the presence of (a) 0 mM (b) 1 mM (c) 2 mM (d) 5 mM (C_2H_5)₄N⁺Br⁻ at $\lambda_{max} = 264$ nm in the aqueous media.

the driving force of micellization [56]. These parameters are the standard Gibbs' free energy change of micellization, ΔG_m^0 , the standard enthalpy change of micellization, ΔH_m^0 and the standard entropy change of micellization, ΔS_m^0 , which are reported in Table 4. The standard Gibbs' free energy change of micellization, ΔG_m^0 can be evaluated by using Eq. (1).

$$\Delta G_m^0 = (2 - \alpha) RT (\ln X_{CMC}) \tag{1}$$

where *R* is gas constant, *T* is temperature and α is degree of counter ion dissociation, *X*_{CMC} is the value of CMC in the mole fraction unit.

The standard enthalpy change of micellization, ΔH_m^0 can be evaluated by using Eq. (2).

$$\Delta H_m^0 = -RT^2 (2-\alpha) [d(\ln X_{CMC})/dT]$$
⁽²⁾

where all the symbols have usual meaning described before. From the Table 4, it can be observed that the standard Gibbs' free energy change of micellization, ΔG_m^0 as well as the standard enthalpy change of micellization, ΔH_m^0 are having negative values for all the studied systems indicating the process of micellization is spontaneous and exothermic in nature. Both these parameters become more



Fig. 6. Plot of (a) standard free energy of micellization ΔG_m^0 (b) standard enthalpy of micellization ΔH_m^0 (c) standard entropy of micellization ΔS_m^0 of [C₁₄mim][Br] solutions in the presence of 0 mM, 1 mM, 2 mM and 5 mM of (C₂H₅)₄N⁺Br⁻ at different temperatures 298.15 K, 308.15 K and 318.15 K in the aqueous media.

negative on the addition of organic electrolyte and with the increase in temperature. The variation in these parameters toward the more negative value is more significant in case of addition of organic electrolyte to the system as compared to that with the increase in temperature which indicates that the addition of electrolyte makes the micellization process more spontaneous and exothermic. This is because the organic electrolyte reduces the repulsions between the head groups of [C₁₄mim][Br]. The repulsion between the head groups is one of the major factors opposing micellization.

The standard entropy change of micellization, ΔS_m^0 can be evaluated by using the values of the standard Gibbs' free energy change of micellization, ΔG_m^0 and the standard enthalpy change of micellization, ΔH_m^0 by using Eq. (3).

$$\Delta S_m^0 = \left(\Delta H_m^0 - \Delta G_m^0\right) / T \tag{3}$$

The entropy change of micellization, ΔS_m^0 is found to be large positive value at all concentrations of (C₂H₅)₄NBr and at all the studied temperatures. The value of entropy change of micellization, ΔS_m^0 decreases with the addition of organic electrolyte and with the increase in temperature which indicates that the micellization process shifts from entropy to enthalpy driven. Similar behavior is observed for conventional surfactants [57,58]. The variation of these parameters with the change in concentration of $(C_2H_5)_4NBr$ as well as with the change in temperature has been presented in Fig. 6.

3.5. FT-IR spectroscopy

FT-IR spectral study of solutions in the presence of 0 mM, 1 mM, 2 mM and 5 mM (C_2H_5)_4NBr at concentrations of [C_{14} mim][Br] below CMC, at CMC and above CMC have been carried out and presented in Figs. S1, S2, S3 and S4 shown in supporting information. The peak observed in the wavenumber range 3000–3600 cm⁻¹ is due to N—H stretching of imidazolium ring. The variation in the peak for different concentrations of [C_{14} mim][Br] in absence and presence of organic electrolyte in aqueous media has been shown in Fig. 7 and the wavenumbers are reported in Table 7. The spectroscopic study confirms the structural alterations prevailing in the system constituting SAIL [C_{14} mim][Br] and organic electrolyte (C_2H_5)_4NBr. The observed variations in the wavenumber indicate that various molecular scale interactions are occurring between SAIL and organic electrolyte [59].



Fig. 7. FT-IR spectra of $[C_{14}mim][Br]$ solutions in the presence of (a) 0 mM (b) 1 mM (c) 2 mM (d) 5 mM $(C_2H_5)_4N^+Br^-$ in the wavenumber range 3000–3600 cm⁻¹ at different concentrations of $[C_{14}mim][Br]$.

Wavenumber obtained from FT-IR spectra recorded in the presence of 0 mM, 1 mM, 2 mM and 5 mM of $(C_2H_5)_4N^+Br^-$ at different concentrations of $[C_{14}mim][Br]$ in the aqueous media.

$\begin{array}{l} [C_{14}mim][Br] \ + \ concentrations \ of \\ (C_{2}H_{5}) \\ _{4}N^{+}Br^{-} \end{array}$	[C ₁₄ mim] [Br]/(mM)	Wavenumber/cm ⁻¹
$[C_{14}mim][Br] + 0 mM of (C_2H_5)$	1.262	3309
$_4N^+Br^-$	2.524	3275
	3.786	3315
$[C_{14}mim][Br] + 1 mM of (C_2H_5)$	1.068	3274
$_4N^+Br^-$	2.137	3264
	3.205	3256
$[C_{14}mim][Br] + 2 mM of (C_2H_5)$	0.908	3272
$_4N^+Br^-$	1.815	3274
	2.723	3280
$[C_{14}mim][Br] + 5 mM of (C_2H_5)$	0.682	3275
$_4N^+Br^-$	1.363	3276
	2.045	3270

4. Conclusion

In the current study, the effect of adding various concentrations of organic electrolyte $(C_2H_5)_4$ NBr on the micellization behavior of SAIL $[C_{14}mim][Br]$ have been analyzed by using various techniques

such as electrical conductivity measurement, refractive index measurement, UV-visible spectroscopy and FT-IR spectroscopy. The modulation in the aggregation behavior of SAIL [C₁₄mim][Br] has been observed on addition of organic electrolyte and with the change in temperature as depicted in Fig. 8. The results obtained by employing various techniques are quite comparable to one another. The decrease in value of CMC is observed by using (C_2H_5) ₄NBr as an additive indicating the addition of electrolyte favors the process of micellization as observed for various conventional ionic surfactants [60-62] and cationic SAILs [63,64]. The temperature dependence of CMC obtained by using electrical conductivity measurement have been employed to calculate various thermodynamic parameters of micellization and the trends obtained are explained in terms of change in concentration of organic electrolyte as well as temperature of the system. The standard Gibbs' free energy of micellization, ΔG_m^0 and standard enthalpy of micellization ΔH_m^0 have large negative value indicating the process of micellization is feasible and exothermic in nature. The values of standard entropy of micellization ΔS_m^0 reveals that the aggregation of [C₁₄mim] [Br] shifts from entropy driven to enthalpy driven with high contribution of organic electrolyte in the solution, indicating synergism in micellization process. Thus our study is conductive to adjust the CMC value of SAIL [C14mim][Br] aqueous solutions to the specific value by addition of electrolyte as well as by adjusting temperature for potential application of SAIL [C₁₄mim][Br] in variety of fields.



Fig. 8. Scheme showing the modulation in the aggregation behavior of [C14mim][Br] with the addition of electrolyte as well as with the change in temperature.

CRediT authorship contribution statement

Harsh Kumar: Conceptualization, Resources, Supervision, Writing review & editing. Gagandeep Kaur: Investigation, Writing - original draft. Priya: Investigation, Writing - original draft.

Declaration of competing interest

Authors declare no conflict of interest.

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Appendix A. Supplementary data

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