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Micellar Properties of Cationic Surfactants in Pure and mixed States.

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Final Report

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Abstract

To elucidate the role of organic solvents, in altering the micellization and interfacial behavior of Ionic Liquid based Surfactants (ILBSs), here we had investigated the effect of formamide (FA), glycerol (GLY), ethylene glycol (EG) and 1-propanol (PRO) on the aggregation and interfacial behavior of 1-tetradecyl-3-methylimidazolium bromide ($C_{14}mimBr$) and 1-hexadecyl-3-methylimidazolium bromide ($C_{16}mimBr$) ILs, in aqueous solution by conductometric and tensiometric techniques at 298.15 K. The aggregation behavior has been determined by studying the changes in critical micelle concentration (cmc), degree of counter ion binding (β), gibbs free energy of micellization (ΔG_m^0) and interfacial behavior by studying various surface parameters such as surface excess concentration (Γ_{max}), minimum area per surfactant molecule (A_{min}) at the air/solvent interface and surface pressure at the cmc (π_{cmc}). Micellization behavior was mainly studied in light of altering the relative permittivity of the medium and displacement of water layer by the organic solvent layer, which disfavors the micellization and as a result increases cmc. Effect of solvophobic parameter (S_p) and packing parameter (P) on the aggregation was also examined. The effect of organic solvents on the aggregation behavior and surface activity of ILBSs in aqueous medium is compared with the conventional cationic surfactants with similar alkyl chain.

Keywords: Critical micelle concentration, Relative permittivity of organic solvents, Ionic Liquid Based Surfactants, 1-tetradecyl-3-methylimidazolium bromide, 1-hexadecyl-3-methylimidazolium bromide.

Research Highlights

1. Organic solvent influences the micellization and surface activity of ionic liquid based surfactants.
2. Increasing organic solvent composition in water, cmc increases.
3. Organic solvent, disfavoring the micellization, displaces water layer at the interface.
4. Aggregation behavior of ILBSs is compared with conventional cationic surfactants.

We are Thankful to Dr. Naved Malek, Applied Chemistry Department, S. V. National Institute of Technology, Surat- 395 007, India for providing us instrumental facilities.

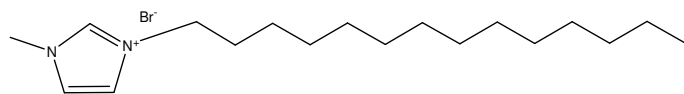
Introduction

Ionic liquids (ILs), composed of organic cations and organic/inorganic anions, are interesting greener replacements for traditional volatile organic compounds (VOCs) in several industrial applications and in fundamental research due to their unique physicochemical properties [1-8]. The long chain imidazolium based ionic liquids possesses better surface active properties than the conventional cationic surfactants [9-14] and found applications in various fields of science, including colloidal science [15, 16], catalysis [17-19], nanotechnology [20-24] and biomedicine [25,26] to name a few. Among these bunches of applications, several applications needs either water free or water-poor media [39] such as the mixture of water-organic solvent media. Among the possible alternatives to get best fit for such applications, traditional strategy to get newer ILs with structural variables such as alkyl chain length variations, various cations and/or anions [27-38] does not solve the purpose. The best possible way to alter the micellization behavior of these ionic liquid based surfactants (ILBSs) and make them a better choice for such applications requiring water poor media is by changing the polarity of the aqueous medium by the addition of organic solvents.

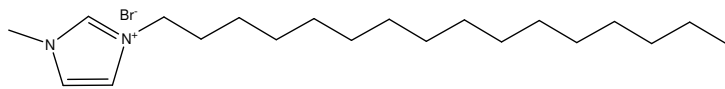
In this context, Wang et al. [40, 41] had studied the aggregation behavior of 1-dodecyl-3-methylimidazolium bromide, ($C_{12}mimBr$) in various water-organic solvents mixtures and reported that with increasing the organic solvent proportion in water, there appears significant increase in cmc and decrease in aggregation number (N_{agg}) and size of the aggregates. Recently, micellization and surface adsorption behavior of $C_{12}mimBr$ was studied in aqueous solution in the presence of several organic solvents and the results have been compared with the traditional cationic surfactant with same alkyl chain length. The results show that the solvents having larger dielectric constant act as co-solvents and the more hydrophobic solvents acts as co-surfactants [42]. Han and his co-workers [43] investigated the aggregation behavior of 1-butyl-3-methylimidazolium tetrafluoroborate (C_4mimBF_4) and 1-butyl-3-methylimidazolium hexafluorophosphate (C_4mimPF_6) in organic solvents by UV-Vis spectroscopy and conductivity measurements and concluded that aggregation depends on the dielectric constant of the solvents. The Phase behavior of ternary systems involving IL, water and different long chain alcohols was investigated by polarized optical microscopy and small-angle X-ray scattering techniques [44]. Effect of organic solvent addition on the aggregation behavior of 1-hexadecyl-3-

butylimidazolium bromide and 1,3-didodecylimidazolium bromide in water was studied by Pino et al [45]. The aggregation behavior of 1-dodecyl-3-methylimidazolium chloride was studied in various concentrations of water-methanol mixtures and the role of methanol as co-surfactant at lower concentration and as co-solvent at higher concentration [46]. As per our knowledge, further literature studying the aggregation behavior of ILBSs in presence of organic solvents in aqueous medium is not available.

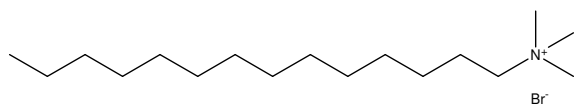
To gain further insight into the influence of organic solvent addition to the micellization and interfacial behavior of ILBSs in aqueous medium, here we have investigated the micellization and interfacial behavior of 1-tetradecyl-3-methylimidazolium bromide ($C_{14}mimBr$) and 1-hexadecyl-3-methylimidazolium bromide ($C_{16}mimBr$) in water in the presence of different organic solvent with variable polarity (Formamide (FA), glycerol (GLY), ethylene glycol (EG), 1-propanol (PRO)) by electrical conductivity and surface tension measurements at 298.15 K. In addition to investigating relevant micellization and surface properties of these ILBSs, we have compared the micellization properties with the conventional cationic surfactants having similar carbon chain length i.e. Tetradecyltrimethylammonium bromide, ($C_{14}TAB$) and Cetyltrimethylammonium bromide, ($C_{16}TAB$). The aim of this work is to understand the factors influencing the micellization of ILBSs in different composition of solvents. This would extend our knowledge on the aggregation behavior of ILBSs by solvent incorporation.



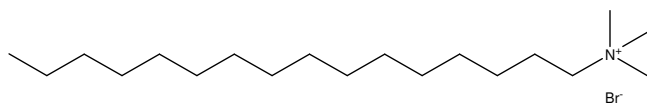
1-Tetradecyl 3-methyl imidazolium bromide



1-Hexadecyl 3- methylimidazolium bromide



Tetradecyltrimethyl ammonium bromide



Cetyltrimethyl ammonium bromide

Scheme 1: Structures of C₁₄mimBr, C₁₆mimBr, C₁₄TAB, and C₁₆TAB.

Experimental Procedures

Materials

The cationic surfactants tetradecyltrimethyl ammonium bromide (C_{14} TAB) and cetyltrimethyl ammonium bromide (C_{16} TAB) were purchased from Aldrich LTD ($\geq 99\%$) and used as received. ILBSs (C_{14} mimBr and C_{16} mimBr) were synthesized as per the previously published procedure[47-50], by reacting N-methyl imidazole(0.10 mol) with respective alkyl bromides (0.13 mol) in toluene for 24 h at 80°C . The resulting salts were recrystallized from ethyl acetate three times to yield white crystalline solids. The products were dried in vacuum for 48 hours prior to use. Karl-Fischer analysis (Metrohm, 890 Titrando) of the samples indicated that the water content was reduced to less than 100 ppm for both of the ILBSs. The mass fraction purities of the obtained ILBSs are greater than 99.5 %. The prepared ILBSs were characterized using ^1H NMR (Bruker 400 MHz) to confirm the absence of any major impurity. Absence of minimum around the breakpoint in the surface tension graph confirms the absence of any surface impurity in the synthesized ILs. Formamide (Merck, 99%), Glycerol (Merck, 99%), Ethylene glycol (Merck, 99%), 1-propanol (Merck, 99%), double distilled deionized water was used from chemical lab. Stock solutions of organic solvents were prepared using double distilled deionized water. The conductivity of the water was $3.1\text{-}3.4 \mu\text{Scm}^{-1}$ throughout the experiments.

Methods

Electrical Conductivity Measurements:

Aqueous solutions of C_n TAB & C_n mimBr ($n=14$ and 16) were prepared by weight using an analytical balance with a precision of ± 0.0001 g (B 204-S, Mettler Toledo, Switzerland, operated in a dry box) in Millipore grade double distilled deionized water. Electrical conductivities were measured at 298.15 ± 0.1 K by a digital microprocessor based conductivity meter (EUTECH PC 6000) from Eutech Instruments (Singapore) having a sensitivity of $0.1 \mu\text{Scm}^{-1}$ with an accuracy of 0.5%. The temperature was maintained constant within 0.1 K using constant temperature bath. The dip type conductivity probe (EC-CONSEN 21B) provided with the instrument has an inbuilt temperature probe. Prior to measurements, probe was calibrated with the aqueous KCl solutions

in the concentration range of 0.01–1.0 molkg⁻¹. At least three repetitive measurements were made for each concentration and only the mean values were taken into consideration.

Surface Tension Measurements:

The tensiometric experiments were performed using a platinum ring by the ring detachment method with a Kruss (Germany) Model K9 tensiometer at 298.15 K ±0.1 K. The temperature was maintained constant within 0.1 K using a constant temperature bath. Double distilled deionized water having surface tension of ±72.5 mNm⁻¹ at 298.15 ±0.1 K was used for calibrating the instrument. Surfactant concentrations were varied by adding concentrated surfactant solution in small installments, and the readings were noted after thorough mixing and temperature equilibration. The measured surface tension values were corrected according to the procedure of Harkins and Jordan in-built in the instrument software. The accuracy of γ measurements was within 0.1 mN m⁻¹.

Results and Discussions

Electrical Conductivity Measurement

The representative plots for the specific conductivity of the studied C₁₄mimBr, ILBSs in the presence of different composition of the most (FA, $\epsilon = 111$) and the least (Pro, $\epsilon = 20.45$) polar organic solvent used in the present investigation are drawn in Fig 1. With increasing the FA content, conductivity increases whereas reverse trend is observed for the organic solvents having relative permittivity less than the water, i.e. PRO. This is due to the fact that with increasing relative permittivity of the solution (i.e. by FA content), cation-anion interaction in the solution decreases, which leads to the higher mobility of the monomers and hence conductivity increases. Reverse is the case for the organic solvents with lesser relative permittivity than water [51, 52]. Comparing the specific conductivity of the conventional surfactants with ILBSs having similar alkyl chain length (Fig. S1), it was observed that with increasing the size of the cations, ionic solvation and the limiting ionic conductivity decreases, which reduces the charge transport as well as the mobility and as a result conductivity decreases in ILBSs [52].

The critical micelle concentration (cmc) values of the ILBSs(C_n mimBr, $n= 14$ and 16) and the conventional surfactants (C_n TAB, $n= 14$ and 16) in water-organic solvent mixtures with different compositions were determined from the conductivity plot. As observed (Figs. S2 (a-d)), the break point in the plot, which is routinely used to determine the cmc, is not clearly defined. In this case, cmc and counter-ion binding (β) determined by this method may lead to high degree of uncertainty. To avoid such erroneous data, we have determined the cmc and β for the studied surfactants and ILBSs in different mixed solvents by the Carpena [53] method. As per the proposed method, the experimental data were fitted to a simple non-linear function, which was obtained by direct integration of the Boltzmann type sigmoid function from Origin Pro 8 programme. The cmc and β of C_n TAB and C_n mimBr ($n=14$ and 16) in aqueous and different mixed solvents are presented in Table 1 and found to be in good agreement with the literature [52, 54-63].

Table 1: Critical micelle concentration CMC, counter-ion binding β , standard Gibbs energies of micellization ΔG_m^0 and solvophobic parameter Sp for the C_n TAB and $[C_n\text{mim}][\text{Br}]$ (n=14 and 16) in different solvents at 298.15 K.

Surfactant/ ILBSs	System	Solvent (v/v) %	cmc (mmol.dm ⁻³)		β	ΔG_m^0 (kJ mol ⁻¹)	Sp	
			Cond.	ST				
C_{14} TAB	H ₂ O	0	3.66	3.45	0.70	-40.40	1.000	
	Formamide	10	5.55	5.42	0.69	-38.70	0.945	
		20	5.89	5.80	0.67	-37.80	0.889	
		30	6.75	6.55	0.64	-36.56	0.832	
	Glycerol	10	5.50	5.25	0.68	-38.61	-	
		20	6.39	6.14	0.65	-37.09		
		30	6.73	6.42	0.63	-36.43		
	EG	10	4.66	4.18	0.65	-38.43	0.914	
		20	5.71	5.20	0.60	-36.41	0.856	
		30	6.39	6.18	0.57	-35.29	0.797	
	1-Propanol	10	3.97	3.75	0.59	-37.51	0.892	
		20	5.03	4.83	0.48	-34.21	0.811	
		30	6.77	6.03	0.32	-29.45	0.715	
	C_{16} TAB	H ₂ O	0	1.00	0.92	0.44	-38.99	-
		Formamide	10	1.55	1.51	0.42	-36.88	0.945
20			2.33	2.29	0.40	-34.99	0.889	
30			2.98	2.90	0.36	-33.21	0.832	
Glycerol		10	1.37	1.06	0.34	-35.32	-	
		20	1.94	1.13	0.31	-34.77		
		30	2.17	1.80	0.23	-31.61		
EG		10	1.14	0.98	0.29	-34.55	0.914	
		20	1.26	1.06	0.28	-34.03	0.856	
		30	1.96	1.13	0.22	-30.99	0.797	
1-Propanol		10	1.11	0.90	0.25	-33.62	0.892	
		20	1.21	1.01	0.22	-32.39	0.811	
		30	1.41	1.11	0.18	-30.88	0.715	
C_{14} mimBr		H ₂ O	0	2.61	2.43	0.75	-43.22	-
		Formamide	10	3.43	3.21	0.77	-42.50	0.945
	20		3.78	3.46	0.74	-41.52	0.889	
	30		4.04	3.96	0.72	-40.62	0.832	
	Glycerol	10	3.11	2.95	0.74	-42.22	-	
		20	3.58	3.20	0.73	-41.37		
		30	3.89	3.71	0.71	-40.54		
	EG	10	2.78	2.62	0.71	-41.96	0.914	
		20	3.43	3.01	0.67	-40.13	0.856	
		30	3.73	3.59	0.62	-38.67	0.797	
	1-Propanol	10	2.68	2.52	0.62	-39.79	0.892	
		20	3.30	2.84	0.59	-38.27	0.811	
		30	3.60	3.15	0.56	-37.25	0.715	
	C_{16} mim Br	H ₂ O	0	0.66	0.76	0.67	-46.87	-
		Formamide	10	0.76	0.87	0.65	-45.76	0.945
20			0.94	0.97	0.59	-43.38	0.889	
30			1.13	1.08	0.54	-41.66	0.832	

	Glycerol	10	0.74	0.86	0.62	-45.19	-
		20	0.85	0.92	0.57	-43.24	
		30	1.04	1.02	0.52	-40.42	
	EG	10	0.70	0.80	0.60	-44.81	0.914
		20	0.83	0.86	0.55	-42.64	0.856
		30	1.03	0.91	0.50	-40.18	0.797
	1-Propanol	10	0.68	0.76	0.56	-43.86	0.892
		20	0.76	0.80	0.52	-42.07	0.811
		30	0.85	0.90	0.45	-39.71	0.715

In the context of our investigation, it is illustrative to compare the effect of organic solvent addition on the micellization of ILBSs, with that of conventional surfactant, a representative member of that family whose aggregation behavior in mixed solvent system has been studied earlier as well as here [54-70]. As reported in Table 1, cmc of the aqueous as well as the mixed solvents for ILBSs are lower than their analogous conventional surfactants, which indicate the superior surface activity of the former [42,71]. The only structural dissimilarity is of head group, the methylimidazolium head group, which is less polar and reduces the electrostatic repulsion between the ionic head groups making the micellization process more spontaneous and resulted in lower cmc.

To get further insight into the micellization behavior of ILBSs in different solvent media of varying polarity, here we have examined the effect of different organic solvent compositions at fixed temperature of 298.15 K. With increasing concentration of the organic solvents (Table 1, Fig. 2), cmc of the investigated ILBSs and cationic surfactants increases, similar to C₁₂TAB [72], C₁₄TAB [26, 72-75], C₁₆TAB [54, 72] and for various ILBSs [40-46]. The formations of aggregates in these amphiphiles are the result of the balance between the two opposite effects including the electrostatic repulsion between the ionic head groups and/or attractive interaction between the hydrophobic chains [40, 42, 80-83]. Here, the elevation in the cmc with increasing the hydrophobicity of the medium (by increasing the organic solvent content) can be explained by two factors: (i) with reducing the polarity of the medium, the repulsion between the ionic head group increases and attractive hydrophobic interaction between the alkyl chains of the surfactants increases, which eventually disfavor the micellization, and (ii) the solubility of the surfactants increases with reducing the cohesive energy density of the mixture [73]. In other words, addition of the organic solvents will diminish the hydrophobic effect by breaking the water structure and increases the cmc [84].

Results from Table 1 shows that cmc and β increases more in case of FA than in GLY, EG and PRO for the studied systems. The value of β decreases with increasing the organic solvent composition as well as with decreasing the relative permittivity of the solvent, which indicates the less favorable aggregation process. Decrease in the β values indicates the weaker binding of the anions on the aggregate surfaces.

For the sake of comparison, we have computed the change in the cmc on the addition of different organic solvents at fixed concentration. For instance, for the addition of 10 wt% of the organic solvents cmc increases 27 %, 37%, 31% and 15% for FA, 23%, 27%, 19%, and 12% for GLY, 16%, 14%, 7% and 5% for EG and 8%, 11%, 3% and 3% for PRO for the C₁₄TAB, C₁₆TAB, C₁₄mimBr and C₁₆mimBr respectively. The results are not surprising as with decreasing the relative permittivity of the solution, cmc decreases in order of FA>GLY> EG> PRO. Ruiz et al investigated similar observation for the conventional surfactant C₁₄TAB in different composition of the polar solvents [85].

The effect of organic solvent composition on the aggregation of the studied surfactants/ILBSs can be quantified by the Gibbs energy of micellization, ΔG_m^0 , calculated from the cmc and β values by [40, 83, 87]:

$$\Delta G_m^0 = (2 - \alpha) RT \ln X_{cmc} = (1 + \beta) RT \ln \frac{C_m}{55.4} \quad (1)$$

Where, X_{cmc} is the cmc in mole fraction unit, C_{cmc} is that in mol dm⁻³, R is the gas constant, T is the temperature, α is the micellar ionization degree, and 55.4 comes from that 1 dm³ of water corresponds to 55.4 moles of water at 298.15 K. cmc values are in the molar fraction scale.

For neat C₁₄TAB and C₁₆TAB, ΔG_m^0 are in good agreement with the literature [73, 88, 89]. With increasing alkyl chain length, both in conventional surfactants and ILBSs, ΔG_m^0 becomes more negative indicating favorable aggregation in higher alkyl chain length surfactants [89]. For the addition of 20 wt% EG, the ΔG_m^0 for C₁₄TAB (-36.41 kJmol⁻¹) and C₁₆TAB (-34.03 kJmol⁻¹) and are in good agreement with previous studies [52, 86]. For C₁₆mimBr, ΔG_m^0 changes from -44.81 to -40.18 kJmol⁻¹ for the addition of 10 wt% to 30 wt% EG, which is similar to its

analogous single chain cationic surfactant *i.e.* C₁₆TAB (Table 1). ΔG_m^0 for C₁₂mimBr for 10 wt% addition of EG in aqueous solution was reported to be -36.0 kJ mol⁻¹ [40], whereas for C₁₄mimBr and C₁₆mimBr we obtained the results to be -41.96 kJ mol⁻¹ and -44.81 kJ mol⁻¹ respectively, the more negative values for the higher alkyl chain length ILBSs indicate that with increasing alkyl chain length, aggregation becomes more favorable. For the addition of 10 wt% EG, similar results for the single chain cationic surfactants, *i.e.* C₁₂TAB[94], C₁₄TAB[74] and C₁₆TAB[88] were reported.

As reported in Table 1, ΔG_m^0 increases with increasing the organic solvent composition in the mixture, suggesting the less favorable aggregation [40-42, 46, 55-70, 88-89]. Further, with increasing the organic solvent content in the medium, similar to β , ΔG_m^0 increases. The reasonable argument for this is the fact that, the transfer of the alkyl chain of surfactant/ILBS, which is principally located in the bulk phase, to the micellar core and the alkyl chains in the head groups of the surfactant/ILBS from the bulk phase into the micellar surface is less favorable [68, 87-97]. This prediction has the experimental evidence by the surface tension results we obtained in the later stage of the manuscript.

To understand the interaction between the alkyl chains of the amphiphiles with the solvents, it is necessary to understand the mixture hydrophobicity [80]. Solvophobic parameter (S_p) is used to measure the above-mentioned interaction and was defined by Abraham et al [90]. S_p values for the pure solvents are found in literature, whereas for the mixtures most recently, Wang et al [40] have developed a correlation method for the prediction of the S_p values at any composition of the organic solvent mixtures with water. The linear relationship derived by the aforementioned authors between the S_p and the volume fraction of the organic solvents added in to the water is used here (Table 1).

With decreasing S_p values (Table 1), cmc increases which indicates the less favorable aggregation. With decreasing S_p values, the interaction of the IL alkyl chain with organic solvents increases and increases the cmc. The knowledge of S_p values for the particular solvent composition will help us to modulate the aggregation property of the ILBSs as well as the conventional surfactants for the particular application. S_p values for the GLY are not reported due to the unavailability in the literature. In a similar fashion, the S_p values are directly

proportional to the β values. With increasing the solvent solvophobicity, the anions bind weakly and are responsible for the less favorable aggregation. Rodriguez et al [91] and Wang et al [40] observed similar observation for the conventional surfactants and ILBSs respectively in various organic mixtures with varying polarity.

Surface Tension Measurement

Surface activities of surfactants and ILBSs in pure water as well as in water-organic solvent mixtures were evaluated by measuring surface tension at 298.15 K. In general, surfactants orient at the air-solution interface and reduces the surface tension till the concentration reaches to the maximum. The concentration after which surface tension does not decrease further is called the cmc and the corresponding surface tension is known as γ_{cmc} , which is the measure of the surfactant efficiency to accommodate at the air-solution interface. The less the γ_{cmc} , the more the surface active the amphiphile is cmc of the surfactant and ILBSs in aqueous as well as in the mixed solvent, obtained through the γ versus log [surfactant/ILBSs] plot are depicted in Table 2 and are in good agreement with the literature [86,92,93] and with the conductivity method used in the current investigation.

The ability of the ILBSs to decrease the surface tension of water is higher than that of the corresponding conventional surfactant with the similar alkyl chain length. This fact sheds the light on the better surface activity of the latter [42]. A careful examination of the FigsS3 (a-d) reveals that as the organic solvent composition increases, surface tension decreases. The cmc and γ_{cmc} values for the corresponding ILBSs and conventional surfactants are listed in Table 2. Lower cmc and γ_{cmc} values for ILBSs than the conventional surfactants (Table 2) indicate the better surface activity of the former. Micelle formations in the surface-active molecules are due to the contribution of the electrostatic and hydrophobic interactions[93]. The reason for the better activity in ILBSs is relatively smaller electrostatic repulsion between the bulky head groups of the cations. The delocalized positive charge on the imidazolium ring and the ubiquitous hydrogen bonds among the imidazolium cations [94, 95] reduces the electrostatic repulsion and hence the cmc.

Table 2: Critical Micellar Concentration (cmc), Excess Surface Concentration (Γ_{\max}), Minimum Area Per Molecule (A_{\min}), Surface Pressure at the cmc (Π_{cmc}), and Gibbs Energy of Adsorption (ΔG_{ads}^0) for the C_n TAB and $[C_n\text{mim}][\text{Br}]$ ($n=14$ and 16) in different solvents at 298.15 K.

Surfactant/ ILBSs	System	Solvent (v/v) %	CMC	γ_{CMC}	Π_{cmc}	10^6 Γ_{\max}	A_{\min}	ΔG_{ads}^0	P	
			mmol.dm ⁻³		Nm ⁻¹	mol m ⁻²	nm ² molec ule ⁻¹	kJ mol ⁻¹		
C_{14} TAB	H ₂ O	0	3.45	40.00	32.50	2.18	0.80	-38.83	0.26	
	Formamide	10	5.42	41.70	18.10	1.32	1.25	-35.67	0.17	
		20	5.80	41.90	18.90	1.09	1.52	-38.66	0.14	
		30	6.55	42.10	21.00	0.92	1.81	-43.28	0.12	
	Glycerol	10	5.25	41.40	22.10	1.68	0.99	-35.13	0.21	
		20	6.14	41.50	19.80	1.53	1.08	-33.74	0.19	
		30	6.42	41.70	18.10	1.40	1.19	-33.36	0.17	
	EG	10	4.18	40.40	28.70	1.97	0.84	-36.96	0.25	
		20	5.20	40.60	27.70	1.78	0.90	-36.42	0.23	
		30	6.18	40.70	24.60	1.55	1.07	-35.78	0.20	
	1-propanol	10	3.75	31.70	10.40	1.06	1.57	-31.85	0.13	
		20	4.83	31.00	8.80	0.90	1.85	-29.43	0.11	
		30	6.03	28.10	7.70	0.73	2.27	-27.24	0.09	
	C_{16} TAB	H ₂ O	0	0.92	40.80	31.40	2.30	0.72	-38.55	0.29
		Formamide	10	1.51	42.50	17.10	1.78	0.93	-32.46	0.23
20			2.29	42.60	17.90	1.54	1.08	-32.75	0.19	
30			2.90	42.80	20.50	1.43	1.17	-34.13	0.18	
Glycerol		10	1.06	41.80	21.50	2.09	0.80	-32.72	0.26	
		20	1.13	41.90	19.20	1.91	0.81	-31.90	0.26	
		30	1.80	42.20	18.00	1.74	0.95	-30.08	0.22	
EG		10	0.98	41.10	28.30	2.21	0.75	-34.99	0.28	
		20	1.06	41.30	26.70	2.02	0.82	-34.79	0.25	
		30	1.13	41.50	24.00	1.81	0.89	-32.66	0.24	
1-propanol		10	0.90	32.30	10.20	1.13	1.47	-30.94	0.14	
		20	1.01	31.40	8.20	0.99	1.67	-29.13	0.13	
		30	1.11	28.60	7.10	0.92	1.80	-27.59	0.12	
C_{14} mimBr		H ₂ O	0	2.43	39.10	33.70	1.98	0.84	-42.86	0.25
		Formamide	10	3.21	37.30	22.20	1.54	1.08	-39.60	0.19
	20		3.46	37.50	23.40	1.43	1.16	-40.85	0.18	
	30		3.96	37.70	25.70	1.37	1.21	-42.34	0.17	
	Glycerol	10	2.95	36.90	26.80	1.75	0.95	-40.47	0.22	
		20	3.20	37.10	24.40	1.59	1.05	-40.03	0.20	
		30	3.71	37.40	23.00	1.45	1.15	-39.60	0.18	
	EG	10	2.62	36.40	33.00	1.89	0.88	-42.53	0.24	
		20	3.01	36.80	31.60	1.74	0.95	-42.19	0.22	
		30	3.59	36.90	28.70	1.56	1.06	-41.03	0.20	
	1-Propanol	10	2.52	33.00	9.80	0.75	2.21	-37.10	0.09	
		20	2.84	29.40	9.50	0.68	2.45	-37.00	0.08	
		30	3.15	26.20	9.00	0.66	2.52	-35.92	0.08	
	C_{16} mimBr	H ₂ O	0	0.76	38.70	34.20	2.09	0.79	-46.03	0.27
		Formamide	10	0.87	36.50	22.90	1.72	0.96	-42.08	0.22
20	0.97		36.80	23.90	1.59	1.05	-42.48	0.20		

		30	1.08	37.10	26.10	1.45	1.14	-44.03	0.18
	Glycerol	10	0.86	36.20	27.30	1.85	0.90	-43.17	0.23
		20	0.92	36.40	25.30	1.66	1.00	-42.50	0.21
		30	1.02	36.70	23.60	1.55	1.07	-41.28	0.20
		10	0.80	35.90	33.60	1.95	0.85	-45.52	0.25
	EG	20	0.86	36.10	31.90	1.80	0.92	-44.67	0.23
		30	0.91	36.20	29.60	1.65	1.01	-43.64	0.21
		10	0.76	29.40	12.90	0.81	2.05	-44.98	0.10
	1-Propanol	20	0.80	28.60	10.80	0.71	2.33	-42.76	0.09
		30	0.90	25.80	9.70	0.69	2.39	-39.91	0.09

As reported in Table 2, with increasing concentration of the organic solvents, γ_{cmc} decreases more (except for FA), which indicates more close packing of the molecules at the interface and/or decreased water-water interaction due to the incorporation of the organic solvents [102]. This result also suggests that with increasing organic solvent composition, the water at the interface is displaced by the surfactant/ILBSs layer [42, 45, 46]. Pino et al [45] studied the effect of various organic solvents on the γ_{cmc} values of the long chain imidazolium based surfactant and observed two opposite trends irrespective to the solvent relative permittivity.

Surface tension data are used to calculate several surface parameters such as, the surface pressure at the cmc or the effectiveness of surface tension reduction (π_{cmc}), the maximum surface excess concentration (Γ_{max}) and the area occupied per molecule (A_{min}) at air-water interface.

The surface pressure at the cmc (π_{cmc}), a property of the surface-active agents which indicate the maximum reduction of the surface tension of the medium [96] was obtained by using the following equations:

$$\pi_{CMC} = \gamma_0 - \gamma_{cmc} \quad (2)$$

Where, γ_0 and γ_{cmc} are the surface tension of the solvent and surfactant/ILBSs solution at the cmc, respectively. The values of π_{cmc} (Table 2), which depends on the hydrophobicity of the medium decreases with increasing the organic solvent composition with lower relative permittivity than water, whereas for the FA, π_{cmc} increases with increasing its composition in water. Therefore, these ILBSs reduce the surface tension of the organic solvent less effectively with increasing the organic solvent composition in the solution [42, 45]. Also the values of π_{cmc}

decreases with increasing the number of alkyl chain length for conventional surfactant and increase with increasing the number of alkyl chain length for ILBSs. This is may be due to the adsorption efficiency of surfactant/ILBSs at air-solution interface increases with increasing the number of carbon atom, due to an increase in the hydrophobic interaction between surfactant/ILBSs monomers.[86, 97-100]. The efficiency of the micellization decreases in the presence of high composition of the organic solvents. For the specific composition of the organic solvent addition, π_{cmc} for the conventional surfactants and for the ILBSs increases in order of EG > Gly > FA > Pro.

Area per molecule at air/water interface and the maximum surface excess concentration (Γ_{max}) of the surfactant systems at the air/water interface are calculated by the application of Gibbs adsorption isotherm [101-102] as:

$$\Gamma_{max} = -\frac{1}{2.303nRT} C \xrightarrow{\text{lim}} CMC \left(\frac{\partial \gamma}{\partial \log C} \right) \quad (3)$$

Where, Γ_{max} is surface excess, R is the universal gas constant (8.314 Jmol⁻¹K⁻¹), C is the concentration of surfactant in bulk solution, and γ is the surface tension.

The effective area of surfactant molecule at air/water interface, A_{min} can be calculated by

$$A_{min} = 1 / (N_A \Gamma_{max}) \quad (4)$$

Where, N_A is Avogadro's number (6.022 × 10²³ mol⁻¹).

The values of Γ_{max} and A_{min} for the conventional surfactants and ILBSs in aqueous as well as water-organic solvent media are reported in Table -2 and are compared with the available literature and are in good agreement [93, 97]. The values of Γ_{max} for the conventional surfactants and ILBSs increases with increase the number of alkyl chain length indicates that more molecules adsorb at air/water interface, which is the result of higher hydrophobic interaction [86, 97-100]. With increasing organic solvent composition and the decreasing relative permittivity, Γ_{max} decreases and A_{min} shows the reverse trend than the Γ_{max} . The plausible reason for such behavior is the reduction of the hydrophobic interactions between the head groups of the surfactants molecules and displacement of the water layer from the air/solution interface by more hydrophobic solvent thereby inducing the weaker adsorption tendency [45, 103].

The Gibbs energy of adsorption (ΔG_{ads}^0) was determined from [64,86]:

$$\Delta G_{ads}^0 = \Delta G_m^0 - \frac{\Pi_{cmc}}{\Gamma_{max}} \quad (5)$$

Where the standard state in the surface phase is defined as the surface covered with a monolayer of surfactant at a surface pressure equal to zero. All the values of ΔG_{ads}^0 reported in Table 2 are negative, which shows that adsorption takes place spontaneously. As reported in Table 2, with increasing organic solvent composition, ΔG_{ads}^0 becomes less negative for the solvents having relative permittivity lesser than water (i.e GLY, EG and PRO) whereas for FA, reverse trend was observed. The values of ΔG_{ads}^0 reflect the efficiency of the surfactant to get adsorbed at the surface, which decreases with the addition of the organic solvents [81]. This investigation reveals the aggregation differences between the surface-active ILBSs and the traditional surfactants. Hydrogen bonds were suggested to play a dominant role in the aggregation of ILBSs in addition to coulombic and hydrophobic interactions. Compared with the traditional cationic surfactants, ILBSs displays a stronger aggregation due to the formation of the hydrogen-bonded network, which will results in the loose arrangements of imidazolium rings in the sub-aggregates of ILBSs. The higher negative value for ΔG_{ads}^0 denotes the higher efficiency of the surfactant to get adsorbed at the surface [82].

The above discussion has demonstrated that aggregation of cationic surfactant and ILBSs takes place in both aqueous and non-aqueous solutions. Alkyl chain length, cationic structure, and addition of organic solvents were found to have a vital effect on various thermodynamic and surface adsorption parameters. Judicious selection of these parameters along with the solvents can modulate the aggregation behaviors of ILBSs in solutions.

Packing Parameter (P)

The structure of the surfactant self-assembly or micelles influences the properties of the surfactants solution and consequently, the performance of surfactants in various applications to a larger extent. It is desirable to know the molecular structure of the surfactants which governs the application by the shape and size. In this connection, Tanford [104,105] explain various factors

which influences the formation of aggregates in the solution, their shape and size and most importantly why the aggregates attain finite size and particular shape. By applying thermodynamic principals and molecular packing considerations, Israelachvili, Mitchell and Ninham[106] proposed the concept of molecular packing parameter. By applying the concept one can predict the size and shape of the aggregate at equilibrium. Various groups had tried in past to predict the size and shape of the conventional surfactants aggregates by means of packing parameter [107-113] defined as:

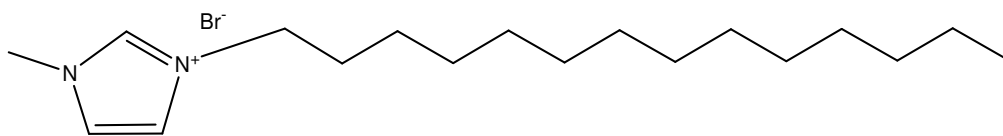
$$p = \frac{V_o}{lcA_{min}} \quad (6)$$

Where, V_o is the volume of the hydrophobic chain and can be determined by Tanford's equation as, [104,105], $V_o = (0.0274 + 0.0269 n_c)$, l_c is the maximum effective length or called as the critical chain length and can be determined by: $l_c \leq l_{max} \approx (0.154 + 0.126 n_c)$ [106]. According to the prediction of Israelachvili et al, for $P < 1/3$, the structure of the micelle will be spherical, for $1/3 < P < 1/2$, micelles will be nonspherical, for $1/2 < P < 1$, the micellar shape will be vesicles or bilayers and for $P > 1$, inverted structures will be predicted. From Table 2, it is predicted that all the conventional surfactants and ILBSs are spherical in shape [107,108]. With increasing the organic solvent content, the packing of the aggregates decreases and loosely packed structure were formed of the type spherical in nature. Sharma et al [112] observed similar results for the addition of $C_{14}mimBr$ the conventional surfactant $C_{14}TAB$. With increasing EG and DMSO content in $C_{12}TAB$, Das et al observed decrease in the packing of the aggregates and the shape of the aggregates were found to be spherical [81].

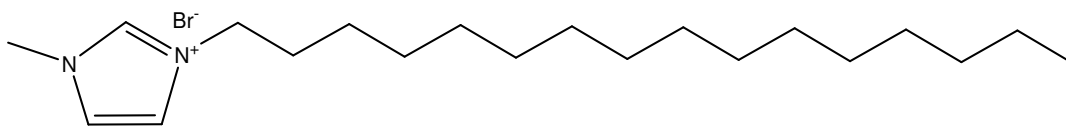
Conclusion

In the present investigation, we have examined the micellization and interfacial behavior of ionic liquid based surfactants (ILBSs), C_nmimBr ($n=14$ and 16) in the presence of several organic solvents in water through conductivity and surface tension measurements at 298.15K. The application of the study gives scientific investigators to use the present systems in the micellar systems needs water poor media. It is found that cmc increases by increasing the organic solvent content in aqueous solutions. Incorporating the solvents having higher relative permittivity makes the system more conductive whereas the less conductive organic solvent incorporation

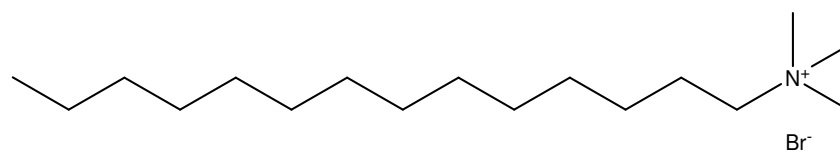
leads the system to be as relatively less conductive than the aqueous system with unfavorable micellization. Increasing the organic solvent content weakens the binding of the anions on the aggregate surfaces and makes the micellization process less unfavorable. Similarly the results of Gibbs energy of micellization also provide information related to the less favorable micellization behavior of the ILBSs in the presence of organic solvents. In the presence of organic solvents, the cmc values increase with decreasing solvophobic parameters, indicating that the aggregation of ILBSs is dominated by the interactions between alkyl chain of the IL and the solvents. The better surface activity of the ILBSs than the conventional cationic surfactants with same alkyl chain length is also studied in the present investigation by studying various surface parameters. Increasing the organic solvent content in water reduces the effectiveness of the ILBSs. Higher content of the organic solvents decreases the tendency of the surfactant molecules to get adsorb on the surfaces. The results of the Gibbs energy of adsorption also shed the light of the organic solvent content in the aqueous ILBSs solution. Overall, the study denotes the role of the organic solvents on the micellization and interfacial behavior of the ILBSs in aqueous medium. The results will help the researchers to regulate the various aggregation parameters and interfacial phenomena of the ILBSs for the better tailor made properties of these new types of the surfactants which are higher surface active than the conventional cationic surfactants. The knowledge will open up the new era for the new ionic liquid–oil microemulsions systems and expand the potential applications of the ILBSs [113].



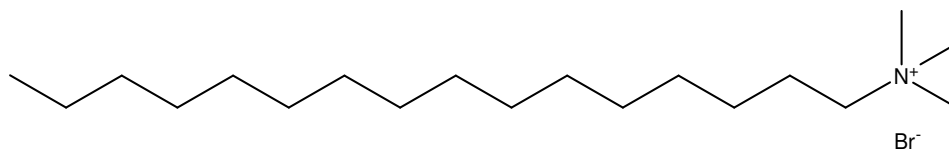
1-Tetradecyl 3-methyl imidazolium bromide



1-Hexadecyl 3- methylimidazolium bromide



Tetradecyltrimethyl ammonium bromide



Cetyltrimethyl ammonium bromide

Scheme 1: Structures of C₁₄mimBr, C₁₆mimBr, C₁₄TAB, and C₁₆TAB.

Calculations

The surface parameters are calculated as per the following relations [1-4]:

Effectiveness of surface tension reduction or The surface pressure at the cmc (π_{cmc}), a property of the surface-active agents which indicate the maximum reduction of the surface tension of the medium was obtained by using the following equations:

$$\pi_{cmc} = \gamma_0 - \gamma_{cmc} \quad (1)$$

Where γ_0 and γ_{cmc} are the surface tension of the solvent and surfactant/ILBS at cmc, respectively.

Area per molecule at air/water interface and the maximum surface excess concentration (Γ_{max}) of the surfactant systems at the air/water interface are calculated by:

$$\Gamma_{max} = -\frac{1}{2RT} \left(\frac{\partial \gamma}{\partial \ln C} \right)_T \quad (2)$$

Where, Γ_{max} is surface excess, R is the universal gas constant (8.314 Jmol⁻¹K⁻¹), C is the concentration of surfactant in bulk solution, and γ is the surface tension.

The effective area of surfactant molecule at air/water interface, A_{min} can be calculated by

$$A_{min} = 1 / (N_A \Gamma_{max}) \quad (3)$$

Where, N_A is Avogadro's number (6.022×10²³ mol⁻¹).

The Gibbs energy of adsorption (ΔG_{ads}^0) was determined from:

$$\Delta G_{ads}^0 = \Delta G_m^0 - \frac{\pi_{cmc}}{\Gamma_{max}} \quad (4)$$

Where the standard state in the surface phase is defined as the surface covered with a monolayer of surfactant at a surface pressure equal to zero.

The Gibbs energy of micellization, ΔG_m^0 , calculated from the cmc and β values by:

$$\Delta G_m^0 = (2 - \alpha) RT \ln X_{cmc} = (1 + \beta) RT \ln \frac{C_m}{55.4} \quad (5)$$

Where, X_{cmc} is the cmc in mole fraction unit, C_{cmc} is that in mol dm^{-3} , R is the gas constant, T is the temperature, α is the micellar ionization degree, and 55.4 comes from that 1 dm^3 of water corresponds to 55.4 moles of water at 298.15 K. cmc values are in the molar fraction scale.

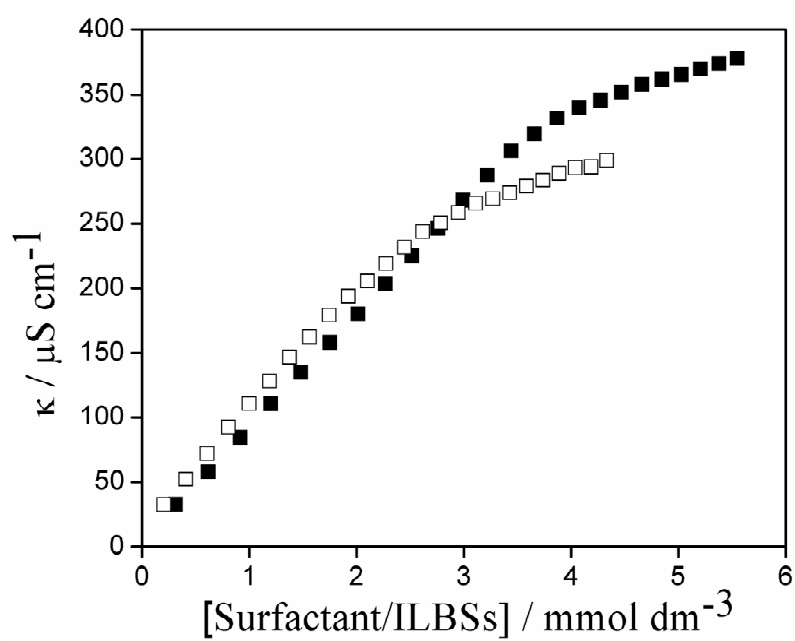


Fig S1: Plot of specific conductance (κ) vs concentration of (■) C₁₄mimBr and (□) C₁₄TAB in water at 298.15 K.

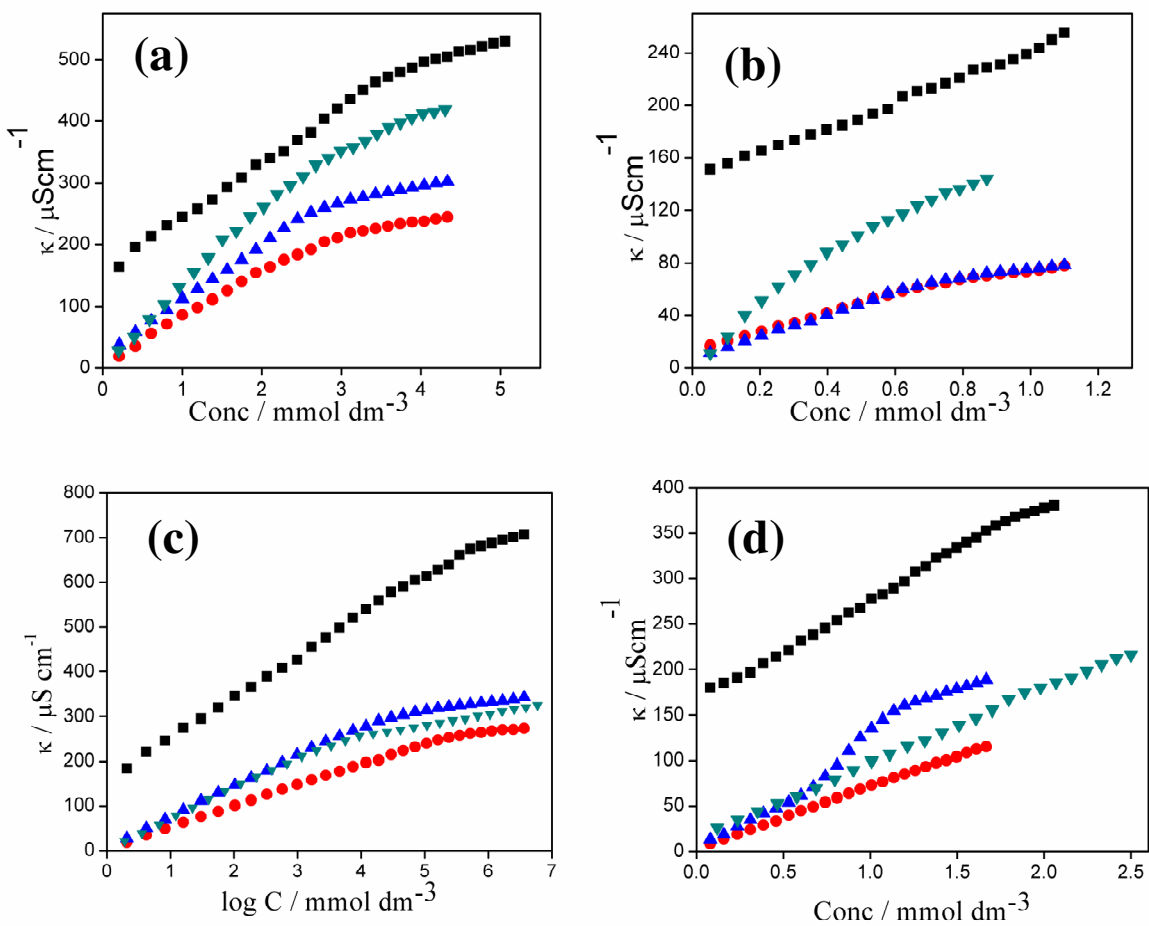


Fig S2: Plot of specific conductance (κ) vs concentration of (a) $\text{C}_{14}\text{mimBr}$ (b) $\text{C}_{16}\text{mimBr}$, (c) C_{14}TAB and (d) C_{16}TAB in 10% addition of (■FA, ●GLY, ▲EG, ▼PRO) at 298.15 K.

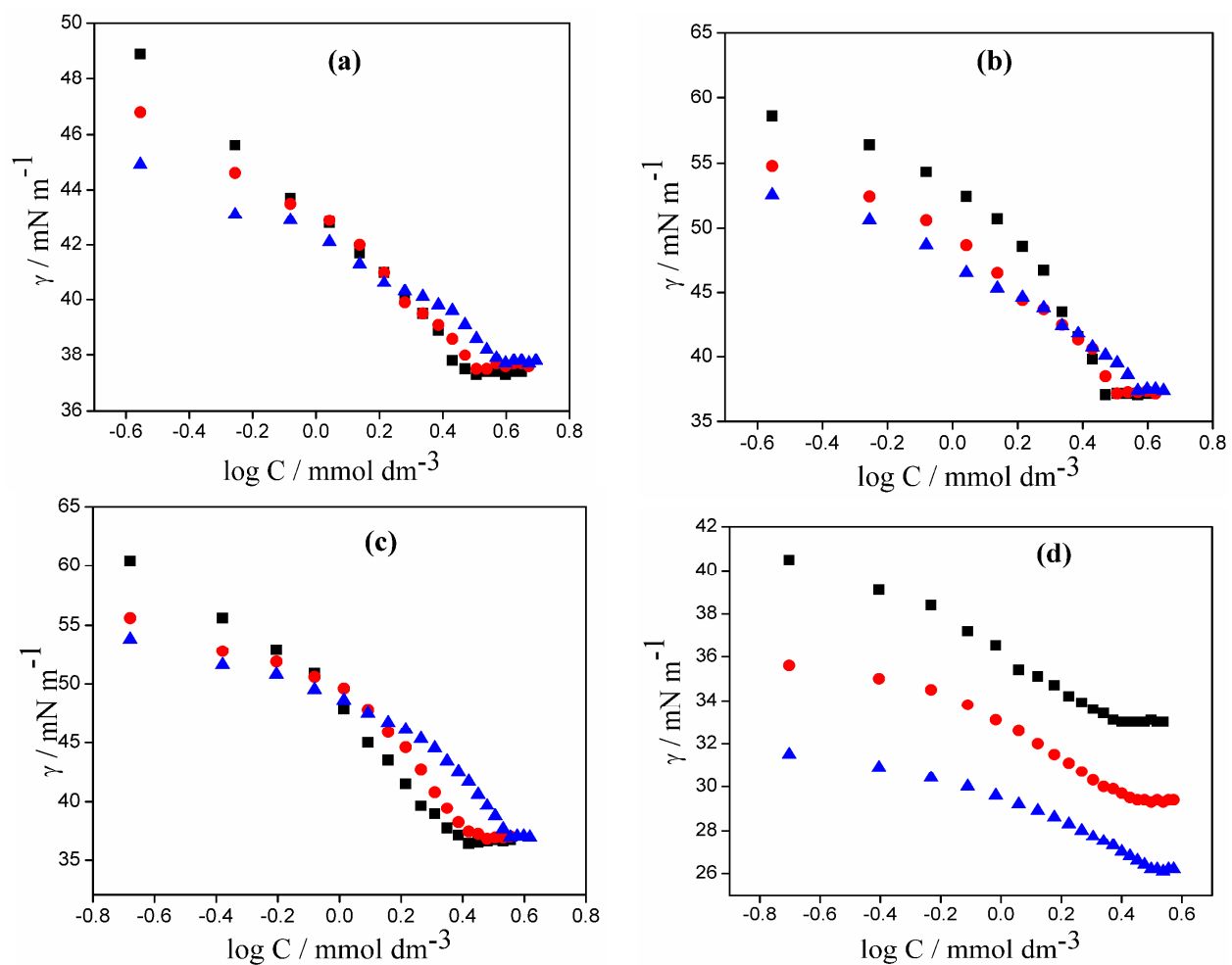


Fig S3: Plot of surface tension (γ) vs concentration of $[\text{C}_{14}\text{mim}][\text{Br}]$ in (a) Formamide, (b) Glycerol, (c) EG and (d) n-Propanol solvent at various composition (\blacksquare 10 wt%, \bullet 20wt%, \blacktriangle 30 wt %) at 298.15 K.

Calculation Purpose References

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