

Interaction between amphiphilic ionic liquid 1-butyl-3-methylimidazolium octyl sulfate and anionic polymer of sodium polystyrene sulfonate

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Abstract

The physicochemistry of interaction of the ionic liquid (IL), 1-butyl-3-methylimidazolium octylsulfate (C₄mim) (C₈OSO₃) with the anionic polymer sodium polystyrene sulfonate, (NaPSS) has been studied using tensiometry, conductometry and fluorimetry. The critical aggregation concentration (*cac*), the standard Gibbs free energy ΔG_m^0 , the standard enthalpy change ΔH_m^0 , and standard entropy change ΔS_m^0 , upon aggregation for the IL in solutions have been derived from the conductance data. Further to get the deeper insights into the aggregation process spectroscopic study using fluorescence measurements have been carried out. The aggregation behaviour observed from conductance, surface tension and fluorescence probe has been found to be in good agreement with each other. Behaviour of fluorescence probe confirms the binding interactions between IL and the polyelectrolyte

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1. Introduction:

Ionic liquids (ILs) have been intensively investigated in recent years. They are liquid around or below 100° C, and have unique properties such as nonvolatility, high stability, adjustable polarity, high ionic conductivity, and recyclability [1-12]. Besides, compared with conventional surfactants, the ionic liquid surfactants show several advantages due to the existence of imidazolium head groups. So they have promising applications like detergency [13], cosmetics [14], foods [15], paints [16], coatings [17], pharmaceutical [18] and nanotechnology [19]. Polyelectrolyte-ILs interactions have been widely studied for many years employing both classical and modern techniques. Das *et al.* investigated the interaction of an anionic polymer sodium carboxymethylcellulose (NaCMC) with 1-hexadecyl-3-methylimidazolium chloride [C16mim][Cl] in aqueous medium using electrical conductivity and surface tension measurements. They also investigated ion-association behaviour of [C16mim][Cl] in the pre-micellar region, and the counter-ion condensation behaviour of [NaCMC] [20]. Garcia *et al.* studied the binding of an anionic ionic liquid 1-butyl-3-methylimidazolium octyl sulfate, [C4mim][C8SO4] with a cationic surfactant hexadecyltrimethylammonium (CTAB) using surface tension, electrical conductivity, absorbance and dynamic light scattering (DLS) measurements and concluded that the *cac* values of this IL increase after surfactant adding, preventing the formation of the CTA-octylSO4 complexes [21]. Mahajan *et al.* have studied the interaction of poly sodium 4-styrene sulphonate (NaPSS), with cationic surface active imidazolium, [C_nmim][Cl] (n = 10, 12, 14) and demonstrated the effect of alkyl chain length on NaPSS/IL interactions [22]. Pal's group have studied the aggregation behaviour of 1-octyl-3-methylimidazolium bromide [C8mim][Br] and sodium polystyrene sulfonate (NaPSS) in aqueous solution by conductivity, surface of tension and fluorescence probe techniques, demonstrating the formation of amphiphillic aggregates in the mixtures of IL/NaPSS [23]. We have examined the IL/polyelectrolyte interaction in mixed aqueous solutions of cationic IL, [C4mim][C8OSO3] and anionic polyelectrolyte, NaPSS combining various techniques: tensiometry, conductimetry, and fluorimetry. The aggregation of the IL, [C4mim][C8OSO3] in aqueous solutions is strong enough to form micelles above their *cac* [24,25]. Both the cation and anion of [C4mim][C8OSO3], an amphiphillic IL are responsible for absorption at the air-water interface. The interpretation of the binding behaviour makes the way smoother for enhanced understanding of the mechanism of polyelectrolyte-ILs systems and will become more advantageous for upcoming applications.

2. Materials and methods:

An electronic balance (Japan, Model GR-202) made by A & D company, with precision of ±0.01mg is used to measure the required weights of components.

2.1 Materials:

The materials 1-butyl-3-methylimidazolium octylsulfate (C4mim)(C8OSO3), sodium polystyrene sulfonate (NaPSS) and pyrene were purchased from Sigma Aldrich, USA. All the solutions were prepared in triply distilled water while pyrene was prepared in methanol. All the chemicals were used without further purification.

2.2 Surface tension measurements:

Surface tension was measured on Du Nouy type tensiometer (Hardson and Co., Kolkata) using the ring detachment method. Temperature has been controlled using a thermostatic bath and double-jacketed dilution cell with an uncertainty of 0.01 K. All measurements were repeated at least thrice at temperature 298.15 K and the mean value was considered.

2.3. Conductivity measurements:

Electrical conductivities were measured at different temperature with a digital conductivity meter CM-183 microprocessor based EC-TDS analyzer with ATC probe and conductivity cell having platinized platinum electrodes which were purchased from Elico Ltd., India. The measurements have been performed in a double walled water jacketed flow dilution cell with an uncertainty of 1×10^{-2} K at a temperature range from 288.15 to 308.15 K. Prior measurements, cell was calibrated with the aqueous KCl solutions in the concentration range of 0.01-1.0 mol kg⁻¹. Three measurements were made for each concentration and only the mean values were considered. The uncertainty in conductivity measurements was found to be less than $\pm 4\%$.

2.4. Fluorescence measurements:

Fluorescence spectra were taken on model RF-5301Pc with blazed holographic grating excitation and emission monochromators fitted with 150W xenon lamp purchased from Shimadzu and using quartz cuvette. The pyrene solution was prepared in methanol as stock solution and fresh solutions of (C₄mim)(C₈OSO₃) with NaPSS at different concentrations were prepared in doubly distilled de-ionized degassed water. The emission spectra of pyrene was recorded in the wavelength range of 350-500 nm at an excitation wavelength of 334 nm and fixing the slit width of emission and excitation to 3 and 3 nm respectively. the ratio (I_I/I_{III}) of the fluorescence intensities of the first vibronic peak (373 nm, I_I) to third peak (384 nm, I_{III}) was calculated, it is very sensitive to the polarity of surroundings [26].

3. Results and discussion:

3.1 Effect of NaPSS concentration on the (C₄mim)(C₈OSO₃)-NaPSS interaction using Surface tension technique:

The surface tension measurements were made to evaluate the surface activity of the IL in aqueous NaPSS solutions and also to determine the critical aggregation concentration (cac). Tensiometric profiles of [C₄mim][C₈OSO₃] in NaPSS solutions are compared in Figure 1.

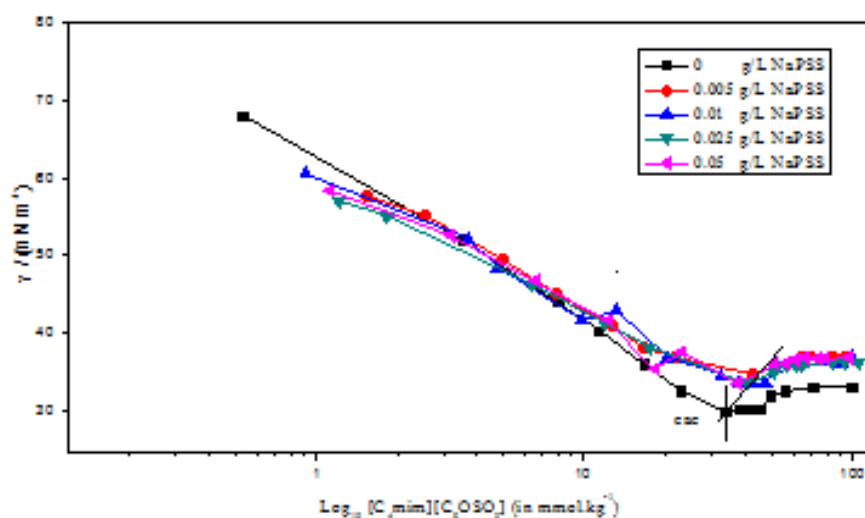


Fig. 1. Surface Tension graphs between γ (in mN m⁻¹) and (C₄mim)(C₈OSO₃) (in mmol kg⁻¹) at 288.15 K for different NaPSS concentrations: (■), 0.0 g/L; (●), 0.005 g/L; (▲), 0.01 g/L; (▼), 0.025 g/L; (◄), 0.05 g/L.

The large decrease of the surface tension of all studied systems observed in this study after adding of IL can be attributed to this possible effect : the adsorption of the aggregates and or a modification of the equilibrium between isolated and aggregates molecules. With further addition of IL, γ remains constant in a narrow range up to that concentration and then starts increasing. At cac, also called as critical aggregation concentration (cac) the $[C_8mim]^+$ started interacting with the NaPSS chain in bulk forming small assemblies as a consequence of initial monomeric adsorption leading to increase in local IL concentration in vicinity of polymer backbone. A decrease in surface tension of IL solution upon addition of NaPSS has been shown in the very dilute IL. Indeed, while $[C_4mim][C_8OSO_3]$ did not exhibit any preference of its NaPSS sequences for the surface, both NaPSS/IL mixtures segregate surfactant monomers at the interface. The obtained cac value of $[C_4mim][C_8OSO_3]$ in aqueous solutions is given in Table 1.

Table 1: The critical aggregation concentration (cac) at different molalities for various NaPSS concentrations measured by Fluorescence and Surface Tension methods

[NaPSS] (g /L)	cac (mmol kg ⁻¹) (Fluorescence)	cac (mmol kg ⁻¹) (Surface Tension)
0.000	37.3	32.9
0.005	38.7	41.2
0.010	39.9	38.9
0.025	41.4	38.8
0.050	47.4	37.1

The order of cac values resulting from surface tension measurements for IL in presence of different concentration of NaPSS is 0 g/L < 0.005 g/L < 0.01 g/L < 0.025 g/L < 0.05 g/L. The observed cac sequence can be correlated to the hydrophobicity of constituent ions. At cac, the interfacially NaPSS-IL (monomer) complex starts transforming into NaPSS-IL (aggregate) complex with a decreased interfacial activity as indicated from increase in surface tension. The aggregate is supposed to be highly surface active and forms at a very low concentration because of the presence of electrostatic interaction between the polyelectrolyte and IL. This effect was already reported in earlier study where the tensiometric profiles of the NaPSS- $[C_8mim][Br]$ system were found to be much similar to our system. Increasing of the concentration of polyelectrolyte leads a prominent lowering in surface tension at lower IL concentrations as compared to the polyelectrolyte free case which is due to the co-adsorption of $[C_8mim][Br]$ and NaPSS at the interface [23]. Fluorescence measurements (discussed later) also display the formation of hydrophobic groups due to decrease in polarity. Similar type of behaviour is also observed in case of Gelatin-(C_4mim) (C_8OSO_3) system [33].

3.2 Conductance measurements:

The electrical conductivity for solutions of $[C_4mim][C_8OSO_3]$ in aqueous solutions of NaPSS at different concentration (0.005 g/L 0.01 g/L, 0.025 g/L and 0.05 g/L) are presented in Figures(2-4). The variation of κ is linear with increase in (C_4mim) (C_8OSO_3) and a steep change in value of κ is observed in figures (2-4). The cac values obtained from the break points at three different temperatures at four different concentrations are given in Table 3. Below cac, the specific conductance increases with a steep slope which is due to the contribution of more free-moving ions. While above cac, the aggregates formed with larger size (due to attraction of a fraction of counter ions on the micellar surface) reduce the number of current carriers and they have low mobility resulting in the increase in

conductivity but with a slower rate. The ratio of post-aggregation region to the pre-aggregation region gives the value of degree of dissociation, α [34-36]. The cac value of ($\approx 37 \text{ mmol kg}^{-1}$) at 298.15 K is obtained for the IL (C_4mim)(C_8OSO_3) which is somewhat lower than the conventional surfactant (Na)(C_8OSO_3) ($\text{cac} \approx 110 \text{ mmol kg}^{-1}$) [24], demonstrating that long-chain imidazolium ILs have superior capability for the formation of aggregates. The resulted lower cac value IL (C_4mim)(C_8OSO_3) may be due to the more effective screening of the intramolecular electrostatic repulsion of large size, hydrophobic imidazolium counter ions.

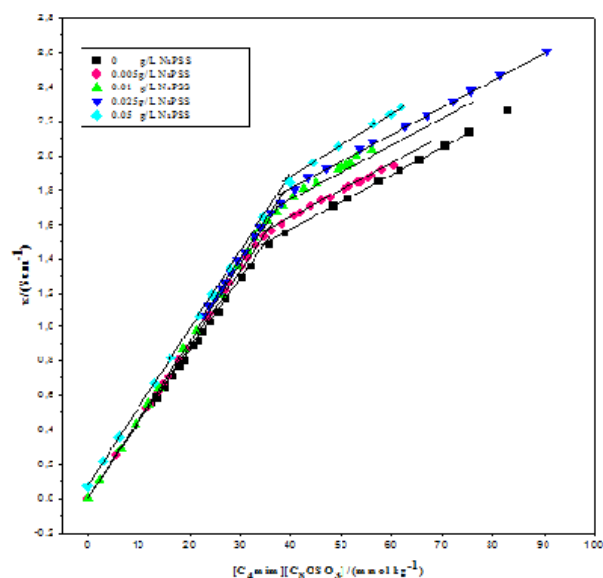


Fig. 2. Conductivity graphs between $\kappa/(\text{S cm}^{-1})$ and $(\text{C}_4\text{mim})(\text{C}_8\text{OSO}_3)$ (in mmol kg^{-1}) at 288.15 K for different NaPSS concentrations: (■), 0.0 g/L; (●), 0.005 g/L; (▲), 0.01 g/L; (▼), 0.025 g/L; (◆), 0.05 g/L.

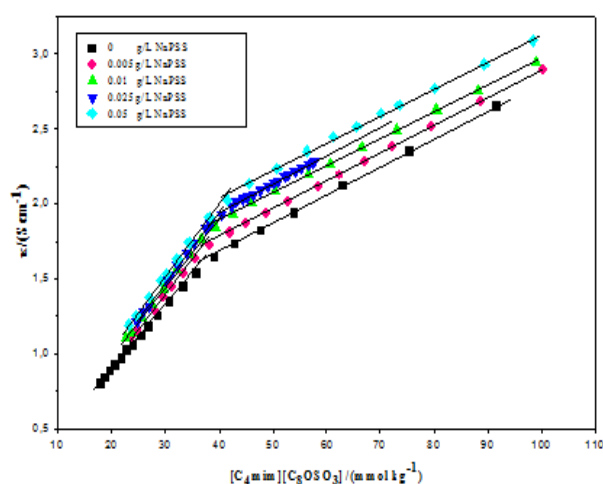


Fig. 3. Conductivity graphs between $\kappa/(\text{S cm}^{-1})$ and $(\text{C}_4\text{mim})(\text{C}_8\text{OSO}_3)$ (in mmol kg^{-1}) at 298.15 K for different NaPSS concentrations: (■), 0.0 g/L; (●), 0.005 g/L; (▲), 0.01 g/L; (▼), 0.025 g/L; (◆), 0.05 g/L.

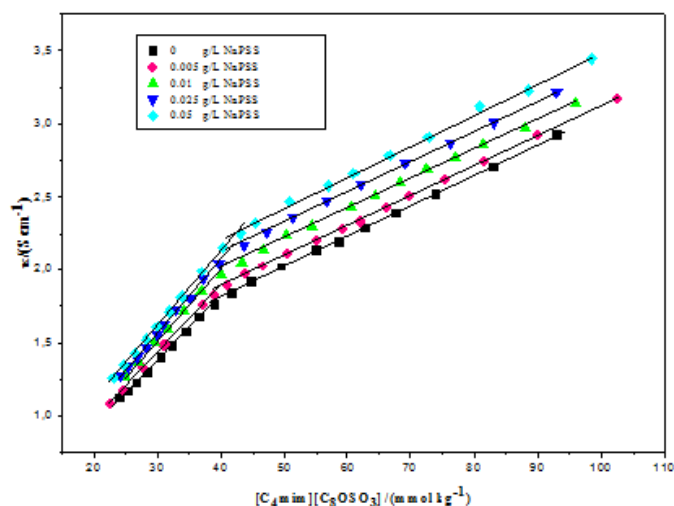


Fig. 4. Conductivity graphs between $\kappa/(\text{S cm}^{-1})$ and $(\text{C}_4\text{mim})(\text{C}_8\text{OSO}_3)$ (in mmol kg^{-1}) at 308.15 K for different NaPSS concentrations: (■), 0.0 g/L; (●), 0.005 g/L; (▲), 0.01 g/L; (▼), 0.025 g/L; (◆), 0.05 g/L.

From Fig. 2-4, it is clear that the cac of the $[\text{C}_4\text{mim}][\text{C}_8\text{OSO}_3]$ increases with an increase in the concentration of the NaPSS. This is due to the fact that there is an increase in the binding sites available for the IL monomers or micelle-like aggregates (not the true micelles) where they can bind with the polyelectrolyte. Therefore, it is quite obvious that on increasing concentration of polyelectrolyte more amount of the IL is required for binding. After binding of all sites, the IL molecules become independent to form micelles. The higher value of α of the complex micelles indicates that due to the interaction of IL with polyelectrolyte the degree of ionic dissociation increases. With increase in temperature the cac value increases as expected for conventional surfactants [37]. High temperature causes the disruption in water structures and results in the increase solubilization of surfactant molecules, along with delaying of aggregation process. To understand the driving force of aggregation, various thermodynamic parameters of aggregation from charge pseudo-phase separation model of micelle formation are calculated using equations (1) – (3):

$$\Delta G_m^0 = (2 - \alpha)RT \ln X_{\text{CAC}} \quad (1)$$

$$\Delta H_m^0 = -RT^2 \left[(2 - \alpha) \frac{d \ln X_{\text{CAC}}}{dT} + \ln X_{\text{CAC}} \frac{d(1 - \alpha)}{dT} \right] \quad (2)$$

$$\Delta S_m^0 = \frac{\Delta H_m^0 - \Delta G_m^0}{T} \quad (3)$$

where α is the degree of dissociation, R is gas constant, T is temperature and X_{CAC} is the cac expressed in terms of mole fraction, standard free energy change ΔG_m^0 , the standard enthalpy change ΔH_m^0 , and standard entropy change ΔS_m^0 , related with aggregation behavior of $(\text{C}_4\text{mim})(\text{C}_8\text{OSO}_3)$ in the solutions have been obtained and presented in Table 2. From Table 2, it is clear that α value increases with increase in temperature and decreases irregularly with increase in concentration of NaPSS. With increase in the concentration of NaPSS in the system the dissociation of IL decreases due to the interactions of the cationic part of IL to the anionic part of NaPSS and IL, leading to the decrease in value of α . As can be seen, the standard Gibbs free energy changes with different NaPSS concentrations are all negative, indicating that the formation of aggregates is spontaneous. The values of standard enthalpy change ΔH_m^0

are positive as well, implying that the aggregate formation process is endothermic. The entropy change, ΔS_m^o for the aggregation process is large and positive. When the concentration approaches cac, water structure around the monomers get highly disrupted due to movement of monomers towards each other.

Table 2: The Critical aggregation concentration (cac) of IL at different g/L of NaPSS at temperatures 288.15-318.15 K and at pressure $p = 0.1$ MPa and the corresponding values of various thermodynamic parameters of aggregation obtained from equations (1)-(3).

[NaPSS] (g /L)	cac ^a (mmol kg-1) (Conductance)	α	ΔG_m^0 (kJ. mol-1)	ΔH_m^0 (kJ .mol-1)	ΔS_m^0 (kJ. mol ⁻¹)
288.15 K					
0.000	34.8	0.396	-28.34	39.13	234.15
0.005	35.5	0.348	-29.11	39.67	238.69
0.010	37.5	0.371	-28.48	12.55	142.38
0.025	38.5	0.350	-28.77	30.06	204.14
0.050	39.3	0.371	-28.31	12.32	141.02
298.15 K					
0.000	36.9	0.459	-27.94	17.87	153.66
0.005	37.3	0.415	-28.71	24.60	178.80
0.010	39.3	0.384	-29.05	29.61	196.76
0.025	40.1	0.396	-28.76	10.99	133.34
0.050	41.5	0.381	-28.89	16.48	152.16
308.15 K					
0.000	39.2	0.480	-28.27	65.49	304.24
0.005	39.4	0.448	-28.83	37.29	214.58
0.010	40.4	0.433	-29.01	11.66	131.97
0.025	41.4	0.409	-29.35	23.00	169.90
0.050	42.5	0.406	-29.29	32.60	200.87

3.3 Fluorescence measurements:

By this technique one can obtain a measure of the effective polarity of that portion of the aggregates where the fluorescer is located. The most widely used probe is pyrene, this measure for pyrene is provided by the ratio of the first and third fluorescent peaks. The intensity ratio of first to third vibration peaks of pyrene, I_I/I_{III} is strongly sensitive in the vicinity of the polarity of the surrounding environment and as the solvent polarity decreases, this ratio also decreases [38-39]. Relative intensity of vibronic bands I_I/I_3 of pyrene fluorescence in NaPSS [C₄mim][C₈OSO₃] solutions as a function of IL concentration is plotted in Figure 5. The ratio I_I/I_{III} remains constant up to a certain concentration and then decreases quickly; this fairly drastic change implies the onset of aggregation, which again attains a constant value with further increase in concentration. In the solution when the concentration of IL is not so high the aggregation process has not been yet started, the pyrene sense the medium as polar. Increasing IL concentrations lead to the decomposition of the pyrene aggregates due to incorporation of the pyrene into the cavities of the aggregates and pyrene at this stage sense the non-polar nature resulting in the decrease of the ratio I_I/I_{III} . The mid-point of the sharp decrease region in the plot gives the cac of the system. The cac data calculated from the

fluorescence technique is presented in Table. 2 and value of cac for aqueous-IL system is in good agreement with the values obtained from conductance and surface tension, also from the literature [33].

It was observed that the addition of NaPSS leads to an increase in the cac as a result of the electrostatic shielding between NaPSS and IL, somewhat delays the aggregation process as pyrene still sensing the medium as polar. After the commencing of aggregation phenomenon the medium changes from polar to non-polar as is sensed by the pyrene and due to enhanced hydrophobic interactions in the system.

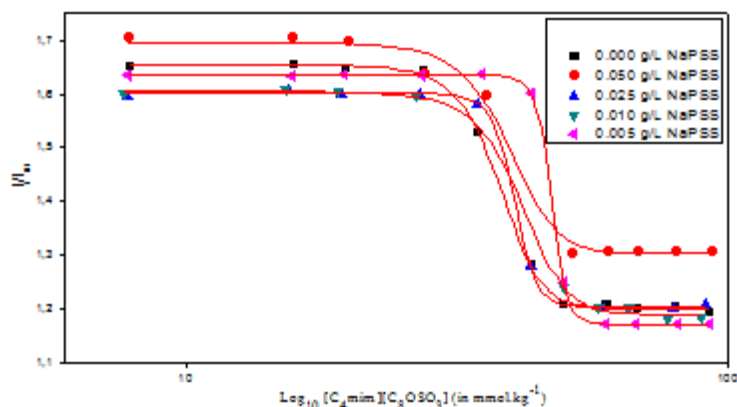


Fig. 5. Sigmoidal curves in the plots of I_I/I_{III} ratio versus $\log_{10} [(C_4mim)(C_8OSO_3)]$ where the break in the curves signifies the starting of aggregation phenomenon of IL with different concentrations of NaPSS: (■), 0.0 g/L; (●), 0.005 g/L; (▲), 0.01 g/L; (▼), 0.025 g/L; (◄), 0.05 g/L

4. Conclusion:

The interaction of NaPSS with $(C_4mim)(C_8OSO_3)$ was studied in aqueous solution using conductometry, tensiometry and fluorimetry. The obtained cac values were correlated very well with the reported values using different techniques. The thermodynamic parameters obtained for $(C_4mim)(C_8OSO_3)/NaPSS$ systems at different temperatures show that the micellization phenomenon is spontaneous process as all the values of ΔG_m^0 are negative. The positive values of (ΔH_m^0) , indicate that the micellization process is an endothermic phenomenon and the large positive values of ΔS_m^0 indicate that the aggregation is entropy driven process over the whole temperature range studied. Further, surface tension and fluorescence spectroscopy help in better understanding Surface tension further fluorescence probe help in better understanding of the interaction between IL and the polyelectrolyte.

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