



Micellization behavior of cetyltrimethylammonium bromide in the absence and presence of sodium polystyrene sulfonate in water and methanol-water mixture: A conductivity approach

Ajaya Bhattarai

Department of Chemistry, M. M. A. M. C., Tribhuvan University, Biratnagar, Nepal

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ABSTRACT

Different micellization properties of cetyltrimethylammonium bromide (CTAB) in the absence and presence of 0.0001 monomol·L⁻¹ and 0.001 monomol·L⁻¹ of sodium polystyrene sulfonate (NaPSS) in water, 0.1 and 0.2 volume fraction of methanol-water mixture at 298.15 K such as the critical aggregation concentration (*cac*), critical micellar concentration (*cmc*) and the apparent critical micellar concentration (*cmc*^{*}) have been discussed from the conductivity study. The values of standard free energies of micellization (ΔG_m^0), the standard free energy of surfactant tail transfer ($\Delta G_{\text{trans}}^0$), influence of NaPSS concentration and CTAB/NaPSS molar ratio, slopes (*S*₁ and *S*₂), correlation of ΔG_m^0 with relative permittivity (*D*), Reichardt's parameter (*E*_T (30)), viscosity (η_0), Hildebrand parameter (δ), solvophobic parameter (*S*_p), correlation of degree of association (α) with *S*_p, correlation of ΔG_m^0 with volume fraction of methanol, gibbs energy difference (ΔG_{ps}^0), degree of binding (β), free energy of binding (ΔG_b^0), the standard Gibbs energy (ΔG_t^0), correlation of $\frac{\kappa_0}{\kappa_{\text{cmc}}}$, $\frac{\text{cmc}}{\text{cac}}$, $\frac{\text{cac}}{\text{cmc}^*}$, $\frac{\Delta G_t^0}{\Delta G_m^0}$, $\frac{\Delta G_b^0}{\Delta G_m^0}$, $\frac{\Delta G_{\text{ps}}^0}{\Delta G_m^0}$ with volume fraction of methanol, correlation of (*cmc/cac*) and (*cac/cmc*^{*}) with volume fraction of methanol and variation of *cac* with charge density are also included in this study.

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1. Introduction

Surfactants are chemical substances which when present at low concentration in a system adsorb on the surfaces, thus altering its free energy to a certain extent [1]. A characteristic feature of surfactants is the ability to form micelles. In polar as well as nonpolar solvents, the solutions of surfactants spontaneously link into a particular structure defined as micelles above a particular concentration called the critical micelle concentration [2,3].

Polyelectrolytes are charged polymers containing charged polymer chains (macroion) and small counterions of opposite charge in polar solvents [4]. For example, sodium polystyrene sulfonate (NaPSS).

The adding of additives into associates of amphiphiles will change its physicochemical properties, for instance, the degree of ionization, reaction rates as well as clouding or phase separation [5–7].

There have been huge works regarding the interaction between NaPSS and cationic surfactants in aqueous solutions by different methods [8–25]. These studies may be utilized for the development of industrial as well as biological processes. NaPSS contains hydrophobic phenyl moiety and hydrophilic sulfonate group. Therefore, NaPSS can

interact with cationic surfactants by hydrophobic as well as electrostatic forces [21,24,26]. The self-aggregation is possible for less relative molecular mass NaPSS in its aqueous state, whereas more relative molecular mass NaPSS does not show such action. The conductivity of pure water changes after adding NaPSS but the surface tension remains the same. Hence, NaPSS is not a surface-active polymer [27–29] but it is highly sensitive with conductance measurement. So, we decided to use less amount of NaPSS in comparison with CTAB which is a very surface-active surfactant and acts as a popular cationic surfactant. CTAB is highly soluble in polar and nonpolar solvents and forms normal and reserve micelles [30,31]. CTAB is one of the most frequently used surfactants in many industrial processes and everyday life [32].

The huge works have been noticed for the interaction between NaPSS and CTAB. Kaczmarek et al. [33] used the conductivity techniques to study the effect of ionic strength on CTAB-NaPSS formation of the complex by using 80 ppm NaPSS/0.5 mM CTAB composition that corresponds to charge neutral polyelectrolyte/surfactant complex. Kogej and Kserjanc showed that NaPSS can induce aggregation of CTAB into micelles at a concentration much lower their *cmc* [34]. Kogej and Skerjanc concluded that stable aggregates between the polyelectrolyte into the surface of the micelle-like surfactant aggregates [34] with the help of fluorescence and conductivity studies. In their works of conductivity, it was observed that the conductivity values of CTAB in the presence

E-mail address: bkajaya@yahoo.com.

of NaPSS somehow higher than the conductivity of CTAB in absence of NaPSS. Moreover, there was the single break in the conductivity curve of CTAB and it was known as *cmc* whereas there were two breaks in the conductivity curves of CTAB in the presence of NaPSS, they named the first break as critical aggregation concentration (*cac*) and the second break as the apparent critical micelle concentration (*cmc**) when CTAB completely forms the complex with NaPSS and then the complexation is complete and free micelles observe in the system at *cmc** that is somehow more in NaPSS solutions than the *cmc* of pure surfactants at 298.15 K [34]. They observed that the *cmc* of CTAB: 0.95 mol/kg (fluorimetry) and 0.94 mol/kg (conductivity) and $\Delta G_m^o = -17.3 \text{ kJmol}^{-1}$ (fluorimetry). But when $5 \times 10^{-4} \text{ M}$ NaPSS, $cmc^* \times 10^3 = 1.25$ (conductivity), degree of Binding (β) = 0.62 (conductivity) was obtained by using Eq. (1):

$$\beta = cmc^* - cmc / m_p \quad (1)$$

where m_p = polyelectrolyte concentration.

By extending the work of Kogej and Kserjanc [34], we have taken CTAB and NaPSS in water and methanol-water mixture at 298.15 K and study conductivity for the calculation of different properties. Also, we have used Eq. (1), to obtain the degree of binding (β) from our study.

It may be possible to calculate the degree of binding of CTAB to NaPSS, that is given by the ratio of CTAB bound amount [CTAB_b] to NaPSS monomolar concentration [NaPSS_m] [35,36]: $\beta = \frac{[CTAB_b]}{[NaPSS_m]}$.

In NaPSS; PSS, a strong anionic polyelectrolyte with aromatic benzene rings carrying the charged sulfonate groups, which assign the poly (styrenesulfonate anion), PSS⁻, a concealed hydrophobic character. However, the concealed hydrophobic character of NaPSS comes into effect when "external" hydrophobic domains are present in the system, as is the case in mixed solutions with surfactants when surfactant molecules form self-associated structures having a hydrophobic core. It was recognized early by Kwak et al. [25] that styrene sulphonate, SS⁻, groups of the PSS chain are incorporated into the hydrophobic interior of such surfactant aggregates.

The standard free energy of micellization is as

$$\Delta G_m^o = RT \ln cmc \quad (2)$$

An analogous expression can be written for the free energy change of surfactant binding to the polyelectrolyte.

$$\Delta G_b^o = RT \ln cac \quad (3)$$

The free energy change for the process free micelles → polyion-bound micelles are then related to the ratio between *cac* and *cmc* through

$$\Delta G_{mb}^o = RT \ln \left(\frac{cac}{cmc} \right) \quad (4)$$

where ΔG_{mb}^o (kJ/mol) is a measure of the stability enhancement of the polyion-induced micelles relative to the free ions. Large negative ΔG_{mb}^o values indicate that micelles formed in the polyion domain are more stable than the free ones. The lower is the *cac* relative to the *cmc*, the more negative is ΔG_{mb}^o , and the more suitable is the polyion and surfactant ion interaction [37]. CTA⁺ cation interacted strongly with PSS⁻ anion [38].

If we go depth for conductivity studies rather than conventional surfactants with NaPSS and its related compounds, there were two breaks for the values of critical aggregation concentration (*cac*) and critical micelle concentration (*cmc*) of aqueous 1-octyl-3-methylimidazolium bromide solutions in different concentration of NaPSS [39] whereas the values of critical micelle concentration (*cmc*) and various breakpoints (*C*₁, *C*₂, *C*₃) of aqueous 1-dodecyl-3-methylimidazolium bromide solutions in different concentrations of poly(4-styrenesulfonic

acid-co-maleic acid) sodium salt were observed in the literature [40]. The conductance of poly(4-styrenesulfonic acid-co-maleic acid) sodium salt with 1-dodecyl-3-methylimidazolium bromide was higher than 1-dodecyl-3-methylimidazolium bromide. In the literature [41]; *cac*, *psc* (polymer saturation concentration), *cmc** was observed whereas Kogej and Skerjanc [34] used NaPSS (70,000) and CTAB and the trends of specific conductivity graphs of two breaks (*cac* and *cmc**) are found to be similar with our study at 298.15 K without *psc*. But they used only one concentration of NaPSS whereas we used two concentrations of NaPSS. The same pattern (*cac* and *cmc**) was observed by Singh et al. of sodium salt of carboxymethylcellulose with 1-dodecyl-3-methylimidazolium chloride and its ester and amide counter-parts ionic liquids [42] by conductivity study.

As we know conductivity measurement is a useful method of carrying experiments between highly active and less inactive components [35].

Although considerable attention has, so far, been paid to the investigations on the polymer-surfactant interactions in aqueous solutions [8–25]. Such studies in mixed solvent media are scarce [36,43].

In a binary mixture of two solvents, the relative permittivity of the system may be varied conveniently by making the different solvent composition. Hence the polyelectrolyte-surfactant interactions can be modified by making different the solvent composition due to the fact that the dominating electrostatic contributions to these interactions are largely influenced by the dielectric constant of the media. In particular, such study can give information about the influence of electrostatic effects on polyelectrolyte-surfactant interactions and on surfactant aggregation mediated by the polyelectrolyte as a function of the dielectric constant of the media.

We have noticed less literature regarding the investigations with limited ideas on physicochemical behavior of CTAB in the presence of NaPSS by conductometry [26,30] and there was no reported work in the methanol-water system.

The understanding of the surface and volumetric properties of CTAB in the presence of various kinds of substrates is very useful. Among the substrates added to the aqueous solution of CTAB, the short-chain alcohols especially methanol plays a very important role [32,44,45]. The isotherm of surface tension, density, viscosity, and the light scattering clearly prove that methanol forms some aggregates [46].

The conductivity isotherm of aqueous CTAB solution and methanol mixture suggest that the dissociation of CTAB in methanol is close to that in water. At the CTAB concentration higher than its *cmc*, the conductivity of the solution increases as a function of methanol concentration and it is higher in the "pure" methanol solution of CTAB than in the aqueous one. It should be assumed that the CTAB conductivity analysis in methanol and the properties of the water and methanol mixture could be helpful to better understand the behavior of CTAB and NaPSS mixture in water + methanol [46,47]

Our aim is to investigate the aggregation properties of CTAB in the absence and the presence of a varying concentration of NaPSS in water and in the methanol-water mixture by conductivity methods such as *cac*, *cmc* and *cmc**.

The major purpose of this study is to see thermodynamic properties such as ΔG_m^o , ΔG_{trans}^o , gibbs energy difference (ΔG_{ps}^o), degree of binding (β), the free energy of binding (ΔG_b^o) and the standard Gibbs energy (ΔG_t^o). Also, to study the influence of NaPSS concentration and CTAB/NaPSS molar ratio and study of CTAB-NaPSS slopes (*S*₁ and *S*₂). The study of correlation of ΔG_m^o with solvent parameters such as relative permittivity (*D*), Reichardt's parameter (*E*_T (30)), viscosity (η_o), Hildebrand parameter (δ) and volume fraction of methanol for CTAB and CTAB-NaPSS system is the noble investigations. The more interesting works is to see the correlation of ΔG_m^o with solvophobic parameter (*S*_p), the correlation of degree of association (α) with *S*_p, the correlation

of $\frac{\kappa_o}{\kappa_{cmc}}$, $\frac{cmc}{cac}$, $\frac{cac}{cmc^*}$, $\frac{\Delta G_t^o}{\Delta G_m^o}$, $\frac{\Delta G_b^o}{\Delta G_m^o}$, $\frac{\Delta G_{ps}^o}{\Delta G_m^o}$ with volume fraction of methanol,

the correlation of (cmc/cac) and (cac/cmc^*) with the volume fraction of methanol and eventually to study the variation of cac of CTAB-NaPSS system with charge density of NaPSS is also our goal.

2. Experimental

Methanol (99.0% pure) was purchased from Merck, India which was funded by University Grants Commission of Nepal. The methanol had the density and the coefficient of viscosity as 0.7872 g/cm^3 and $0.5440 \text{ mPa}\cdot\text{s}$ at 298.15 K respectively and are perfectly matched with the literature [48]. The cationic surfactant CTAB was purchased from Aldrich Chemical Company, Inc. CTAB was highly pure ($> 99.0\%$) and used after drying for 1 h. The cmc of CTAB was measured at 298.15 K . The observed cmc of CTAB by conductivity is 0.9 mM which was matched with the literature [49]. The methanol-water mixtures were prepared up to 0.2 volume fraction of methanol at 298.15 K by maintaining at a constant temperature in thermostat [50] by using triple distilled water. Precipitation in the system above 0.2 volume fraction of methanol prevented us to go beyond. NaPSS of $70,000 \text{ g mol}^{-1}$ with (1) a degree of sulfonation and (< 1.2) a polydispersity index was obtained from Sigma Aldrich, USA. The molecular weight was checked with Mark-Houwink concept [51]. The purity of NaPSS was also checked by spectrophotometric examination [52]. NaPSS (0.0001 and $0.001 \text{ monomol}\cdot\text{L}^{-1}$) solutions were made in water and methanol-water mixture and used as the solvents for CTAB solutions. The binary mixtures were further used after one day to make the solutions of CTAB. Finally, the volume makeup of the solutions was done at 298.15 K after one day.

The conductance was measured by a digital conductivity meter (Systronics India Ltd.) with a cell constant 1.002 cm^{-1} of 0.01% uncertainty. The calibration of the conductivity cell was done by 0.1 and 0.01 M KCl solutions [53]. Our purpose of using conductivity meter was to check the conductivity of triple distilled water which was $< 0.6 \mu\text{S/cm}$ at 298.15 K and to measure specific conductance of CTAB and CTAB-NaPSS system. The uncertainty of the measurements was within $\pm 3.0\%$.

3. Results and discussion

3.1. Conductivity measurement and thermodynamics properties

In the presence of NaPSS, at first a sharp decline of conductivity of CTAB is noticed and then the movability of CTA^+ is highly diminished due to the electrostatic field of PSS^- . The slow formation of minimicelles takes place. After the minimum, the conductance increases with the increment of the concentration of CTAB. The flexible NaPSS chain folds around CTAB micelles like a counterion cloud. This can be followed by the liberation of counter ions. As a result, the conductance increases (Figs. 1 to 3). The increase of conductance of CTAB by adding NaPSS may be due to the counter ions of both the surfactant and the polyelectrolyte are displaced at the moment of the polyelectrolyte-surfactant complex is formed. These counter ions are far more mobile when liberated than when they were in their bound state to either the surfactant or polyelectrolyte.

If we analyze the specific conductivity graph in the presence of NaPSS, the linear increment with CTAB concentration up to the cac . After this concentration, a lower slope was noticed as compared with the previous one (Figs. 1, 2, 3) conductivity graphs. This is marked by the starting where there are strong electrostatic interactions between CTAB and NaPSS that is due to the liberation of a number of counterions and the linear increment of conductance with an increase of CTAB concentration up to the cac . The mobility of counterion is limited by the redissolution procedure and the conductivity more gradually increased in the second region (cmc^*). Thus, on more addition of CTAB, a huge number of CTAB molecules get absorbed on NaPSS backbone and opens to an increase in +ve charge on NaPSS which shows the

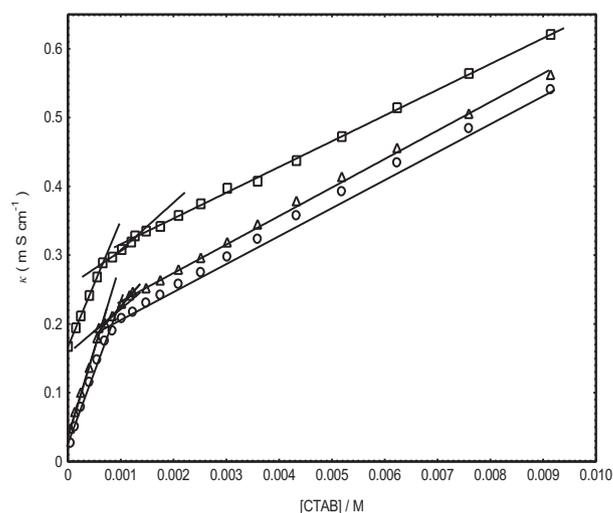


Fig. 1. Variation of the specific conductivity (κ) with the concentration of CTAB in the absence(circle) and presence of NaPSS system in water at 298.15 K , NaPSS concentration being $0.0001 \text{ monomol}\cdot\text{L}^{-1}$ (triangle), $0.001 \text{ monomol}\cdot\text{L}^{-1}$ (square).

increment of specific conductivity, κ . By increasing NaPSS concentration, the cmc of CTAB in all investigated systems also increases. Here the cac is the very important concentration which was observed at the first break point with a white colloidal precipitate of PSS^- and bound CTA^+ ions that quickly vanish on more addition of CTAB. On addition of NaPSS to CTAB solution, the CTAB monomers may jump on the surface of the NaPSS molecule, as a result, a complex of CTAB-NaPSS formed. This complex concentration is called cac .

We observed the cac increment on adding more amount of NaPSS. The reason behind that there is more availability of binding sites for CTAB monomers so that they can bind with NaPSS. On doing so more amount of CTAB is necessary for binding with NaPSS. After binding all sites, the formation of independent micelles of CTAB molecules is observed. In our system we have observed that the degree of ionic dissociation (α) increases from water to methanol-water mixture (Table 1) for the formation of CTAB-NaPSS complex then the interaction between CTAB and NaPSS also increases. α is also associated with cac that is when α increases then cac also increases on the addition of more NaPSS to CTAB-NaPSS system (Table 1). Therefore, the more increment of cac with the addition of more NaPSS is naturally associated with the complexation of a huge amount of CTAB. Hence the higher value of

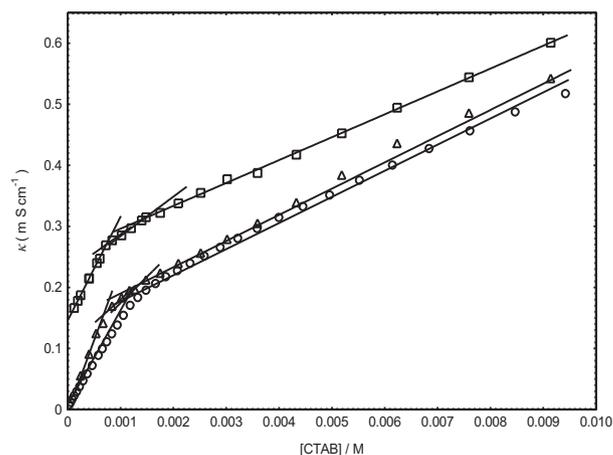


Fig. 2. Variation of the specific conductivity (κ) with the concentration of CTAB in the absence(circle) and presence of NaPSS system in methanol-water mixture containing 0.1 volume fraction of methanol at 298.15 K , NaPSS concentration being $0.0001 \text{ monomol}\cdot\text{L}^{-1}$ (triangle), $0.001 \text{ monomol}\cdot\text{L}^{-1}$ (square).

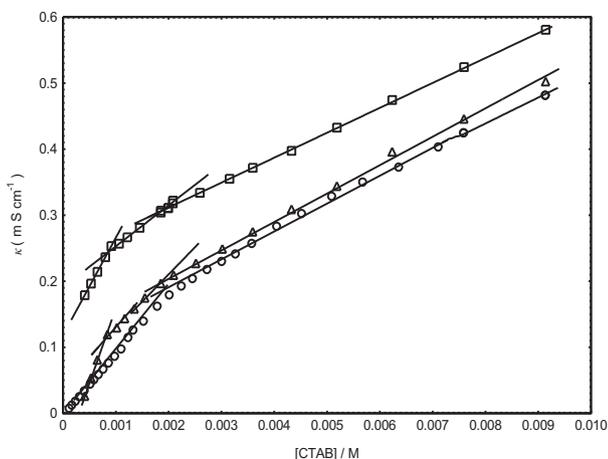


Fig. 3. Variation of the specific conductivity (κ) with the concentration of CTAB in the absence(circle) and presence of NaPSS system in methanol-water mixture containing 0.2 volume fraction of methanol at 298.15 K, NaPSS concentration being 0.0001 monomol·L⁻¹(triangle), 0.001 monomol·L⁻¹(square).

cac may be associated with the weaker association between CTAB and NaPSS [34].

Kogej [38] noticed the complex formation of CTAB-NaPSS and therefore did not observe clearly cac from κ vs c curves but he used molar conductivity Λ vs \sqrt{c} to obtain (cac and cmc^*) whereas Bakshi & Sachar [54] observed κ vs c curves and obtained only cmc^* . We have obtained cac and cmc^* from the easy plot software. This software has the ability to see even the small break in the curves while plotting the data for X and Y-axes. cmc^* values of complex CTAB-NaPSS obtained are always higher than the cmc of CTAB. This indicates the micelle formation in the presence of NaPSS is taking place at higher CTAB concentration due to the formation of CTAB-NaPSS complex which reduces the actual amount of CTAB available for independent micellization.

As methanol is added to CTAB-NaPSS solution, the dielectric constant and degree of the structuring of the solvent are lowered. As more methanol is added, this process continues and the micelles expand (cmc increases). This is due to reduced hydrophobic effect [55]. Similar trends were noticed in the literature [36].

An increase in the cmc and cmc^* values with the increasing amount of the added NaPSS at 298.15 K may be ascribed to the lowering in the amount of free CTAB molecules since more CTAB molecules are required to saturate an increased amount of NaPSS. It is apparent that micellization becomes less spontaneous upon addition of NaPSS to 298.15 K, and that the spontaneity of micellization decreases as the amount of added NaPSS increases [56].

Table 1

The Critical Aggregation Concentration (cac), Critical Micellar Concentration (cmc), and the Apparent Critical Micellar Concentration (cmc^*) obtained for CTAB-NaPSS System from conductometry in water and methanol-water mixture containing 0.1 and 0.2 volume of methanol at 298.15 K containing degree of dissociation (α).

cmc (mM)	[NaPSS] (monomol·L ⁻¹)	cac (mM)	cmc^* (mM)
Water			
1.00 ($\alpha = 0.22$)	0.0001	0.59 ($\alpha = 0.25$)	1.10 ($\alpha = 0.47$)
	0.0010	0.66 ($\alpha = 0.28$)	1.30 ($\alpha = 0.54$)
0.1 Volume fraction of methanol			
1.20 ($\alpha = 0.23$)	0.0001	0.68 ($\alpha = 0.33$)	1.40 ($\alpha = 0.50$)
	0.0010	0.73 ($\alpha = 0.36$)	1.50 ($\alpha = 0.58$)
0.2 Volume fraction of methanol			
1.70 ($\alpha = 0.27$)	0.0001	0.79 ($\alpha = 0.50$)	1.80 ($\alpha = 0.52$)
	0.0010	0.85 ($\alpha = 0.54$)	1.90 ($\alpha = 0.63$)

Errors limits of cac , cmc and cmc^* are within $\pm 3\%$.

With the help of cmc , we can calculate important thermodynamic parameters such as standard Gibbs free energy of micellization [57,58]:

$$\Delta G_m^0 = (2-\alpha)RT \ln X_{cmc} \quad (5)$$

where α is the degree of dissociation, X_{cmc} is mole fraction of surfactant at cmc , R is the universal gas constant and T is the temperature.

In addition, the effect of additives on the micellization process can be studied by means of standard free energy of surfactant tail transfer, ΔG_{trans}^0 is defined by [48]:

$$\Delta G_{trans}^0 = (\Delta G_m^0)_{\text{methanol+water}} - (\Delta G_m^0)_{\text{water}} \quad (6)$$

From the theory of self-assembly [59], the major contribution to the standard free energy of micellization is linked with a transfer of the surfactant tail from solvent into the micelle, ΔG_{trans}^0 .

The ΔG_{trans}^0 values are all positive (ΔG_{trans}^0 in 0.1 and 0.2 volume fraction of methanol for CTAB in absence of NaPSS are 1.41 and 4.22 kJmol⁻¹) whereas for CTAB in 0.0001 monomol L⁻¹ NaPSS are (1.65 and 3.51 kJmol⁻¹) and CTAB in 0.001 monomol L⁻¹ NaPSS are (1.75 and 4.22 kJmol⁻¹) and their values increase with addition of methanol. This indicates the transfer of CTAB tail from the bulk into the micelle is less suitable and hence the binary mixture of organic solvent and water is a better solvent for the CTAB and CTAB-NaPSS complex [60].

The negative value of ΔG_m^0 shows spontaneous and becomes less negative when the addition of NaPSS to CTAB (Table 2). Such types of trends were also found in the literature [40].

As we know that the concentration of the polyelectrolyte plays a more complex impact on the point of aggregation. Till now, there are no details studies of CTAB-NaPSS system in water and methanol-water mixture by conductometric methods. Firstly, we want to see the influence of NaPSS concentration and CTAB/NaPSS molar ratio on the conductance curves.

3.2. Influence of polyelectrolyte concentration and surfactant/polyelectrolyte molar ratio

Fig. 1 represents the conductometric graph of CTAB-NaPSS systems in pure water with monomer concentrations of NaPSS corresponding to 0.0001 monomol·L⁻¹ (triangles) and 0.001 monomol·L⁻¹ (squares). Fig. 4 represents the same values of the conductances plotted as a function of the molar ratio of CTAB to NaPSS monomer concentrations in pure water. It can be seen from Fig. 1 that the breaking points shifted towards higher concentrations value on increasing CTAB concentrations

Table 2

Free energies of micellization (ΔG_m^0), Binding parameter (β), free energy of binding (ΔG_b^0), the standard Gibbs energy (ΔG_t^0), gibbs energy difference (ΔG_{ps}^0), the solvent conductance and the conductance at the cmc of CTAB in the absence and presence of NaPSS at water and methanol-water mixture at 298.15 K.

V.F. of methanol	ΔG_m^0 (kJmol ⁻¹)	(β)	ΔG_b^0 (kJmol ⁻¹)	ΔG_t^0 (Jmol ⁻¹)	ΔG_{ps}^0 (Jmol ⁻¹)	K_0 (mS/cm)	K_{cmc} (mS/c)
CTAB							
0.00	-48.28					0.00059	0.2081
0.10	-46.87					0.00048	0.1750
0.20	-44.06					0.00039	0.1510
CTAB in 0.0001 monomol·L ⁻¹ NaPSS							
0.00	-40.91	1.65	-49.67	-8.76	-1257.83	0.00059	0.2367
0.10	-39.26	1.60	-46.57	-7.32	-1407.93	0.00048	0.2060
0.20	-34.44	1.40	-43.78	-6.39	-1899.64	0.00039	0.1954
CTAB in 0.001 monomol·L ⁻¹ NaPSS							
0.00	-38.66	0.29	-48.34	-9.67	-979.91	0.00059	0.3280
0.10	-36.91	0.26	-45.45	-8.54	-1232.05	0.00048	0.3169
0.20	-34.40	0.24	-42.95	-8.51	-1718.19	0.00039	0.3070

Errors limits of ΔG_m^0 , β , ΔG_b^0 , ΔG_t^0 , ΔG_{ps}^0 , K_0 and K_{cmc} are within $\pm 3\%$, $\pm 4\%$, $\pm 5\%$, $\pm 3\%$, $\pm 5\%$ $\pm 3\%$ and $\pm 3\%$ respectively.

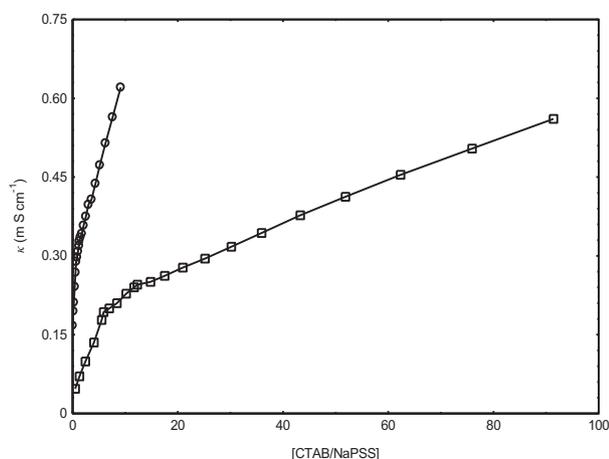


Fig. 4. Variation of κ with [CTAB/NaPSS] in the presence of NaPSS (0.0001 monomol·L⁻¹, squares; 0.001 monomol·L⁻¹, circles) in water at 298.15 K.

when NaPSS concentration is increased. This result can be easily explained by the fact that when the number of NaPSS chains increases in solution, more CTAB molecules are needed to saturate the NaPSS chains and render them sufficiently hydrophobic to be surface active.

More interestingly, Fig. 4 shows that once the conductances presented in Fig. 1 are plotted as a function of the molar ratio of the CTAB concentration to the concentration of NaPSS monomers, all the data points of CTAB in the presence of high concentration of NaPSS look like linear curve without breaks containing higher values of conductance whereas for the low concentration of NaPSS, there is still visible of breaks before and after the cac and cmc^* . Such types of behavior have also been noticed for CTAB in the presence of NaPSS in 0.1 and 0.2 volume fractions of methanol (Figs. 2, 3, 5, 6).

In our study, small aggregates started forming by the interaction of CTAB with NaPSS (0.0001 monomol·L⁻¹ and 0.001 monomol·L⁻¹) and in the first break, there is lower concentration termed as critical aggregation concentration (cac). It seems that higher the concentration of NaPSS, higher will be the cac of the system (Table 1).

The second break in the higher concentration in the conductivity corresponds to the critical micellization concentration for the formation of pure surfactant micelles in presence of the polyelectrolyte; this concentration is, generally, referred to as the apparent critical micellization concentration (cmc^*). The cmc^* is obviously higher than the corresponding cmc (i.e., the cmc of CTAB in absence of NaPSS) (Table 1). The cmc^* value obtained is always found to be higher than the cmc value in a given solvent medium and at a given temperature for the

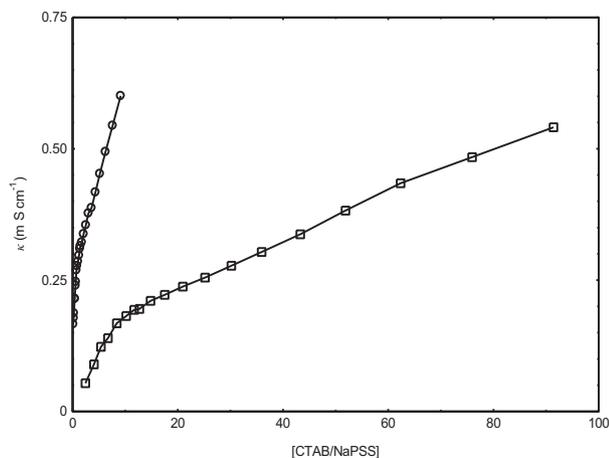


Fig. 5. Variation of κ with [CTAB/NaPSS] in the presence of NaPSS (0.0001 monomol·L⁻¹, Closed triangles; 0.001 monomol·L⁻¹, Closed squares) in 0.1 methanol-water at 298.15 K.

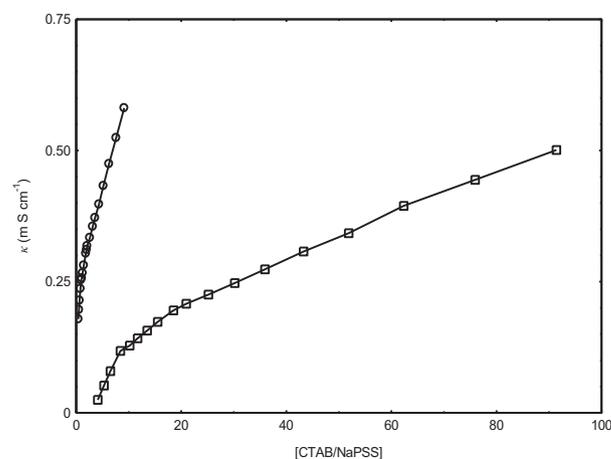


Fig. 6. Variation of κ with [CTAB/NaPSS] in the presence of NaPSS (0.0001 monomol·L⁻¹, Closed triangles; 0.001 monomol·L⁻¹, Closed squares) in 0.2 methanol.

two polyelectrolyte concentrations investigated. This demonstrates that the micelle formation in the presence of the polyelectrolyte is taking place at higher surfactant concentration due to the consumption of surfactant ions for the formation of polyelectrolyte-surfactant complex, which reduces the actual amount of surfactant molecules available for independent micellization.

Chakraborty et al. [41] reported conductometric profiles with three breaks for NaCMC-CTAB interactions thus signifying the importance of both hydrophobic and electrostatic interactions. They calculated the cmc (mM) of CTAB at 25 °C by (0.959) conductivity with cac (0.113), $psc = 0.662$, $cmc^* = 1.10$. Similarly, Shah et al. [61] calculated the cmc (mM) of CTAB at 25 °C in water by (0.97 mM) conductometry, $\Delta G_m^o = -49.90$ kJmol⁻¹. These data of cmc and ΔG_m^o almost matched with our system without polymer (Table 1).

3.3. Variation of the slopes of conductance curve with the volume fraction of methanol

The close observation of Figs. 1-3 show that the slopes in the pre- cmc region is high as compared with the slopes in the post- cmc region and gives the smallest value of α (Table 1). The higher slope in the pre- cmc region is associated with the high value of conductivity which is observed before the micellization takes place that is the number of current carrier molecules increases with the addition of CTAB and hence conductivity quickly increases. But after the micellization, the movement of micelles becomes the slow and lesser number of current carriers are present in the solution and have less value conductivity and hence lower slopes are seen in the post- cmc region (Fig. 7).

When we see the curves of CTAB and CTAB-NaPSS complex, the curves of the CTAB-NaPSS complex was found differ from CTAB. Actually, it is found that the values of conductance increase with the amount of NaPSS. In the low concentration region of CTAB, the curves of the CTAB-NaPSS complex show a linear variation (very low slope). This very low slope is due to a strong interaction between the CTAB and NaPSS. CTA⁺ cations slowly come to the complex on the anionic sites of NaPSS. Then there is a change in the slope of the conductivity at a concentration lower than cmc of CTAB alone. This change in slope is marked to the critical aggregation concentration [62].

The slope (S_1) for cac and cmc^* formation decreases on increasing of the methanol-water mixture in 0.1 mM NaPSS and 1 mM NaPSS whereas the slope (S_2) for cac and cmc^* formation increases on increasing of methanol-water mixture 0.1 mM NaPSS and 1 mM NaPSS. cac slopes are sharp in comparison with cmc^* slopes upon addition of larger values of methanol. The slopes of complex (CTAB-NaPSS) are always found to be positive in methanol-water mixtures, indicating strong ion-ion interactions. Here the strong ion-ion interactions give to

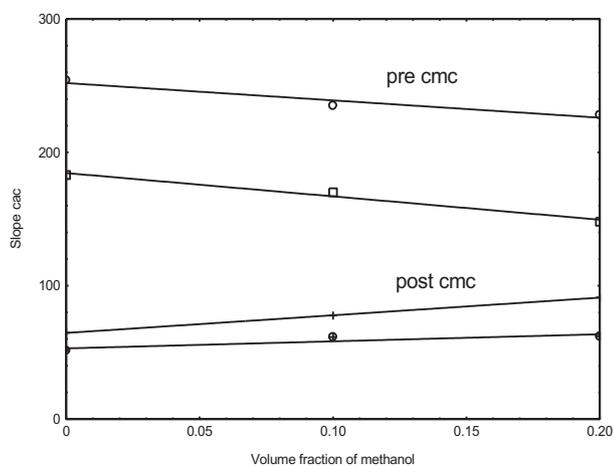


Fig. 7. Variation of the slope of cac with the volume fraction of methanol; CTAB in the presence of $0.0001 \text{ mol}\cdot\text{L}^{-1}$ NaPSS for pre cmc (circle), presence of $0.001 \text{ mol}\cdot\text{L}^{-1}$ NaPSS for pre cmc (square), CTAB in the presence of $0.0001 \text{ mol}\cdot\text{L}^{-1}$ NaPSS for post cmc (crosses) and presence of $0.001 \text{ mol}\cdot\text{L}^{-1}$ NaPSS for post cmc (crosses circle).

sufficient counterion binding on the NaPSS chain by CTAB. We observed S_2 for cac and cmc^* , the slopes are found to increase in the mixture of water and methanol. When methanol becomes rich, that indicates greater counterion binding [50]. That is why it was possible to study the micellization behavior of single cationic CTAB in methanol-water mixture up to higher volume fraction of methanol [61,63] whereas in mixed surfactant systems as cationic rich and anionic rich was limited to 0.3 volume fraction of methanol [64]. As the concentration of methanol increases, the formation of the micelle is very difficult to predict due to the solubilization of micelle [65]. For CTAB-NaPSS system, 0.2 volume fraction of methanol is limited due to precipitation in the solution (Fig. 8).

3.4. Correlation of $\frac{k_o}{k_{cmc}}$ with the volume fraction of methanol

In the year 2012, Mukhim and Ismail [66] proposed that the ratio of the solvent surface tension to the limiting surface tension at the cmc , $\frac{\gamma_o}{\gamma_{cmc}}$ to describe the solvophobic effect [67]. But here we tried to see the ratio of the solvent conductance to the conductance at the cmc

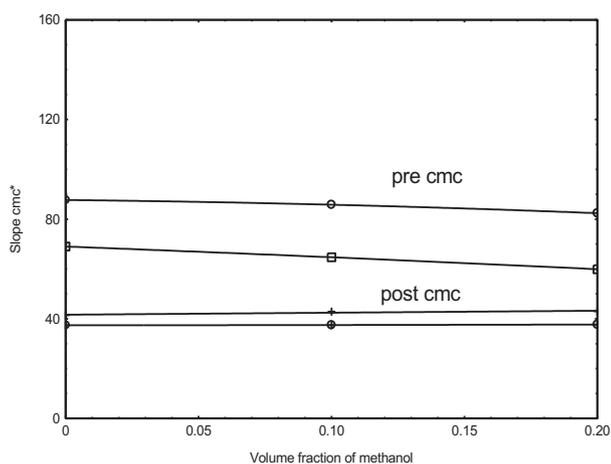


Fig. 8. Variation of the slope of cmc^* with volume fraction of methanol; CTAB in the presence of $0.0001 \text{ mol}\cdot\text{L}^{-1}$ NaPSS for pre cmc (circle), presence of $0.001 \text{ mol}\cdot\text{L}^{-1}$ NaPSS for pre cmc (square), CTAB in the presence of $0.0001 \text{ mol}\cdot\text{L}^{-1}$ NaPSS for post cmc (crosses) and presence of $0.001 \text{ mol}\cdot\text{L}^{-1}$ NaPSS for post cmc (crosses circle).

with volume fraction of methanol. Fig. 9 shows that the variation of the ratio of the solvent conductance to the conductance at the cmc with the volume fraction of methanol for CTAB and CTAB-NaPSS system. The fittings are from the polynomial equations having correlation coefficients, $r^2 = 1$. The highest ratio values are for CTAB in the presence of $0.001 \text{ mol}\cdot\text{L}^{-1}$ NaPSS and look like linear variation whereas the least ratio values are for CTAB in the absence NaPSS with looks like linear variation. But the convex curve is observed for CTAB in the presence of $0.0001 \text{ mol}\cdot\text{L}^{-1}$ NaPSS. Thus, on the addition of more amount of NaPSS, the curve shifted towards high ratio values.

3.5. Correlation of cmc/cac with the volume fraction of methanol

Here the cmc/cac ratio provides the interacting strength between CTAB and NaPSS. NaPSS-induced micelle was found to be very stable in comparison to free micelle of CTAB [68]. The binding of CTAB to NaPSS was happened to be through solubilization of the benzene rings of the NaPSS in the micelles. The conductivity is such study which confirmed the strong complexation between NaPSS and CTAB. Here the cac obtained from conductivity is sharper than other methods. Cac is thus an analog of cmc but in solutions of CTAB with added NaPSS and we have observed the value of cac lower than the cmc of CTAB in water and methanol-water mixture (Table 1).

As we observed from Table 1, that the cac values are always higher in CTAB with $0.001 \text{ mol}\cdot\text{L}^{-1}$ NaPSS in comparison to CTAB with $0.0001 \text{ mol}\cdot\text{L}^{-1}$ NaPSS. So, obviously, the ratio of cmc to the cac is the lowest for CTAB with $0.001 \text{ mol}\cdot\text{L}^{-1}$ NaPSS in comparison to CTAB with $0.0001 \text{ mol}\cdot\text{L}^{-1}$ NaPSS. Hence the strength of the interaction between CTAB and NaPSS on CTAB with $0.001 \text{ mol}\cdot\text{L}^{-1}$ NaPSS is high in comparison to CTAB with $0.0001 \text{ mol}\cdot\text{L}^{-1}$ NaPSS. If we see the graph (Fig. 10) for CTAB with $0.001 \text{ mol}\cdot\text{L}^{-1}$ NaPSS, the ratio (cmc/cac) increases with the addition of methanol and the nature of the graph is somewhat concave. Similarly, the graph for CTAB with $0.0001 \text{ mol}\cdot\text{L}^{-1}$ NaPSS, the ratio (cmc/cac) increases sharply with the addition of methanol and the nature of the graph is also the concave.

3.6. Correlation of cac/cmc^* with the volume fraction of methanol

The critical aggregation concentration (cac) and the apparent critical micellar concentration (cmc^*) is possible to observe in polymer-surfactant interaction. From Table 1, one can see the cac values are always higher in CTAB with $0.001 \text{ mol}\cdot\text{L}^{-1}$ NaPSS in comparison to CTAB with $0.0001 \text{ mol}\cdot\text{L}^{-1}$ NaPSS. So, obviously, the ratio of cac to the cmc^* is the highest for CTAB with $0.001 \text{ mol}\cdot\text{L}^{-1}$

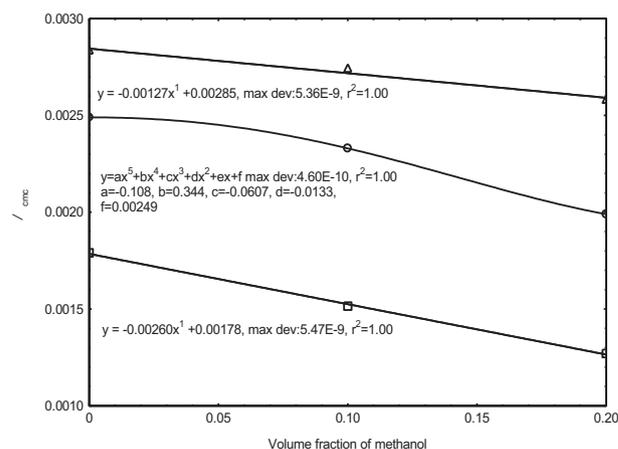


Fig. 9. Variation of $\frac{k_o}{k_{cmc}}$ with the volume fraction of methanol: CTAB in the absence of NaPSS (square) and CTAB in the presence of NaPSS concentration being $0.0001 \text{ mol}\cdot\text{L}^{-1}$ (circle), $0.001 \text{ mol}\cdot\text{L}^{-1}$ (triangle).

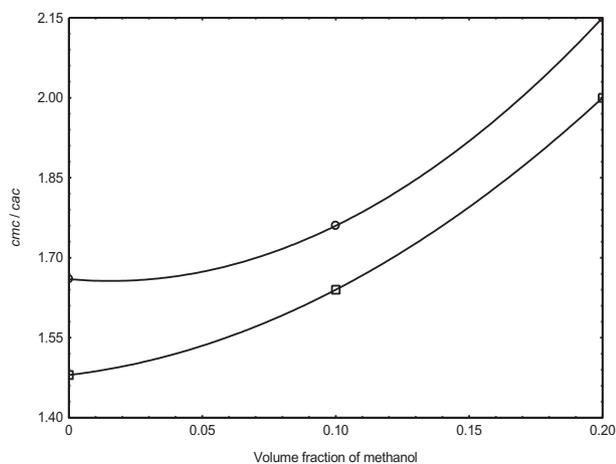


Fig. 10. Variation of $\frac{cmc}{cac}$ with the volume fraction of methanol: CTAB in the presence of NaPSS concentration being $0.0001 \text{ monomol} \cdot \text{L}^{-1}$ (circle) and $0.001 \text{ monomol} \cdot \text{L}^{-1}$ (square).

NaPSS in comparison to CTAB with $0.0001 \text{ monomol} \cdot \text{L}^{-1}$ NaPSS. Hence the strength of interaction between CTAB and NaPSS on CTAB with $0.0001 \text{ monomol} \cdot \text{L}^{-1}$ NaPSS is high in comparison to CTAB with $0.001 \text{ monomol} \cdot \text{L}^{-1}$ NaPSS.

If we see the graph (Fig. 11) for CTAB with $0.001 \text{ monomol} \cdot \text{L}^{-1}$ NaPSS, the ratio (cac/cmc^*) decreases with the addition of methanol and the nature of the graph is somehow convex whereas the graph for CTAB with $0.0001 \text{ monomol} \cdot \text{L}^{-1}$ NaPSS, the ratio (cac/cmc^*) also

decreases with the addition of methanol and the nature of the graph is also convex. But in the graph, the ratio (cac/cmc^*) value for CTAB with $0.001 \text{ monomol} \cdot \text{L}^{-1}$ NaPSS is higher in water and 0.2 volume fraction of methanol whereas in 0.1 volume fraction of methanol in comparison for CTAB with $0.0001 \text{ monomol} \cdot \text{L}^{-1}$ NaPSS collapse (Fig. 11).

The graph pattern of conductivity for NaCMC + CPC [69] was matched with our study containing cac and cmc^* . In some cases, there was a failure to detect the cac by the conductometry [70]. Sharma et al. measured the conductivity of NaPSS with SAIL (active ionic liquids) and found cac and cmc^* [71] where the conductivity of NaPSS + SAIL was found to be higher than SAIL.

3.7. Variation of $\frac{\Delta G_b^0}{\Delta G_m^0}$ with the volume fraction of methanol

The standard free energy of binding (ΔG_b^0) for CTAB-NaPSS has more negative values in water and 0.1 as well as 0.2 volume fraction of methanol in $0.0001 \text{ monomol} \cdot \text{L}^{-1}$ NaPSS in comparison with $0.001 \text{ monomol} \cdot \text{L}^{-1}$ NaPSS. Similarly, CTAB-NaPSS has more negative values in water and less negative values in 0.2 volume fraction of methanol for $0.001 \text{ monomol} \cdot \text{L}^{-1}$ NaPSS and $0.0001 \text{ monomol} \cdot \text{L}^{-1}$ NaPSS. Such type of trends have also in the standard free energy of micellization (ΔG_m^0) but having less negative values for water as well as the methanol-water mixture (Table 2). When we talk about the ratio of $\frac{\Delta G_b^0}{\Delta G_m^0}$ then we see high values for $0.001 \text{ monomol} \cdot \text{L}^{-1}$ NaPSS in comparison with $0.0001 \text{ monomol} \cdot \text{L}^{-1}$ NaPSS for water as well as methanol-water mixture (Fig. 12). But in the case of $0.001 \text{ monomol} \cdot \text{L}^{-1}$ NaPSS, $\frac{\Delta G_b^0}{\Delta G_m^0}$ for CTAB-NaPSS goes decrease from water to 0.1 volume fraction

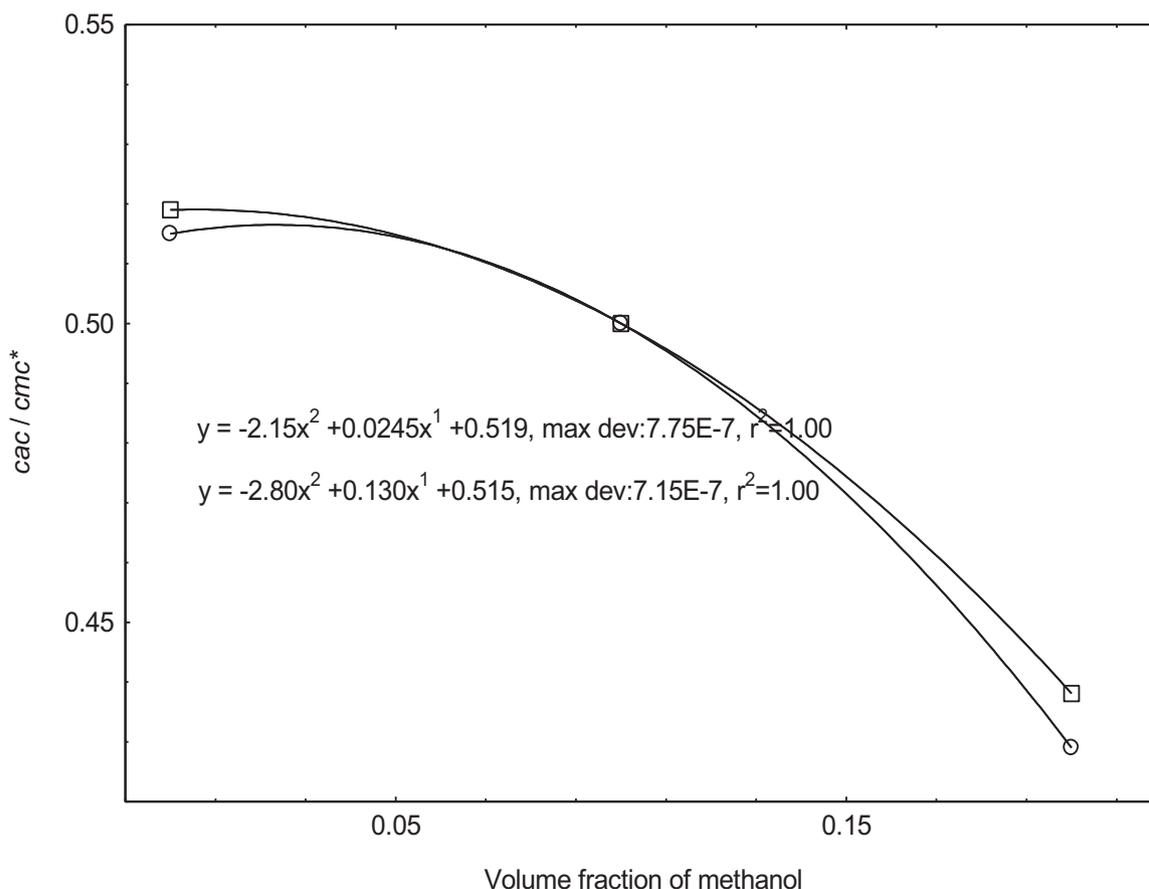


Fig. 11. Variation of $\frac{cac}{cmc^*}$ with the volume fraction of methanol: CTAB in the presence of NaPSS concentration being $0.0001 \text{ monomol} \cdot \text{L}^{-1}$ (circle) and $0.001 \text{ monomol} \cdot \text{L}^{-1}$ (square).

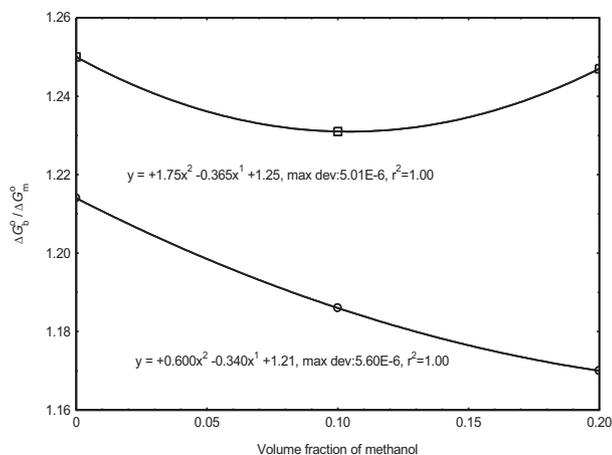


Fig. 12. Variation of $\frac{\Delta G_b^0}{\Delta G_m^0}$ with the volume fraction of methanol: CTAB in the presence of NaPSS concentration being 0.0001 monomol·L⁻¹ (circle) and 0.001 monomol·L⁻¹ (square).

of methanol and then monotonously increases up to 0.2 volume fraction of methanol. So, the nature of the curve looks like concave (Fig. 12). In the case of 0.0001 monomol·L⁻¹ NaPSS, $\frac{\Delta G_b^0}{\Delta G_m^0}$ for CTAB-NaPSS goes to decrease sharply from water to 0.2 volume fraction of methanol. So, the nature of the curve looks like somehow linear (Fig. 12).

3.8. Variation of $\frac{\Delta G_{ps}^0}{\Delta G_m^0}$ with the volume fraction of methanol

It is possible to analyze the intensity of interaction between surfactant and polymer [72] using the Gibbs energy difference as

$$\Delta G_{ps}^0 = RT \ln \left(\frac{cac}{cmc} \right) \quad (7)$$

It is observed from Table 2 that the less negative values of ΔG_{ps}^0 for the addition of NaPSS for CTAB-NaPSS system. Also, ΔG_{ps}^0 for CTAB-NaPSS has the less negative values in water as well as 0.2 volume fraction of methanol in 0.0001 monomol·L⁻¹ NaPSS and 0.001 monomol·L⁻¹ NaPSS in comparison with the standard free energy of micellization (ΔG_m^0). But ΔG_{ps}^0 becomes more negative ongoing from water to 0.2 volume fraction of methanol for 0.0001 monomol·L⁻¹ NaPSS and as well as for 0.001 monomol·L⁻¹ NaPSS (Table 2).

The more negative the value, the more favorable the interaction between CTAB and NaPSS. The reason behind is that there must be the driving force for this interaction to occur, one that is exothermic in its nature. We believe that the interaction happens because the groups, which styrene are very hydrophobic, are incorporated into the micelles. Skerfanc et al. [14] proposed that the hydrophobic interactions between cationic surfactants and NaPSS are more important than the electrostatic ones, also agreeing with a report by Hanson et al. [23].

Here in Table 2, ΔG_m^0 becomes less negative ongoing from water to 0.2 volume fraction of methanol for 0.0001 monomol·L⁻¹ NaPSS and 0.001 monomol·L⁻¹ NaPSS. That is why $\frac{\Delta G_{ps}^0}{\Delta G_m^0}$ ratio values look high for 0.0001 monomol·L⁻¹ NaPSS in comparison with 0.001 monomol·L⁻¹ NaPSS for water as well as methanol-water mixture (Fig. 13). The nature of the curves sharply increase ongoing from water to 0.2 volume fraction of methanol and look like concave for 0.001 monomol·L⁻¹ NaPSS as well as for 0.0001 monomol·L⁻¹ NaPSS (Fig. 13).

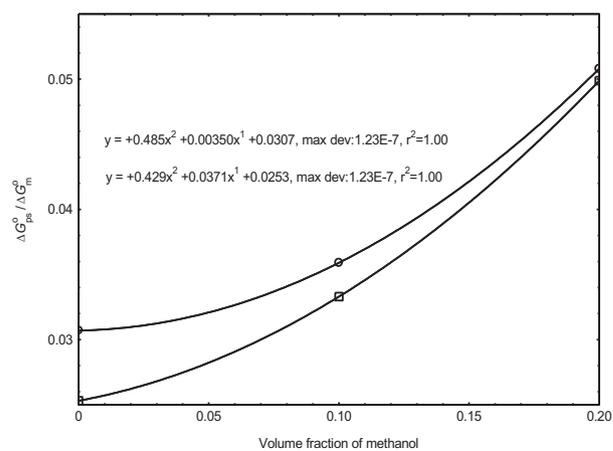


Fig. 13. Variation of $\frac{\Delta G_b^0}{\Delta G_m^0}$ with the volume fraction of methanol: CTAB in the presence of NaPSS concentration being 0.0001 monomol·L⁻¹ (circle) and 0.001 monomol·L⁻¹ (square).

3.9. Variation of $\frac{\Delta G_t^0}{\Delta G_m^0}$ with the volume fraction of methanol

We can calculate the standard free of micellization at cmc* (ΔG_m^0) and the standard free energy of binding (ΔG_b^0);

$$\Delta G_m^0 = (2-\alpha)RT \ln X_{cmc^*} \quad (8)$$

$$\Delta G_b^0 = (2-\alpha)RT \ln X_{cac} \quad (9)$$

Here cac are lower than cmc of CTAB. The polymer charge density parameter, determined by the average linear charge separation on the NaPSS backbone, is one of the decisive factors governing the binding process. So,

$$\Delta G_m^0 = (2-\alpha)RT \ln X_{cmc} \quad (10)$$

$$\Delta G_b^0 = (2-\alpha)RT \ln X_{cac} \quad (11)$$

ΔG_b^0 for CTAB-NaPSS system was found to be more negative than the corresponding values of ΔG_m^0 (Table 2).

On considering the phase separation model for aggregate and micelle formation, the measurement of the interaction force between NaPSS and CTAB can be obtained from the relationship between cac and cmc*. The standard Gibbs energy (ΔG_t^0) required to move 1 mol of free CTAB into the CTAB-NaPSS complexes can be determined [71]:

$$\Delta G_t^0 = \Delta G_b^0 - \Delta G_m^0 \quad (12)$$

The process of micelle formation on NaPSS skeletons by hydrophobic effects and CTAB micellization in presence of NaPSS are spontaneous. In addition, ΔG_t^0 is negative which confirms the feasibility of CTAB-NaPSS complexation before the formation of individual micelles (Table 2). We have found that the decrease of ΔG_t^0 as a function of wt. of NaPSS (Table 2). It, therefore, seems that the aggregation process becomes more spontaneous when NaPSS molecules are more [69]. ΔG_t^0 becomes less negative ongoing from water to 0.2 volume fraction of methanol for 0.0001 monomol·L⁻¹ NaPSS and 0.001 monomol·L⁻¹ NaPSS (Table 2).

$\frac{\Delta G_t^0}{\Delta G_m^0}$ becomes less for 0.0001 monomol·L⁻¹ NaPSS in comparison with 0.001 monomol·L⁻¹ NaPSS for water as well as the methanol-water mixture (Fig. 14). $\frac{\Delta G_t^0}{\Delta G_m^0}$ decreases sharply ongoing from water to 0.2 volume fraction of methanol and the curve looks like somehow

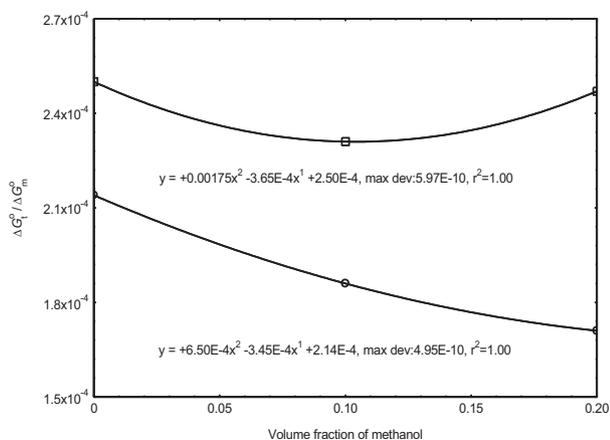


Fig. 14. Variation of $\frac{\Delta G_t^0}{\Delta G_m^0}$ with the volume fraction of methanol: CTAB in the presence of NaPSS concentration being 0.0001 monomol·L⁻¹(circle) and 0.001 monomol·L⁻¹ (square).

linear (Fig. 14) for 0.0001 monomol·L⁻¹ NaPSS whereas $\frac{\Delta G_t^0}{\Delta G_m^0}$ increases monotonously ongoing from water to 0.2 volume fraction of methanol and the curve looks like concave (Fig. 14) for 0.001 monomol·L⁻¹ NaPSS.

3.10. Variation of ΔG_m^0 vs solvent parameters

It is interesting for us to correlate ΔG_m^0 with the different solvent parameters namely Reichardt's parameter viscosity, dielectric constant, [73], the Hildebrand parameter [74]. Because micellization consists of molecular association, the fluidity, polarity and solvent structure are expected to influence the process [65]. Here we use the methanol-water mixture to see the effect of CTAB and CTAB-NaPSS on the ΔG_m^0 values. ΔG_m^0 is the best thermodynamic parameter. Especially for ionic surfactants, the counterion binding influences ΔG_m^0 .

In Figs. 15-18, the dependence of ΔG_m^0 (CTAB and CTAB-NaPSS) on the solvent parameters, $E_T(30)$, η_0 , D , and δ of methanol-water mixture are presented. The $E_T(30)$, η_0 and D were taken from the literature [75], and δ values were calculated with the empirical relationship given elsewhere [61] between δ and dielectric constant which works best for hydrogen bonded liquids:

$$\delta = 0.45D + 18.5 \quad (13)$$

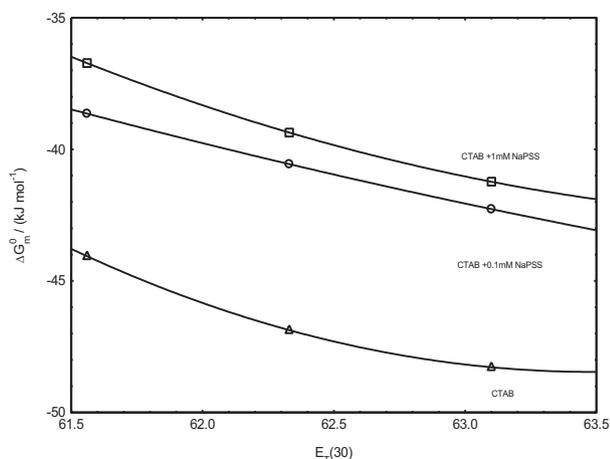


Fig. 15. ΔG_m^0 vs $E_T(30)$ at 298.15 K.

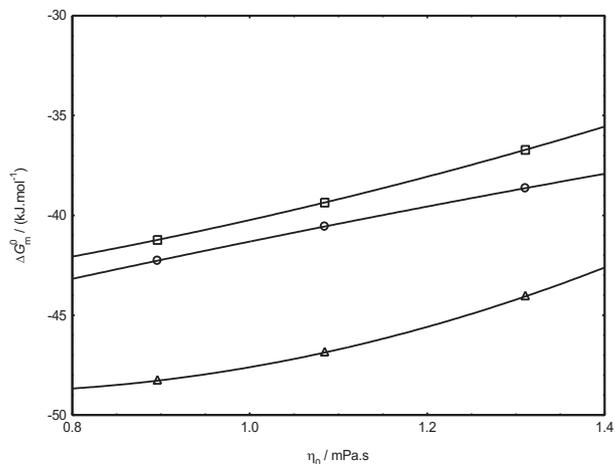


Fig. 16. ΔG_m^0 vs η_0 at 298.15 K: CTAB in the absence of NaPSS(triangle), CTAB in the presence of NaPSS concentration being 0.0001 monomol·L⁻¹(circle) and 0.001 monomol·L⁻¹(square)

The investigated parameters produced curvilinear correlations with ΔG_m^0 for CTAB system in water and methanol-water mixture. Such types of trends were also observed by Pan et al. [65].

In the case of CTAB-NaPSS system, investigated parameters produced different nature of correlations with ΔG_m^0 in water and methanol-water mixture.

For ΔG_m^0 vs $E_T(30)$ at 298.15 K, CTAB in 0.001 monomol·L⁻¹ NaPSS has a high curve in comparison with CTAB in 0.0001 monomol·L⁻¹ NaPSS and look linearly decrease with the addition of methanol. It is observed that both the curves are higher than the curve of CTAB only (Fig. 15). But in the case of ΔG_m^0 vs η_0 , CTAB in 0.001 monomol·L⁻¹ NaPSS has a high curve in comparison with CTAB in 0.0001 monomol·L⁻¹ NaPSS and look linearly increase with the addition of methanol. It is observed that both the curves are higher than the curve of CTAB only (Fig. 16).

For ΔG_m^0 vs $\frac{1}{D}$ at 298.15 K, CTAB in 0.001 monomol·L⁻¹ NaPSS has high curve in comparison with CTAB in 0.0001 monomol·L⁻¹ NaPSS and look increase of concave nature curve with the addition of methanol. It is observed that both the curves are higher than the curve of CTAB only (Fig. 17). But in the case of ΔG_m^0 vs δ , CTAB in 0.001 monomol·L⁻¹ NaPSS has a high curve in comparison with CTAB in

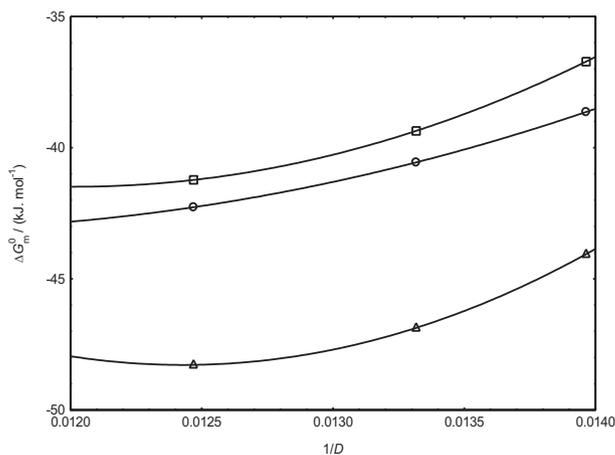


Fig. 17. ΔG_m^0 vs $\frac{1}{D}$ at 298.15 K: CTAB in the absence of NaPSS(triangle), CTAB in the presence of NaPSS concentration being 0.0001 monomol·L⁻¹(circle) and 0.001 monomol·L⁻¹(square).

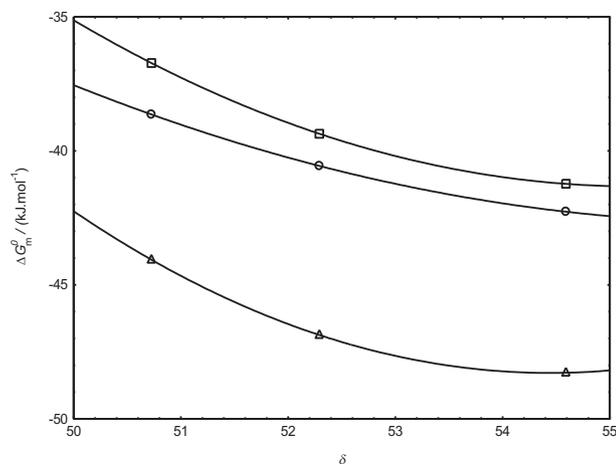


Fig. 18. ΔG_m^0 vs δ at 298.15 K: CTAB in the absence of NaPSS (triangle), CTAB in the presence of NaPSS concentration being $0.0001 \text{ mol} \cdot \text{L}^{-1}$ (circle) and $0.001 \text{ mol} \cdot \text{L}^{-1}$ (square).

$0.0001 \text{ mol} \cdot \text{L}^{-1}$ NaPSS and looks concave nature of curve on decreasing trend with the addition of methanol. It is observed that both the curves are higher than the curve of CTAB only (Fig. 18).

3.11. Correlation of ΔG_m^0 with the solvophobic parameter (S_p)

From the concept of solute-solvent interactions, the interaction of alkyl chain with solvents may be marked by the solvophobicity of hydrocarbon [76]. The solvophobic power of hydrocarbons can be discussed by their solvophobic parameter, S_p , estimated by Gibbs energies of transfer of hydrocarbons from gas into a given solvent [76]. For the binary mixture investigated here, the S_p values are possible to get for methanol-water mixture [76], though their solvent composition is different from those investigated in our work. To handle this issue, the correlation method developed by Wang et al. [77] were used.

It is found that there is a good linear relationship between ΔG_m^0 and the S_p values for water and methanol-water mixture as shown in Fig. 19 for CTAB and CTAB-NaPSS. The high nature of the curve for CTAB-NaPSS system is for $0.001 \text{ mol} \cdot \text{L}^{-1}$ NaPSS in comparison with $0.0001 \text{ mol} \cdot \text{L}^{-1}$ NaPSS. It is observed that both the curves are higher than the curve of CTAB only (Fig. 19).

In the case of α vs S_p , the values of α were taken from the Table 1, and plotted with S_p values of hydrocarbon in methanol-water mixture and found that α of CTAB and CTAB-NaPSS aggregate in the way that the α

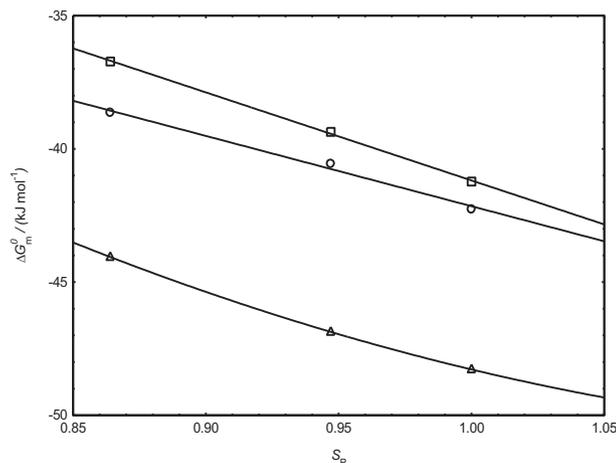


Fig. 19. ΔG_m^0 vs S_p at 298.15 K: CTAB in the absence of NaPSS (triangle), CTAB in the presence of NaPSS concentration being $0.0001 \text{ mol} \cdot \text{L}^{-1}$ (circle) and $0.001 \text{ mol} \cdot \text{L}^{-1}$ (square).

values decrease with increasing S_p values (Fig. 20) whereas the nature of the decrease of the α values are different.

For the CTAB system, α decreases with S_p by a concave curve with the least value in comparison with $0.001 \text{ mol} \cdot \text{L}^{-1}$ and $0.0001 \text{ mol} \cdot \text{L}^{-1}$ NaPSS whereas for CTAB-NaPSS system, α decreases with S_p by a convex curve with the highest value for $0.001 \text{ mol} \cdot \text{L}^{-1}$ NaPSS in comparison with $0.0001 \text{ mol} \cdot \text{L}^{-1}$ NaPSS (Fig. 20). This suggests that the increase of the solvophobic power of alkyl chains in methanol-water solvents would favor the formation of micellization.

3.12. Degree of binding (β)

The binding efficiency can be determined from the shape of the isotherms. At the beginning of the experiment, β is so high that a substantial amount of CTAB is bound to NaPSS. That is seen in a high degree of binding at low NaPSS concentration. On the other hand, the drop in the degree of binding observed as the concentration of the NaPSS increases. As binding occurs due to the electrostatic interaction between the positively charged surfactant head group on the polyion and hydrophobic interactions between the hydrocarbon chains of the surfactant [78].

It is observed from Table 2 that β is high in water and after addition of methanol decreases in both concentrations of NaPSS. Decreasing of β with decreasing the dielectric constant of the solvent was also observed in the literature [36]. Also, β is high in CTAB but decreased in the presence of NaPSS and more decreased with more addition of NaPSS.

3.13. Correlation of cac with charge density

As we have noticed that the cac depends on polyelectrolyte concentration [Table 1]. It was also noticed that the cac depends on the charge density of polyelectrolyte [79]. To know the depth of charge density of NaPSS between the concentration of 0.001 and $0.0001 \text{ mol} \cdot \text{L}^{-1}$, we need to measure the conductance of NaPSS at the range of 0.001 to $0.0001 \text{ mol} \cdot \text{L}^{-1}$ in water and methanol-water mixture at 298.15 K and calculate the fraction of uncondensed counterions. The detailed can be found in the Data in Brief.

Fig. 21 shows that the cac increases with the increase of the charge density for both concentrations of NaPSS. The curves of cac against charge density look linear and parallelly increase for both concentrations of NaPSS. Also, the curve of cac vs ξ for $0.001 \text{ mol} \cdot \text{L}^{-1}$ NaPSS is high in comparison with $0.0001 \text{ mol} \cdot \text{L}^{-1}$ NaPSS. There was an increase of ξ with methanol for higher temperatures [80]. Similarly, we have also observed the same trends of ξ with methanol with

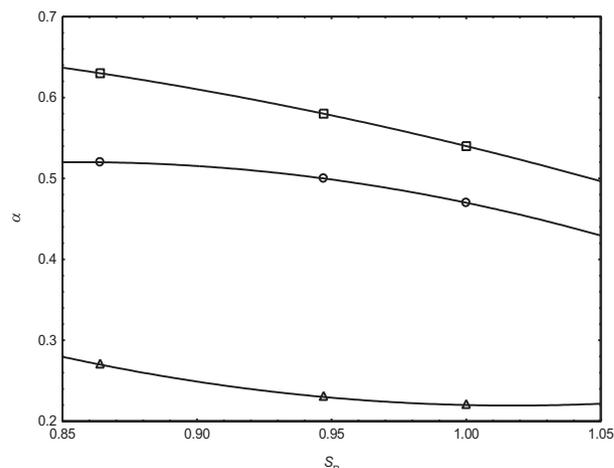


Fig. 20. α vs S_p at 298.15 K: CTAB in the absence of NaPSS (triangle), CTAB in the presence of NaPSS concentration being $0.0001 \text{ mol} \cdot \text{L}^{-1}$ (circle) and $0.001 \text{ mol} \cdot \text{L}^{-1}$ (square).

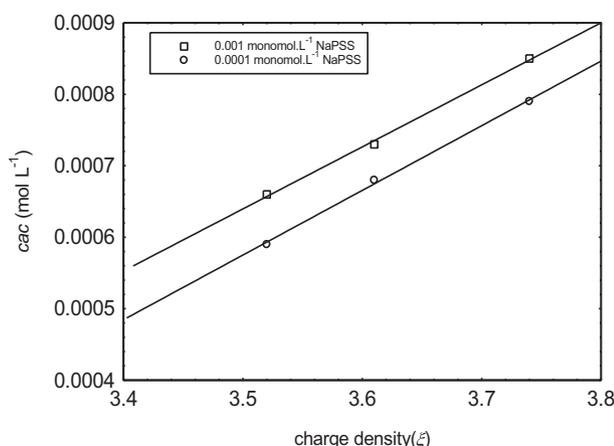


Fig. 21. Effect of the charge density (ξ) of NaPSS on the cac in aqueous CTAB solution in the presence of varying concentrations of NaPSS: 0.0001 monomol·L⁻¹ (circles) and 0.001 monomol·L⁻¹ (squares). Lines are used to guide the eye.

calculated and the best-fitted values of ξ described in the literature elsewhere [81]. Here we used the best-fitted values of ξ for the variation of cac of NaPSS. The best-fitted values of ξ was obtained by the Q-Basic Programming. Among the three solvents system, the cac is the highest at 0.2 volume fraction of methanol on 0.001 monomol·L⁻¹ NaPSS (Fig. 21). Hence it is proved that the cac of CTAB in the presence of NaPSS increases with the addition of methanol and NaPSS (Fig. 21). From Fig. 21 it is apparent that the cac increases with the increase in NaPSS concentration in a given solvent medium at a given temperature. The increase in the cac value with the increase in the polyelectrolyte concentration is obviously, related to the complexation of a greater amount of the surfactant. As the NaPSS concentration increases, more binding sites are available, and hence more surfactant ions would bind to the polyion chain.

Fig. 21 also indicates that at a given temperature and for a constant amount of polyelectrolyte, the cac values increase as the solvent medium becomes richer in methanol i.e., with the decrease in the relative permittivity of the solvent. This might be ascribed to the increase in the solubility of the hydrocarbon tail of the surfactant and polyelectrolyte chain with the increasing amount of methanol in the mixed solvent media. As a result, the bound surfactant ions cluster side by side along the polyion chain and replace equal numbers of counterions from the polyelectrolyte molecule. An increase in the interaction between the polyion chain and surfactant ions with decreasing relative permittivity of the medium might also play an important role.

4. Conclusion

The experimental results for the specific conductance of solutions of the cationic surfactant cetyltrimethylammonium bromide in the presence of the anionic polyelectrolyte sodium polystyrene sulfonate in pure water and methanol-water mixtures have been presented as a function of the surfactant concentration at 298.15 K.

The specific conductance is found to increase with increasing sodium polystyrene sulfonate over the entire concentration range investigated, whereas it is found to decrease as the relative permittivity of the medium decreases.

The cmc is found to increase with the addition of methanol over the entire concentration range investigated in a given mixed solvent medium. At the same time, α , cac and cmc^* are found to increase with the addition of methanol and NaPSS in CTAB-NaPSS system.

Furthermore, the negative decrease of ΔG_m^0 on the addition of methanol and NaPSS in CTAB and CTAB-NaPSS system. Similarly, β decreases with the addition of methanol and NaPSS in CTAB-NaPSS system. The

negative decrease of ΔG_b^0 on the addition of methanol and NaPSS in CTAB-NaPSS system.

But in the case of ΔG_t^0 , there is negative decrease with the addition of methanol whereas the negative increase of ΔG_t^0 with the addition of NaPSS. The negative increase of ΔG_{ps}^0 with the addition of methanol whereas the negative decrease of ΔG_{ps}^0 with the addition of NaPSS. The cac is found to increase linearly of CTAB-NaPSS system with the increase of charge density for 0.0001 monomol·L⁻¹ NaPSS and 0.001 monomol·L⁻¹ NaPSS.

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