

Chapter IX

Sodium Polystyrenesulfonate-Induced Aggregation Behaviour of Cetyltrimethylammonium Bromide in Acetonitrile-Water Mixed-Solvent Media: A Conductivity and Tensiometric Study

Introduction

Interactions between a polyelectrolyte and surfactant in aqueous solutions have been investigated for several decades and are extensively documented.¹⁻⁵ In particular, there have been significant research efforts focusing on the interactions between polyelectrolytes and oppositely charged surfactants in recent years.⁵⁻²³ Indeed such studies can be applied to a large number of industrial as well as biological processes. The association between the polymers and surfactants has been largely rationalized as a consequence of hydrophobic and electrostatic interactions.^{24,25} While interactions between non-ionic polymers and ionic surfactants rely mainly on hydrophobicity,^{2,26} attractive electrostatic forces dominate in the case of polyelectrolytes and oppositely charged surfactants. In the presence of an oppositely charged polyelectrolyte, micelle-like aggregates start to form along the polymer chain surfactant concentration as the surfactant concentration exceeds a critical value referred to as the critical aggregation concentration (*cac*). The *cac* is thus an analog of the critical micellar concentration, *cmc* (the concentration above which micellar aggregates begin to form in a pure surfactant solution),²⁷ but in solutions of surfactants with added polymeric component. A characteristic feature of this parameter is that it is always lower than the *cmc* of the corresponding surfactant. The lower *cac* is particularly pronounced in solutions of polyelectrolytes with opposite charge to the surfactant. With the increase in the surfactant concentration, a second transition known as the polymer-saturation point (*psc*) is obtained. Afterwards, the concentration of surfactant monomer builds up until free surfactant micelles start to form at a concentration commonly known as the apparent critical micellar concentration (*cmc*).

The experimental efforts in this field were first devoted to the determination of binding isotherms,^{4,14,28-30} enthalpies of binding,^{11,31} and various thermodynamic and transport properties^{22,32} in solutions of polyelectrolytes with added surfactants. Different experimental techniques used to study polymer-surfactant interactions include conductometry, tensiometry, viscometry, calorimetry, turbidimetry, volumetry, Nuclear Magnetic Resonance (NMR) measurements, fluorescence, gel permeation chromatography

(GPC), Fourier Transform Infrared (FTIR) spectroscopy, electromotive force (EMF) measurements, light scattering techniques e.g., DLS, SAXS, SANS etc.^{33,34}

Although considerable attention has, so far, been paid to the investigations on the polymer-surfactant interactions in aqueous solutions,¹⁻⁵ such studies in mixed solvent media are scarce.²¹ In mixed solvent systems, however, the dielectric constants of the media can be varied conveniently simply by changing the solvent composition. Hence the polyelectrolyte-surfactant interactions can be modified by changing 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.

Here, we investigate the aggregation behavior of cetyltrimethylammonium bromide (CTAB) in presence of varying concentration of sodium polystyrenesulfonate (NaPSS) in acetonitrile-water mixed solvent media containing 10, and 20 vol% of acetonitrile at temperatures 308.15, 313.15, and 318.15 K by using conductometry and tensiometry. Precipitation in the system above 20 vol% of acetonitrile prevented us to go beyond.

Experimental

Acetonitrile (E. Merck, India, 99%) was distilled with phosphorous pentoxide and then redistilled over calcium hydride. The purified solvent had a density of $0.76570 \text{ g.cm}^{-3}$ and a co-efficient of viscosity of 0.3126 mPa.s at 308.15 K; these values are in good agreement with the literature values.³⁵ Triply distilled water with a specific conductance of less than $10^{-6} \text{ S.cm}^{-1}$ at 308.15 K was used for the preparation of the acetonitrile-water mixed solvents.

The surfactant cetyltrimethylammonium bromide (CTAB) (E. Merck, Germany) has been used as received.

In the conductance method, a concentrated solution of CTAB, prepared in NaCl solution in the mixed solvents, was added in installments with the help of a microsyringe in the NaCl solution in the mixed solvents, placed in a wide mouth test tube fitted with a dip-type conductivity cell of cell constant 1.15 cm^{-1} . After each addition, conductance of the

solution was measured (after thorough mixing and temperature equilibration) with a Pye-Unicam PW9509 conductivity meter at a frequency of 2000 Hz. The cell was calibrated by the method of Lind *et al.*³⁶ using aqueous potassium chloride solutions. The measurements were triplicated. The conductance values were uncertain within the limit 0.01%.

The surface tensions of the surfactant solutions were measured with a Krüss (Germany) K9 tensiometer by the platinum ring detachment method. The tensiometer was connected to a water-flow cryostat to maintain the temperature equilibration. Prior to each measurement, the ring was heated briefly by holding it above a Bunsen burner until glowing. Several independent solutions were prepared and triplicate measurements were performed to check the reproducibility. The uncertainty of the measurements was within $\pm 1 \times 10^{-3} \text{ N}\cdot\text{m}^{-1}$.

Measurements were made at 308.15 K in a thermostated water-bath maintained within $\pm 0.005 \text{ K}$.

Results and Discussion

Critical Micellar Concentrations (cmc) of Pure CTAB

The critical micellar concentrations (*cmc*) of CTAB in absence of NaPSS were determined both from conductometry and tensiometry. These were obtained from the inflections in the plots of specific conductivity versus surfactant concentration. The data points above and below the inflection were fitted to two linear equations, and the *cmc*s were obtained from the intrersection. This method is found to be reliable and convenient for the present system because of the significant variations of specific conductivity with surfactant concentration in the pre- and postmicellar regions which allowed us to draw two unambiguous straight lines above and below the *cmc*. In tensiometry, the *cmc*s were the threshold surfactant concentrations required to saturate the air/solution interface and were obtained from the sharp breaks in the surface tension (γ) versus log[surfactant] profiles. The representative plots for CTAB in 20 vol% acetonitrile at 313.15 K are shown in Figures 1 and 2a for tensiometry and conductometry, respectively. Similar plots were also observed for other systems. The *cmc* values of CTAB in two acetonitrile-water mixtures containing 10 and 20 vol% of acetonitrile at 308.15, 313.15, and 318.15 K are shown in Table 1. It is observed that in a given acetonitrile-water mixture the *cmc* of pure CTAB increases with increasing temperature within the range of temperature under study. Addition of acetonitrile shifts the *cmc* of CTAB to higher values at a given temperature (in water the *cmc*s of CTAB were

reported¹¹ to be 1.007 and 1.0900 mM from conductometry, and 1.102 and 1.200 mM from tensiometry respectively at 308.15, and 313.15 K). The *cmc* values are also found to increase as the medium gets richer in acetonitrile. Two factors must be considered to explain this significant influence of acetonitrile on the *cmc* value of CTAB: (a) the presence of acetonitrile decreases the cohesive energy density, or the solubility parameter, of water, thus increasing the solubility of the monomeric form of the surfactant and hence the *cmc*, and (b) the cosolvent causes a reduction in the relative permittivity of the aqueous phase, favouring the mutual repulsion of the ionic heads in the micelle, thus opposing micellisation and increasing the *cmc*.

Critical Aggregation Concentrations (cac), Polymer Saturation Concentrations (psc), and Apparent Critical Micellar Concentrations (cmc*) of NaPSS-CTAB

The presence of NaPSS in CTAB solutions greatly modifies the tensiometric behavior of the surfactant. The γ -log[surfactant] curves of polyelectrolyte-surfactant systems display three distinct characteristic concentrations where the surface tension changes quite sharply. In presence of NaPSS, the first minimum in the plot is the critical aggregation concentration (*cac*) of CTAB. In this study, small aggregates started forming by the interaction of CTAB with the polyelectrolyte. Two processes, (1) binding of aggregates with NaPSS in the bulk and (2) binding of aggregates with NaPSS at the interface then occurred. The first process did not effect γ , whereas the second dislodged the polyelectrolyte to sink into the bulk from the interface; consequently, the interface was stripped off both from NaPSS and CTAB with an increase in γ until the binding process was complete manifested as a maximum in the tensiometric profiles; this concentration where the binding process was complete is considered as the polymer saturation concentration (*psc*). Upon completion of the process, there was monomer buildup at the interface associated with a decline in γ until free micelles started to form in solution beyond which addition of CTAB can hardly affect the surface tension of the solution. The onset of this plateau in the surface tension curve 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.*, *cmc* of CTAB in absence of NaPSS). These characteristic features of γ versus log[surfactant] have been clearly demonstrated in the representative figure (Figure 1) for NaPSS-CTAB system in acetonitrile-water mixture containing 20 vol% acetonitrile at

313.15 K. These kinds of three-break tensiometric isotherms for interactions of polyvinylpyrrolidone with sodium dodecylsulfate were also reported earlier¹⁰ for polyvinylpyrrolidone (PVP)-sodium dodecylsulfate (SDS) interactions. Park *et. al.*³⁷ also observed such complex tensiograms for aqueous solutions of CTAB in presence of NaPSS. These authors, however, did not report the characteristic CTAB concentrations for aggregate formation, polymer saturation and pure surfactant micelle formation in presence of NaPSS. Tensiometric profiles with lower complexity have also been reported sodium carboxymethylcellulose (NaCMC)-CTAB, and NaCMC-dodecyltrimethylammonium bromide (DTAB) systems^{14,38} Chakraborty *et. al.*,¹¹ on the other hand, reported tensiograms with three breaks for NaCMC-CTAB interactions thus signifying the importance of both hydrophobic and electrostatic interactions. The values of *cac*, *psc*, and *cmc** from tensiometry are listed in Table 1.

We have also arrived at exactly the same conclusions concerning the NaPSS-CTAB interactions from conductometric (specific conductance versus surfactant concentration) profiles (*cf.* the representative Figure 2b for NaPSS-CTAB system in acetonitrile-water mixture containing 20 vol% acetonitrile at 313.15 K). The specific conductance versus surfactant concentration plots exhibit four linear regions (below the *cac*, between the *cac* and *psc*, between *psc* and *cmc**, and above the *cmc**, with gradually decreasing slopes where three distinct breaks are discernible. The three distinct breaks in the conductometric profiles were also observed for aqueous PVP-SDS system.¹⁰ The values of *cac*, *psc*, and *cmc** obtained using conductometric procedure are included in Table 1; these are found to be in good agreement with the respective values derived from tensiometric measurements.

The *cmc** value obtained are always found to be higher than the *cmc* value in a given solvent medium and at a given temperatures for the two polyelectrolyte concentrations investigated. This indicates that the micelle formation in the presence of the polyelectrolyte is taking place at higher surfactant concentration due to the formation of polyelectrolyte-surfactant complex, which reduces the actual amount of surfactant molecules available for independent micellization.

Variations of Critical Aggregation Concentration (cac), Polymer Saturation Concentration (psc), and Apparent Critical Micellar Concentration (cmc^*) of NaPSS-CTAB with Polyelectrolyte Concentration, Temperature, and Solvent Composition of the Mixed Solvent Media

From Table 1 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 bind to the polyion chain.

The cac values are also found to increase with the increase in temperature (Table 1). This means that replacement of the counterions of the polyelectrolyte by the surfactant ions increases with temperature. Another possible reason is the temperature-induced uncoiling of the polyion chain which results in more available binding sites at higher temperature for complex formation. A similar temperature dependence of the cac value for NaCMC-CTAB interaction was also noticed earlier by means of conductometry and microcalorimetry.¹¹

Table 1 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 acetonitrile *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 acetonitrile in the mixed solvent media. As a result, the bound surfactants 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.

The variations of the psc , and cmc^* values for the present system also followed similar trends with polyelectrolyte concentration, solvent composition and temperature as those observed for the cac (mentioned earlier) thus corroborating the main conclusions drawn from the variation of cac .

Conclusions

This chapter reports the aggregation behaviour of CTAB both in absence and in presence varying concentration of NaPSS in acetonitrile-water mixed solvent media at

308.15, 313.15, and 318.15 K. NaPSS induced self-aggregation of CTAB at a concentration much lower than its *cmc* values in the mixed solvent media. The system has evidenced different kinds of interacting features corresponding to polyelectrolyte-induced aggregate formation, CTAB aggregate-NaPSS binding in bulk, CTAB-NaPSS binding at the interface, and free micelle formation in solution. The critical aggregation concentrations (*cac*), polymer saturation concentrations (*psc*), and apparent critical micellar concentrations (*cmc**) for NaPSS-CTAB interactions have been determined from tensiometry and conductometry. Good agreement between the values obtained from these two techniques was found. The results have been discussed in terms of various interactions prevailing in the present system.

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Table 1. The Critical Aggregation Concentration (*cac*), Polymer Saturation Concentration (*psc*), Critical Micellar Concentration (*cmc*), and the Apparent Critical Micellar Concentration (*cmc**) obtained from Tensiometry and Conductometry in Acetonitrile-Water Mixed Solvent Media Containing 10, and 20 Vol Percent of Acetonitrile at 308.15, 313.15, and 318.15 K

T (K)	[NaPSS] % (w/v)	<i>cac</i> (mM)	<i>psc</i> (mM)	<i>cmc</i> (mM)	<i>cmc*</i> (mM)	<i>cac</i> (mM)	<i>psc</i> (mM)	<i>cmc</i> (mM)	<i>cmc*</i> (mM)
		10 Vol Percent Acetonitrile				20 Vol Percent Acetonitrile			
308.15	0.00			3.03 ^a				3.54 ^a	
				3.24 ^b				3.87 ^b	
	0.01	1.45 ^a	3.97 ^a		6.80 ^a	1.54 ^a	5.95 ^a		9.44 ^a
		1.43 ^b	3.75 ^b		7.30 ^b	1.57 ^b	6.17 ^b		10.05 ^b
	0.02	1.71 ^a	4.44 ^a		9.12 ^a	1.86 ^a	6.76 ^a		10.47 ^a
		1.65 ^b	4.53 ^b		8.64 ^b	1.84 ^b	7.27 ^b		10.01 ^b
313.15	0.00			3.62 ^a				4.10 ^a	
				3.44 ^b				4.23 ^b	
	0.01	1.45 ^a	4.43 ^a		7.55 ^a	1.61 ^a	6.60 ^a		9.97 ^a
		1.49 ^b	4.10 ^b		7.60 ^b	1.74 ^b	7.04 ^b		10.22 ^b
	0.02	1.96 ^a	4.84 ^a		9.73 ^a	2.10 ^a	7.94 ^a		10.53 ^a
		1.91 ^b	5.07 ^b		9.50 ^b	2.20 ^b	7.64 ^b		10.98 ^b
318.15	0.00			4.56 ^a				5.24 ^a	
				4.25 ^b				5.13 ^b	
	0.01	1.47 ^a	4.98 ^a		8.34 ^a	1.78 ^a	7.28 ^a		10.23 ^a
		1.50 ^b	4.70 ^b		8.51 ^b	1.81 ^b	7.60 ^b		10.94 ^b
	0.02	1.98 ^a	5.35 ^a		10.45 ^a	2.23 ^a	8.06 ^a		11.63 ^a
		2.01 ^b	5.18 ^b		9.91 ^b	2.25 ^b	7.84 ^b		11.28 ^b

^aValues obtained from tensiometry.

^bValues obtained from conductometry.

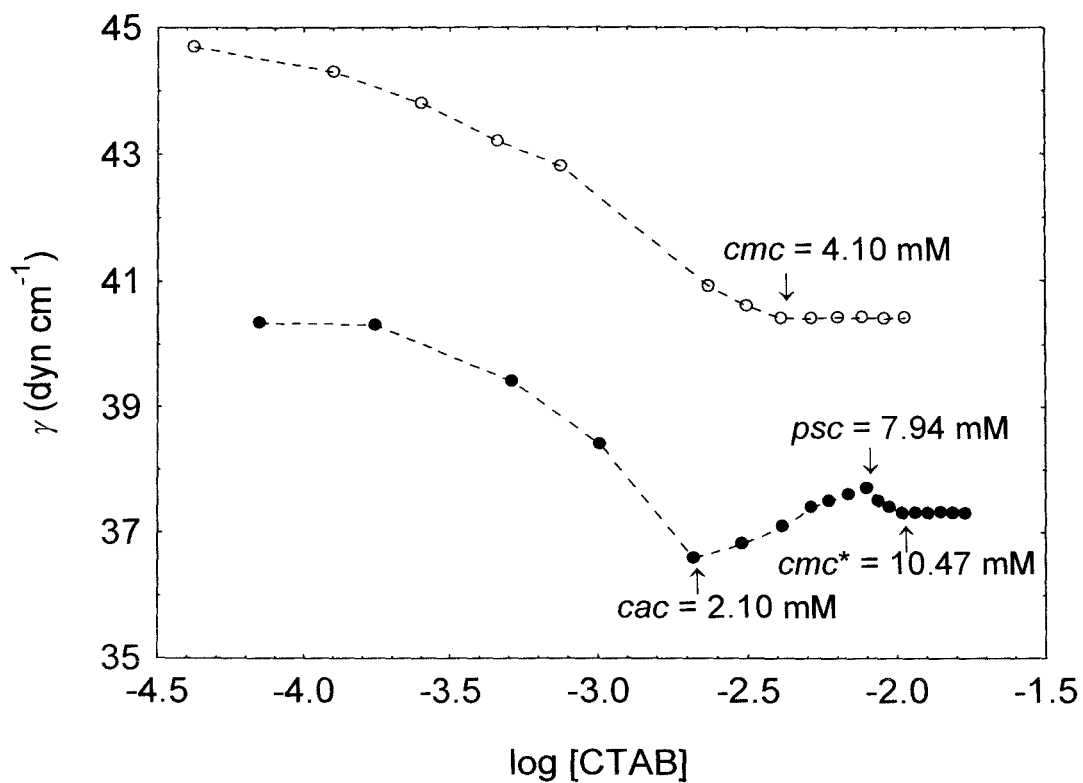


Figure 1. Variation of γ with $\log [\text{CTAB}]$ for CTAB and for NaPSS-CTAB system in acetonitrile-water mixture containing 20 vol percent of acetonitrile at 313.15 K, NaPSS concentration being 0.02% (w/v).

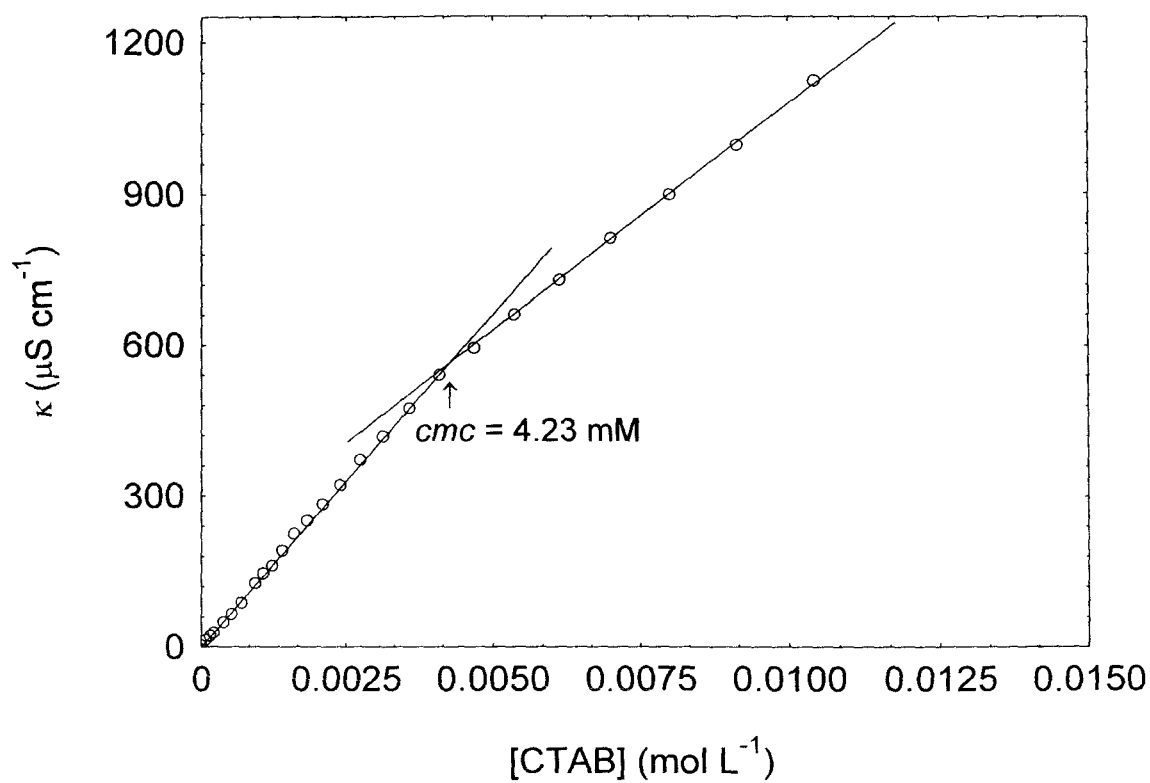


Figure 2a. Variation of the specific conductivity (κ) with the concentration of CTAB in acetonitrile-water mixture containing 20 vol percent of acetonitrile at 313.15 K.

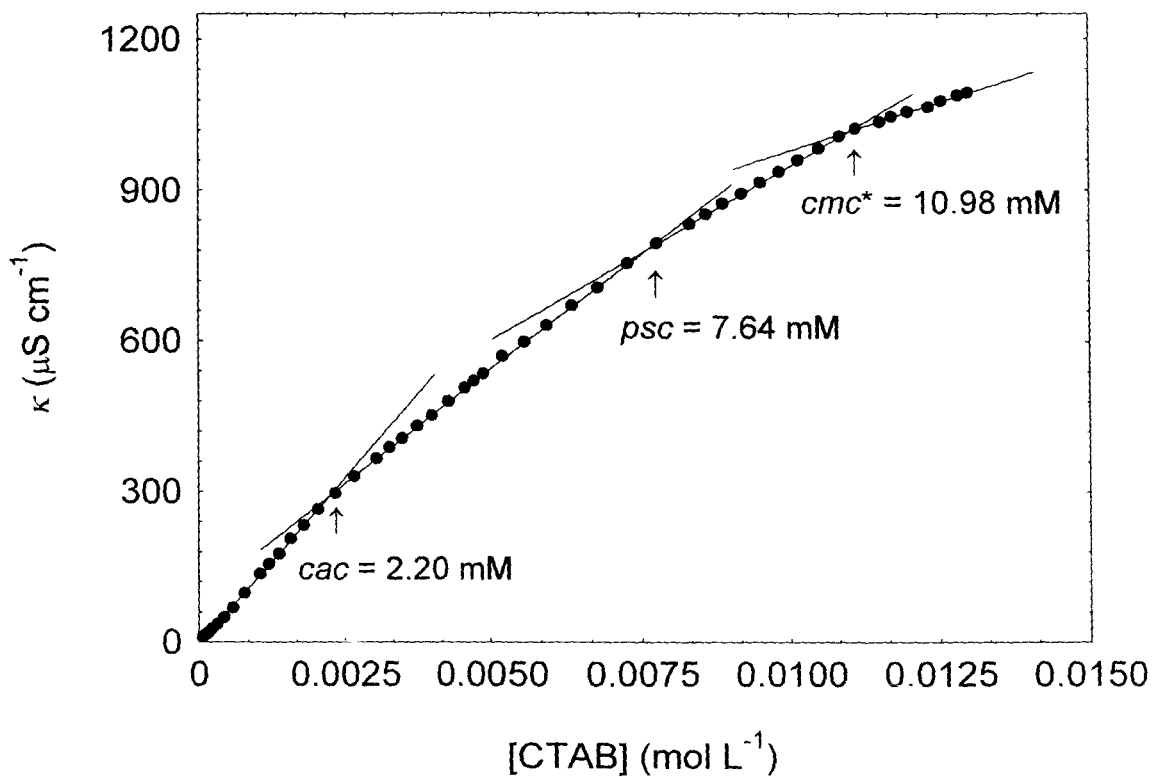


Figure 2b. Variation of the specific conductivity (κ) with the concentration of CTAB in acetonitrile-water mixture containing 20 vol percent of acetonitrile at 313.15 K, NaPSS concentration being 0.02% (w/v).