

Viscosity of Sodium Polystyrenesulfonate in Presence of Cetyltrimethylammonium Bromide in Methanol-Water Mixed Solvent Media

Introduction

Polyelectrolytes and surfactants are often found together in aqueous formulations of cosmetics, detergents, pharmaceuticals, and coatings to simultaneously control surface tension and rheology. Consequently, the interactions between polyelectrolytes and oppositely charged surfactants have been studied extensively.¹⁻¹⁰ In such systems, the balance of hydrophobic and electrostatic interactions between the two species determines the structure and solution behaviour of the system. Owing primarily to the strong electrostatic attraction between these species and the release of their condensed counterions upon binding,^{11,12} there is a strong thermodynamic driving force for association. This is evidenced by the very low critical aggregation concentration (*cac*), the surfactant concentration at which micelles form in the presence of oppositely charged polyelectrolytes.¹³⁻¹⁶ The *cac* is below the concentration where surfactant first forms micelles without polymer present in the system, because the polyelectrolyte stabilizes the charge on the micelle surface and no counterions are required to condense on either the micelle or the section of the polyion that is associated with the micelle.¹¹ Various methods have been employed to determine the *cac*, such as surface tension, conductometry, calorimetry, dye solubilization, binding isotherm measurements using surfactant-selective, solid-state membrane electrodes etc. We have already demonstrated the use of surface tension and conductometry for sodium polystyrenesulfonate (NaPSS)-cetyltrimethylammonium bromide (CTAB) system in methanol-water mixed solvent media at different temperatures. The strong interaction between the polyelectrolyte and oppositely charged surfactant causes precipitation at concentration near the stoichiometric balance point, where equivalent amounts of surfactants and charged monomers are present.

At low polyelectrolyte concentrations with no added salt, there is a semidilute unentangled solution regime that spans a wide concentration range. Addition of surfactant to such solutions lowers the viscosity dramatically.¹⁷⁻²⁴ Abuin and Scaiano¹⁷ showed that this viscosity reduction is far stronger than the simple charge screening resulting from the

addition of monovalent salt. Later, Plucktaveesak *et al.*²⁵ introduced a simple viscosity model to predict the reduction of the viscosity of a polyelectrolyte solution upon addition of oppositely charged surfactant, based upon the scaling theory for viscosity of unentangled semidilute polyelectrolyte solutions.²¹ The model accounts for both changes in the effective chain length of the polyelectrolyte when it wraps around the exterior of the spherical micelles and changes in ionic strength resulting from surfactant and polyelectrolyte counterions. It is important to point out that Plucktaveesak *et al.*²⁵ treat solutions with a stoichiometric excess of charged monomers relative to the oppositely charged added surfactant.

In this chapter, we describe our investigation on the viscosity behaviour of NaPSS in presence of CTAB in methanol-water mixtures in presence of an excess of the polyelectrolyte species. The data obtained were analyzed on the basis of the equation developed by Plucktaveesak *et al.*²⁵

Experimental

Methanol (E. Merck, India, 99% pure) was distilled with phosphorous pentoxide and then redistilled over calcium hydride. The purified solvent had a density of 0.7772 g.cm^{-3} and a co-efficient of viscosity of 0.4742 mPa.s at 308.15 K ; these values are in good agreement with the literature values.²⁶ Triply distilled water with a specific conductance less than $10^{-6} \text{ S.cm}^{-1}$ at 308.15 K was used for the preparation of the mixed solvents. The sodium salt of polystyrenesulfonic acid (NaPSS) employed in this investigation was purchased from Aldrich Chemical Company, Inc. The average molecular weight (M_w) of the sample was 70,000.

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

The stock solutions were freshly prepared for each concentration series to avoid problems of aging and microorganism contamination, which was found to occur with diluted surfactant solutions.²⁷

The viscometric measurements were performed at 308.15 K using a Schultz-Immergut-type viscometer²⁸ with a sintered disc fitted to the widest arm to filter the solution/solvent from dust particles, if any. The measurements were made in a thermostat maintained within $\pm 0.01 \text{ K}$ of the desired temperature by means of a mercury-in-glass thermoregulator, and the absolute temperature was determined by a calibrated platinum resistance thermometer and Muller bridge.^{29,30}

Several independent solutions were prepared, and runs were performed to ensure the reproducibility of the results. To check whether the reduced viscosities depend on the shear

rate in the concentration range investigated; measurements with capillaries of different sizes were performed. This did not lead to different values of the reduced viscosity.

To avoid moisture pick up, all of the solutions were prepared in a dehumidified room with utmost care. In all cases, the experiments were performed at least in three replicates.

Theory

Plucktaveesak *et al.*²⁵ introduced a simple model for the viscosity of polyelectrolyte solution in the presence of an added surfactant based on the scaling theory for the viscosity of unentangled semidilute polyelectrolyte solutions.³¹ A brief description of this approach is given below.

A Zimm model for the viscosity of dilute polyelectrolyte solutions has been proposed by Dobrynin *et al.*³¹ The specific viscosity (η_{sp}) is predicted to scale as the 4/5 power of the degree of polymerization (N) and to decrease as monovalent salt (with molar concentration c_s) is added:

$$\eta_{sp} \approx N^{4/5} \left[1 + \left(\frac{2c_s}{fc_p} \right) \right]^{-3/5} \quad c_p < c^* \quad (1)$$

where f is the fraction of monomers bearing an effective charge (*i.e.*, fraction of uncondensed counterions), and c_p is the molar concentration of monomers. Hence, the term in the parentheses is the ratio of concentration of small ions from added salt ($2c_s$) to that of the free counterions from the polyelectrolyte ($f c_p$). The overlap concentration c^* is the crossover concentration between the dilute and semidilute regimes.³¹

A Rouse model for the viscosity of unentangled semidilute polyelectrolyte solutions has also been proposed by Dobrynin *et al.*³¹ This scaling theory predicts that the specific viscosity (η_{sp}) of the unentangled polyelectrolyte solutions is proportional to the degree of polymerization N of the chains and decreases with addition of monovalent salt (with molar concentration c_s):

$$\eta_{sp} \approx N \left[1 + \left(\frac{2c_s}{fc_p} \right) \right]^{-3/4} \quad c^* < c_p < c_e \quad (2)$$

This equation holds for concentrations above the overlap concentration but below the entanglement concentration c_e .

As oppositely charged surfactant is added to a polyelectrolyte solution, the viscosity of the solution is lowered by two effects. First, the polyelectrolyte loses some of its effective chain length in wrapping around the exterior of the surfactant micelles. It was assumed that one neutralized monomer is bound to each surfactant headgroup in the micelle. It was further assumed that neither the placement of charges along the polyion chain nor the fraction of neutralized monomers is altered by the interaction with the micelle. The polyion chain will wrap efficiently around the micelle, using a section of chain containing a number of neutralized monomers that is equal to the aggregation number of the micelle.

Now, if c is the concentration of the added surfactant, the fraction of polyelectrolyte monomers tied up with micelles is $c/(\alpha c_p)$, where α is the degree of neutralization, so the fraction of polyelectrolyte monomers that are free from micelles (proportional to the effective polyelectrolyte chain length) is $1 - c/(\alpha c_p)$. The second effect is that the ionic strength (the concentration of free ions) in solution increases as surfactant is added. These ions consist of polyelectrolyte counterions released upon interaction with the surfactant micelle, and counterions of surfactant molecules. It was assumed that, for each surfactant molecule bound to a polyelectrolyte monomer, there is effectively one salt molecule added to the solution, comprising the counterion of the polyelectrolyte monomer and the counterion of the surfactant. Since in most cases the critical aggregation concentration (cac) is very small, practically all added surfactant is bound to the polyelectrolyte, making the effective salt concentration c , the concentration of added surfactant. The number density of free polyelectrolyte counterions also diminishes as surfactant is added because the fraction of the chain bound to micelles no longer has free counterions. It was assumed that the fraction of free counterions on the remaining sections of chain is the same as without added surfactant, making the number density of free counterions $fc_p[1 - c/(\alpha c_p)]$. The ratio of salt ions to free polyelectrolyte counterions ($2c_s/fc_p$) in Eqs. (1) and (2) becomes $2c/(fc_p[1 - c/(\alpha c_p)])$. Eqs. (1) and (2) are, therefore, modified to describe the viscosity of polyelectrolyte solutions as oppositely charged surfactant is added:

$$\frac{\eta_{sp}(c)}{\eta_{sp}(0)} = \left[1 - \left(\frac{c}{\alpha c_p} \right) \right]^{4/5} \left[1 + \frac{2c}{f c_p \left[1 - \left(\frac{c}{\alpha c_p} \right) \right]} \right]^{-3/5}$$

$c_p < c^*$ (3)

$$\frac{\eta_{sp}(c)}{\eta_{sp}(0)} = \left[1 - \left(\frac{c}{\alpha c_p} \right) \right] \left[1 + \frac{2c}{f c_p \left[1 - \left(\frac{c}{\alpha c_p} \right) \right]} \right]^{-3/4}$$

$c^* < c_p < c_e$ (4)

$\eta_{sp}(c)$ and $\eta_{sp}(0)$ are the specific viscosities of polymer with and without added surfactant, respectively.

Eq. (4), however, needs modification for surfactant concentration above the critical aggregation concentration and the relevant equation is

$$\frac{\eta_{sp}(c)}{\eta_{sp}(0)} = \left[1 - \delta \left(\frac{c - cac}{\alpha c_p} \right) \right] \left[1 + \frac{2c}{f c_p \left[1 - \delta \left(\frac{c - cac}{\alpha c_p} \right) \right]} \right]^{-3/4}$$

$c^* < c_p < c_e$ and $c > cac$ (5)

The critical aggregation concentration is cac and the fraction of micelle headgroups associated with polyelectrolyte is δ .

Since for the system under investigation, the surfactant concentrations are always smaller than its critical aggregation concentration, we have applied Eq. (4) in order to predict the viscosity data.

Results and Discussion

Figures 1 through 3 show the variation of the specific viscosity of NaPSS [$\eta_{sp}(c)$] as a function of the ratio of the molar concentration of CTAB (c) to the monomolar concentration of NaPSS (c_p) in methanol-water mixed solvent media at 308.15 K in presence of CTAB. For

all of the semidilute solutions studied, the viscosity of the polyelectrolyte–surfactant solutions decreases as c/c_p increases, *i.e.*, as the relative amount of the surfactant increases. Since the concentrations of the surfactant used here are all below its critical aggregation concentration (*cf.* chapter VIII) and since the polyelectrolyte concentrations used are in the semidilute regime, we have analyzed the experimental results on the basis of Eq. (4). The fractions of uncondensed counterions (f) appearing in the equation have been obtained by conductometric measurements described earlier (Chapter IV).

As shown in Figures 1-3, the predictions of specific viscosities are in good agreement with experimental data for all three concentrations of surfactant in all the mixed methanol-water media over the entire c/c_p range investigated.

The aggregation number of ionic surfactant micelles formed in the presence of oppositely charged polyelectrolyte has been reported to be somewhat smaller or somewhat larger than the aggregation number of the micelles formed without polymer present (References 11 and 12, and references therein). Such changes are not fully understood yet. One very nice feature of the model used for the present analysis is that the predictions are insensitive to aggregation number as long as the micelles are still roughly spherical as tacitly assumed in the treatment. Viscosity is determined by the size of the polyion chain in solution. In this model the size of the chain, and hence the viscosity, is determined from the simply from the fraction of monomers associated with micelles, not the details of the micellar size. The superb agreement of our experimental results with the predictions indicates that the basic assumption of simple random placement of spherical micelles in solution holds true for the CTAB micelles formed in methanol-water mixed solvent media in presence of the polyelectrolyte NaPSS. This also rules out the formation of other phases namely, lamellar phases or cubic phases of spherical micelles. Formation of such interesting phases have, however, been reported for polyelectrolyte solutions with high concentrations of added oppositely charged surfactant.³²⁻³⁴ Thus the model for the viscosity of polyelectrolyte solutions in presence of an added oppositely charged surfactant put forwarded by Plucktaveesak *et al.*²⁵ on the basis of the scaling theory for the viscosity of unentangled semidilute polyelectrolyte solutions has been shown to be very successful for the present system under consideration.

Conclusions

This chapter reports the viscometric behaviour of a system consisting of anionic polyelectrolyte NaPSS and a cationic surfactant CTAB in methanol-water mixed solvent media. The experimental results of the specific viscosity of the polyelectrolyte solutions with added surfactant have been nicely described using a simple viscosity model²⁵ based on the scaling theory for viscosity of unentangled semidilute polyelectrolyte solutions.³¹ The present analysis indicated the formation of spherical micelles for the CTAB molecules in methanol-water mixed solvent media in presence of the polyelectrolyte NaPSS.

References

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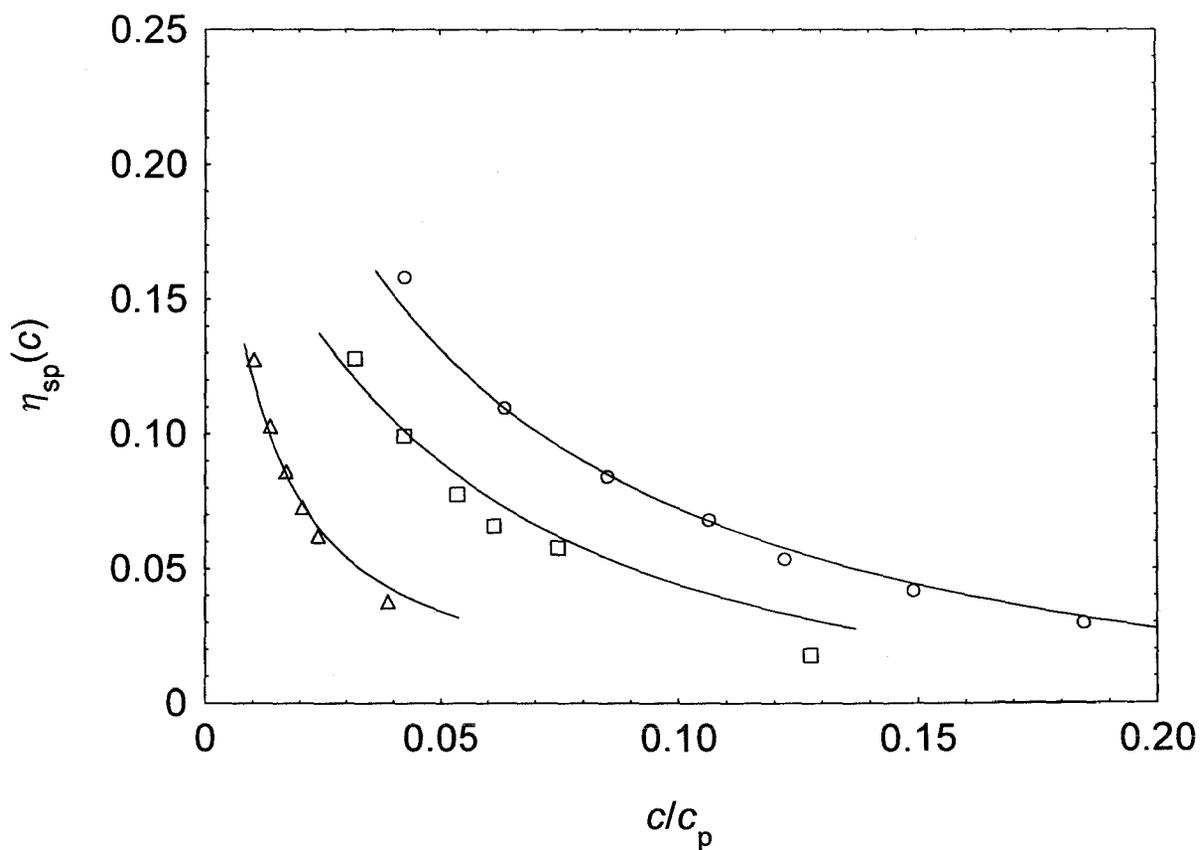


Figure 1. Variation of $\eta_{sp}(c)$ for NaPSS-CTAB system with c/c_p in methanol-water mixture containing 8 mass% methanol at 308.15 K: triangles, 0.0001 mol.L⁻¹ CTAB; squares, 0.0003 mol.L⁻¹ CTAB; circles, 0.0006 mol.L⁻¹ CTAB. Solid lines are calculated ones.

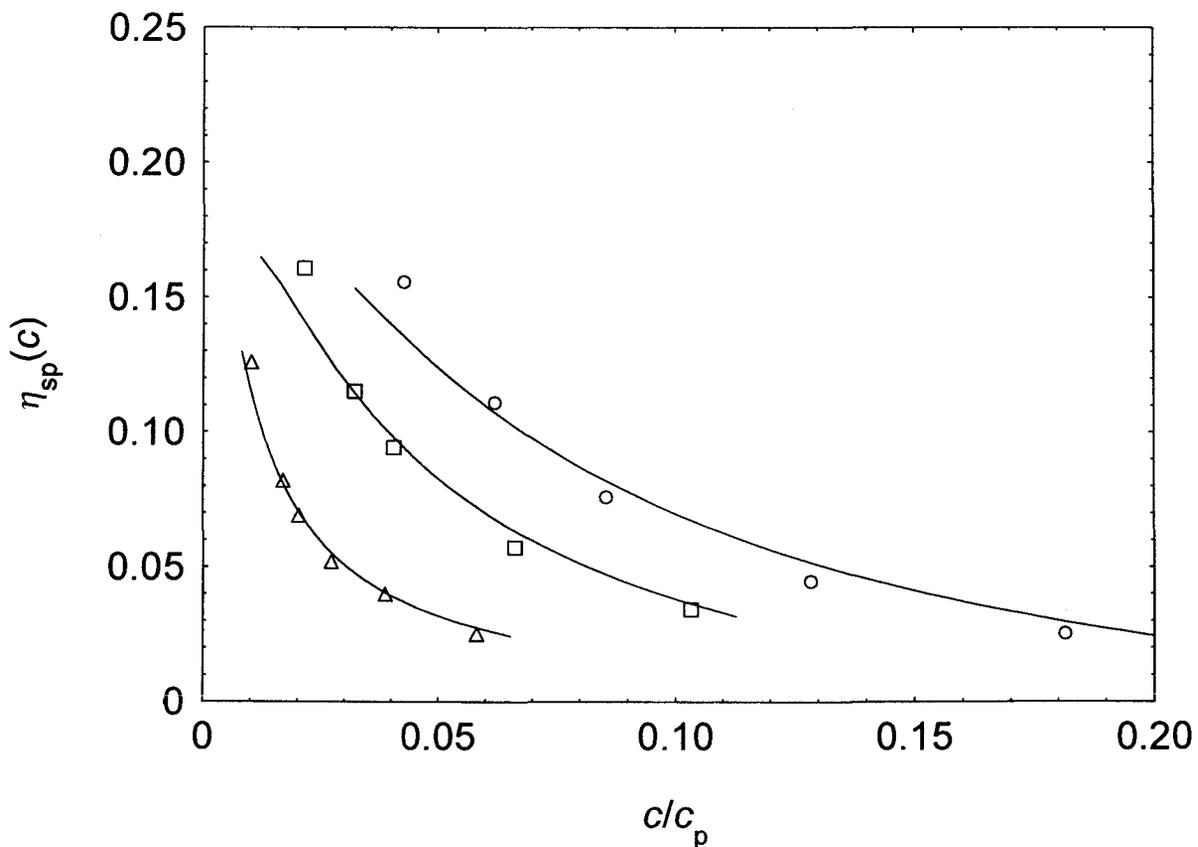


Figure 2. Variation of $\eta_{sp}(c)$ for NaPSS-CTAB system with c/c_p in methanol-water mixture containing 16 mass% methanol at 308.15 K: triangles, 0.0001 mol.L⁻¹ CTAB; squares, 0.0003 mol.L⁻¹ CTAB; circles, 0.0006 mol.L⁻¹ CTAB. Solid lines are calculated ones.

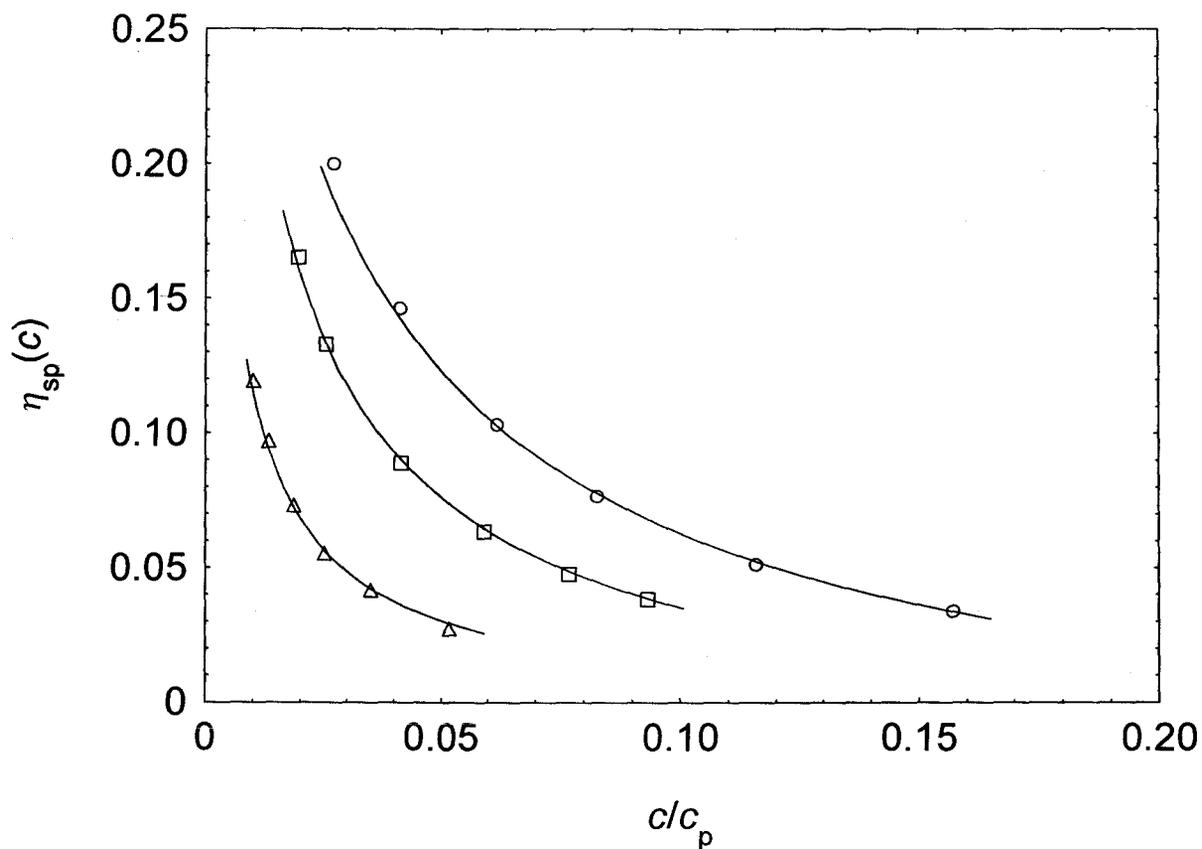


Figure 3. Variation of $\eta_{sp}(c)$ for NaPSS-CTAB system with c/c_p in methanol-water mixture containing 34 mass% methanol at 308.15 K: triangles, 0.0001 mol.L⁻¹ CTAB; squares, 0.0003 mol.L⁻¹ CTAB; circles, 0.0006 mol.L⁻¹ CTAB. Solid lines are calculated ones.