

# Complex Formation Between Cationic Polyelectrolytes and Anionic Surfactants

M. Mihai<sup>\*</sup>, G. Dabija<sup>\*\*</sup>, C. Costache<sup>\*\*</sup>

<sup>\*</sup>Chemical Engineering, University Politehnica of Bucharest, Faculty of Apply Chemistry and Material Science, 1-7 Polizu Street, sect 1, 011061 Bucharest, Romania

<sup>\*\*</sup>Technology of Inorganic Substances and Environmental Protection, University Politehnica of Bucharest, Faculty of Apply Chemistry and Material Science, 1-7 Polizu Street, sect 1, 011061 Bucharest, Romania

**Abstract:** The polyelectrolyte – surfactant complexes formation has been studied. The critical micelle concentration for every polyelectrolyte and surfactant which had been used has been measured on this purpose. The phase behaviour of mixtures of a cationic polyelectrolyte (Praestol 644) and an anionic surfactant (sodium lauryl sulphate – SLS) has been studied. Three phase regions were identified for a given polyelectrolyte concentration, with increasing surfactant concentration. The rheological consequences of interactions of polyelectrolytes with surfactants of the opposite charge are experimentally studied. The results reveal that the Praestol 644 solution has the Bingham pseudoplastic, reopectic and viscoelastic and the complex solutions lose the viscoelastic and rheopectic rheological properties.

**Keywords:** polyelectrolyte, surfactant, complex polyelectrolyte – surfactant, rheology

## 1. Introduction

Polyelectrolytes are used in a number of technical applications, such as water treatment. With polyelectrolytes can change the surface properties of colloids, rheology of solutions, wettability etc. In particular, cationic polyelectrolytes are used in the water treatment because of their ability to interact with negatively charged surfaces. Using surfactants in combination with polyelectrolytes increases the width of the applications even further, and mixtures of polymers and surfactants in aqueous solution have been used for colloidal stabilization or flocculation as well as rheology control.

The interaction between polyelectrolytes and oppositely charged surfactants can be understood considering electrostatic and hydrophobic interactions (Vautrin 2006). At low concentrations, the surfactant binds individually to the polyelectrolyte through electrostatic interactions. A cooperative association occurs at the critical aggregation concentration,  $c_{ac}$ , as the concentration is raised due to hydrophobic interactions between the surfactant tails. This aggregation process leads in some cases to a bead-and-necklace type structure, where surfactant aggregates are located along the polyelectrolyte chain (Bastardo 2005).

The addition of a simple salt lowers the viscosity of polyelectrolyte solutions because salt screens the electrostatic repulsion that expands the size of the polyelectrolyte. The addition of an equivalent amount of oppositely charged surfactant has a larger effect on viscosity (Abuin and Scaiano 1986). This is because flexible polyelectrolytes bind to the spherical surfactant micelles by wrapping around the exterior of the micelle, thereby shortening the effective length of the

polyelectrolyte chain (Konop 1997). The polyelectrolyte stabilizes the large charge on the micelle surface and no counter ion condensation on the micelle surface is needed (Goddard 1993). These effects stabilize the spherical micelles, reflected in micelles forming at a much lower concentration when oppositely charged polyelectrolytes are present (Colby 2000).

## 2. Experimental

The cationic Praestol 644 is a commercial denomination of a copolymer of polyacrylamide with acrylic acid. The association between the cationic polyelectrolyte Praestol 644 and the anionic surfactant sodium lauryl sulphate (SLS) has been studied using the surface tension measurements of the solutions. These are simple measurements that monitor the polyelectrolyte and surfactant aggregates formed in solution.

The rheological behaviour of the solutions are experimentally studied with rheoviscosimetre Rheotest RV

## 3. Results and discussion

In order to study the influence of association degree in micelles of the used substances on the complex formation the micellar critical concentration of each substance was experimentally determined. The results are presented in Figure 1.

The consequences of interactions of polyelectrolytes with surfactants of the opposite charge are presented in figures 2 – 5

The values of the critical aggregation concentrations and of the critical saturation concentration for each solution are presented in the table 1.

TABLE 1. The dependence of the concentrations  $c_{ca}$  and  $c_{cs}$  from the Praestol 644 concentration

c, %	$c_{ca}, 10^{-4}$	$c_{cs}, 10^{-3}$
$1.0 \cdot 10^{-4}$	3.0	5.5
$7.5 \cdot 10^{-4}$	3.0	6.0
$4.4 \cdot 10^{-3}$	3.2	6.0

From the diagram analysis of those figures results that for  $c_{SLS} > 3 \cdot 10^{-4}$  % the surfactant molecules are associated in micelles but the macromolecules of polymer are not associated and the complex forms by engraftment of surfactant micelles on the macromolecules polymer chain. The complex solution superficial tension is lower then the one of the polymer solution. These properties recommend the use of this solution in interfacial liquid – solid processes.

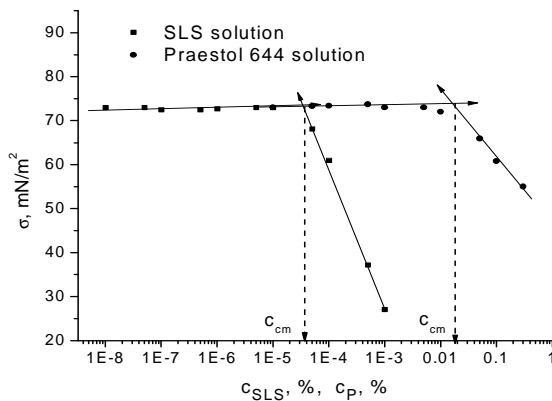


Figure 1. Superficial tension dependence for the Praestol 644, respective SLS aqueous solution

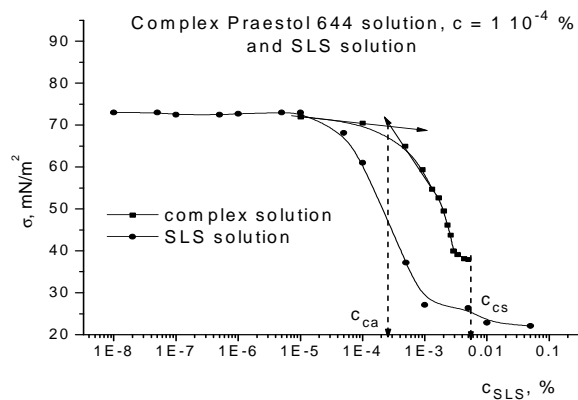


Figure 2. Superficial tension dependence for the aqueous concentration solutions of the Praestol 644 and SLS complex for  $c = 1 \cdot 10^{-4}$  % SLS concentration solutions at 20 °C

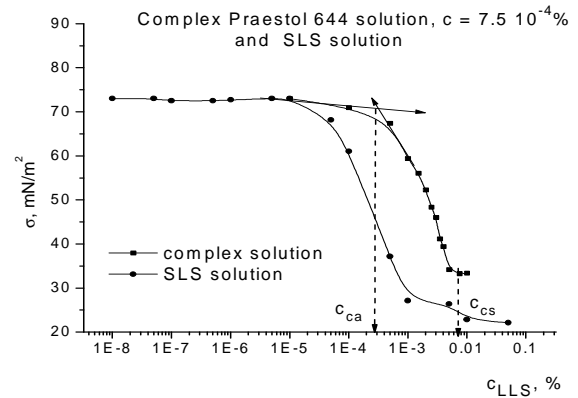


Figure 3. Superficial tension dependence for the aqueous concentration solutions of the Praestol 644 and SLS complex for  $c = 7.5 \cdot 10^{-4}$  % SLS concentration solutions at 20 °C.

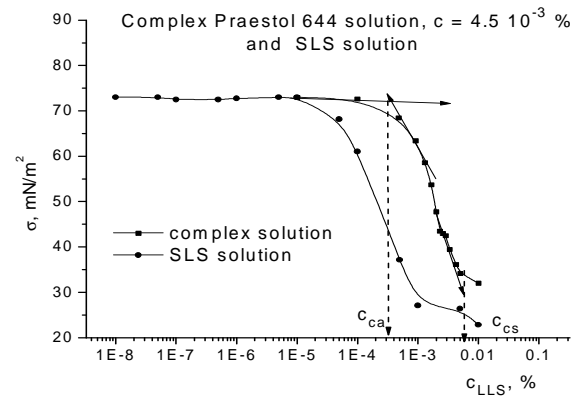


Figure 4. Superficial tension dependence for the aqueous concentration solutions of the Praestol 644 and SLS complex for  $c = 4.5 \cdot 10^{-3}$  % SLS concentration solutions at 20 °C.

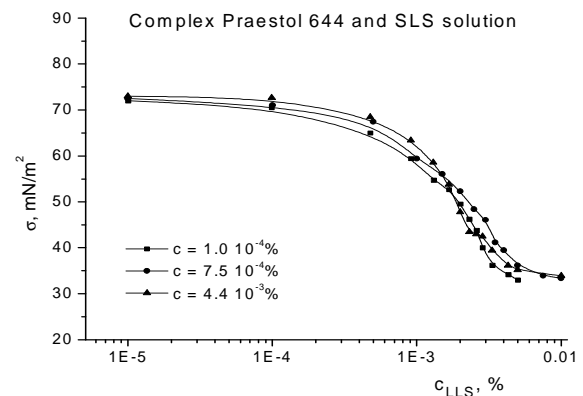


Figure 5. Superficial tension dependence for the aqueous concentration solutions of the Praestol 644 and SLS complex for different SLS concentration solutions at 20 °C

The same results are obtained at higher concentration of the polymer solution, while this concentration is lower than the micellar critical concentration. At concentrations  $c > 10^{-2}$  % of the polymer solution the formed complex precipitates entering in the heterogeneous zone of complex formation. In the analysed situations the concentrations for aggregation and critical concentration of saturation have the same values for every experiment,  $c_{ca} = 3 \cdot 10^{-4}$  %, and  $c_{cs} = 6 \cdot 10^{-3}$  %. It results that between the Praestol 644 solution and SLS there are complexes with good defined structure and composition forming.

The concentrations values of  $c_{ca}$  and  $c_{cs}$  remain constant independent from the quantities ratio of polymer and SLS from the solution. The complexes solutions have the superficial tension lower than the one of the polymer solution, but higher than the one of the surfactant solution. The superficial tension of the solution decreases only after aggregation. In order to highlight the influence of the admixture of surfactant on the polymer solution, the rheogram of the Praestol 644 solution was experimentally determined (figure 6). Figure 6 shows that the Praestol 644 solution has the Bingham pseudoplastic behaviour and the rheological model is  $\tau = 7.27 + 399\dot{\gamma}^{0.39}$ ; has reopectic behaviour at  $\dot{\gamma} < 22s^{-1}$  and viscoelastic behaviour with the relaxation time  $t_r = 1/30 s = 0.033 s$  for going diagram and  $t_r = 1/22 = 0.045 s$  for return diagram.

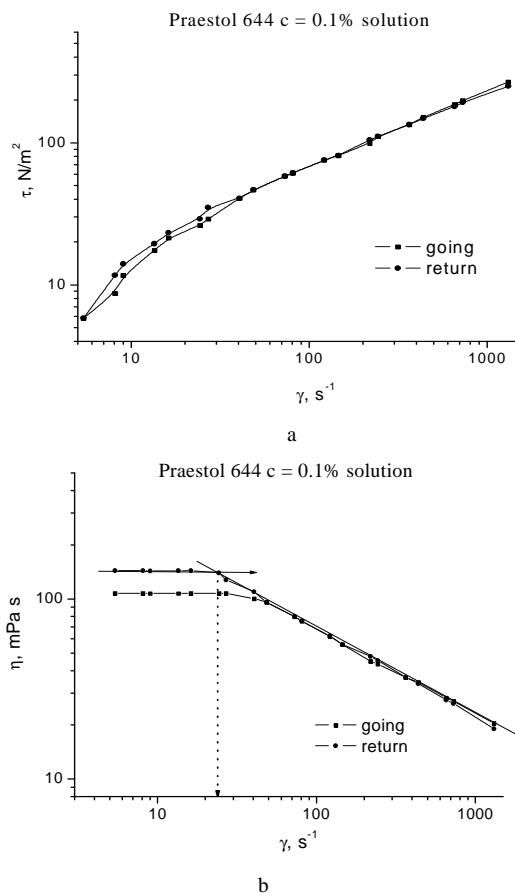


Figure 6. Rheogram of Praestol 644  $c = 0.1$  % solution at  $20\text{ }^{\circ}\text{C}$  in  $\tau = f(\dot{\gamma})$  coordinate (a) respectively  $\eta = f(\dot{\gamma})$  (b)

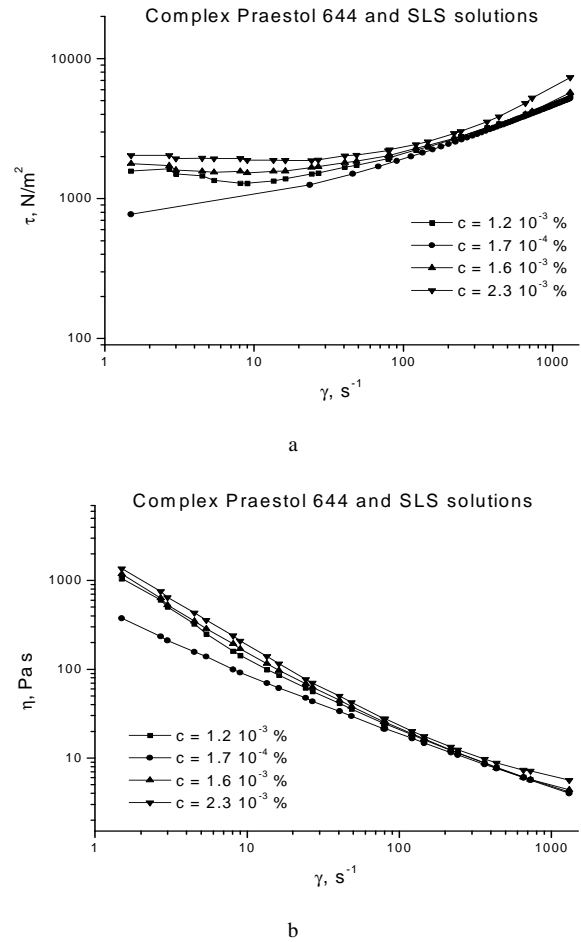


Figure 7. Rheogram of complex solution made with Praestol 644  $c = 0.1$  % for different SLS concentration solutions at  $20\text{ }^{\circ}\text{C}$  in coordinate  $\tau = f(\dot{\gamma})$  (a) and  $\eta = f(\dot{\gamma})$  (b).

The rheograms presented in figure 7 were obtained for the complex solution formed by adding surfactant solution of different concentrations in the polymer solution with constant concentration. The Rheograms were correlated trough nonlinear regression with Ostwald de Waele  $\tau = \tau_0 + \eta_a \dot{\gamma}^n$  model and the model parameters for each studied case are presented in table. The results presented in figure 7 point out that by forming the complex the polymer solution lose the viscoelastic and reopectic properties.

TABLE 2. The dependence of the model parameters from the concentration of the SLS solution

CSLS, %	$\tau_0$	$\eta_a$	n
0	7.27	399.00	0.39
$1.710^{-4}$	599.46	141.59	0.49
$1.210^{-3}$	1312.40	56.82	0.59
$1.610^{-3}$	1545.21	36.09	0.65
$2.310^{-3}$	1882.77	7.46	0.92

The analysis of the values presented in the table point out that if the surfactant concentration rises then the value of the flow threshold of the Bingham solution rises

(constant  $\tau_0$ ), the value of the apparent viscosity of the solution decreases (constant  $\eta_a$ ) and the pseudoplastic character of the solution decreases (constant  $n$ ). The rheological properties of the polymer solution are significantly modified.

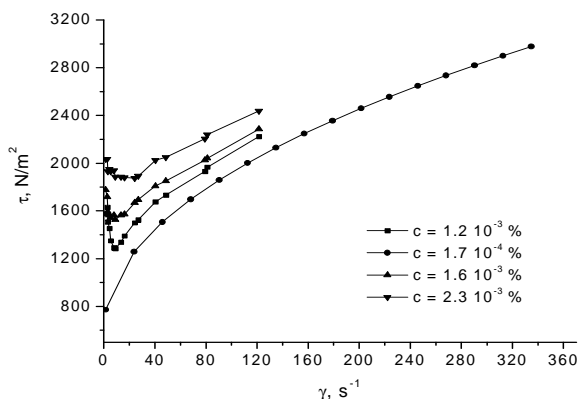


Figure 8. Rheogram of complex solution made with Praestol 644  $c = 0.1\%$  for different SLS concentration solutions at  $20\text{ }^{\circ}\text{C}$  in coordinate  $\tau = f(\gamma)$  at low share rate values

In the rheograms presented in figure 8 it is to be found that at low share rate values the variation law  $\tau = f(\gamma)$  is different from the variation law for higher values of the share rate. The reorganisation of the complex structure formed under the action of the share stress may be the explanation of this fact. It results that a hard-set complex forms, because the resulted rheograms are similar with the polymer solution rheogram. This behaviour is the result of the cationic character of the Praestol 644 solution.

## 4. Conclusions

The interaction between polyelectrolytes and oppositely charged surfactants are experimentally studied. A cooperative association occurs at the critical aggregation concentration,  $c_{ac}$ , when the surfactant aggregates are located along the polyelectrolyte chain.

The rheology of polyelectrolyte solutions are profoundly altered by the presence of surfactants. The addition of an oppositely charged surfactant lowers the viscosity of polyelectrolyte solutions. This is because flexible polyelectrolytes bind to the spherical surfactant micelles by wrapping around the exterior of the micelle.

## REFERENCES

1. Abuin, E. B., Scaiano J. C., *J. Amer. Chem. Soc.*, **1984**, 106, pp. 6274-6683.
2. Konop, A. J., Polyelectrolyte Collapse Induced by Aggregation of Oppositely Charged Surfactant, Masters Thesis, Pennsylvania State University, **1997**.
3. Konop A.J, Colby, R.H., *Langmuir*, **1999**, **15**, pp. 58-65.
4. Goddard, E.D., Ananthapadmanabhan, K.P., Interaction of Surfactants with Polymers and Proteins, CRC Press, London, 1993.
5. Colby, R., XIIIth International Congress on Rheology, Cambridge, UK, **2000**, pp. 414-416.
6. Bastardo, L.A., Self assembly of Surfactants and Polyelectrolytes in Solutions at Interfaces, Doctoral Thesis at the Royal Institute of Technology Stockholm, 2005.
7. Vautrin, C., Stabilité et Structure d'Agrégats Cationiques, Thèse de Doctorat de l'Université Versailles Saint-Quentin-en-Yvelines, **2006**.
8. Monteux, C., Thèse de doctorat de l'Université Paris VI, **2004**.