

# Complex Formation between Weak Anionic Polyelectrolyte and Medium Cationic Surfactant

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*This paper presents the results of an experimentally study about the formation of complexes between a weak anionic polyelectrolyte, a copolymer of acrylamide and sodium acrylate, Praestol 2515 and a medium cationic surfactant, hexadecyl trimethyl ammonium bromide (HTAB). The critical micellar concentrations,  $c_{cm}$ , for anionic polyelectrolyte and cationic surfactant have been computed from the superficial tension – concentration curve. Experiences took place in a system of fixed polymer concentration,  $c_p$ , with increasing amount of surfactant. Two concentrations, critical aggregation concentration,  $c_{ac}$  and critical saturation concentration,  $c_{cs}$  are essential for understanding and studying the interactions between polymer and surfactant and they are determined experimentally. In solutions that have  $c_p < c_{cm}$ , by mixing the polymer with HTAB associated in micelles some complexes are formed that have the same values of  $c_{ca}$  and  $c_{cs}$ . In the solutions that have  $c_p > c_{cm}$ , other complexes are formed with different values of the  $c_{ca}$  and  $c_{cs}$ . The changes in the rheological behaviour of the complex solutions formation were also experimentally studied. The Praestol 2515 polymer solution is Bingham pseudoplastic type, without a rheological characteristic dependent on time or viscoelastic properties. By adding HTAB surfactant some complexes are formed with apparent viscosity and flow threshold lower than those of the pure polymer solution as long as  $c_{HTAB}$  is greater than  $c_{cs}$  and greater than those of the pure polymer solution when  $c_{HTAB}$  is less than  $c_{cs}$ . For all cases, the flow index remains practically constant. The rheograms show that the complexes are stable and resistant to moderate shear stress and therefore they can be used also in processes that involve intensive shear rate flow. For the solid – liquid interface processes are recommended the complexes formed between polymers solution with  $c_p < c_{cm}$  and surfactants solution with  $c > c_{cs}$ .*

*Keywords.: anionic polyelectrolyte, hexadecyl trimethyl ammonium bromide, HTAB, cationic surfactant*

The polymers and tensioactive substances are often associated in industrial applications due to some remarkable synergetic properties of these combinations. The complexes formed by means of these mixtures have better tensioactive properties than the participating single substances thus being preferred in the interface processes of the disperse systems; the rheological properties of these complexes thus formed are superior to the initial polymer and will facilitate the access of these complexes towards the interface [1]. The interaction between the two types of molecules is manifested by means of specific associations and new and original structures which can lead to significant synergetic effects. In the case of the systems which yield a great ratio between surface and volume (i.e. disperse systems) the interfacial phenomena have an important role because they control the processes which take place within these systems [2]. The polymer characteristics determine the association with the tensioactive substances for specific industrial applications. The preferred polymers in such type of associations are those soluble in water, non-toxic and environmentally friendly. The water soluble polymers may also be largely used for certain applications in biology, medicine, as well as in hygiene, in food and detergents industry, and for the treatment of the wastewaters [3, 14-20]. The formed complex is obtained either by attaching the globular micelles of tensioactive substance by means of forces of electrostatic attraction on the amphiphile chain of a

polymer, or by attaching the non-associated tensioactive substance to the globular micelles of the amphiphile polymer due to the electrostatic attraction too [2-6]. The outcome in the forms of complexes in a polymer – surfactant solution is observed by mean of the changes in the physical properties of this particular solution such as the superficial tension, the viscosity or the electric conductivity [7].

The interaction between water-soluble weak anionic polymer and medium cationic surfactants has been observed so far to be nonexistent or very weak contrary to the case of anionic surfactants where many investigations have shown clear evidence of interaction [4, 7].

This paper presents the results of an experimentally study of the complex formation in aqueous solution between a weak anionic polyelectrolyte, a copolymer of acrylamide and sodium acrylate (Praestol 2515) and a medium cationic surfactant, hexadecyl trimethyl ammonium bromide (HTAB).

## Experimental part

The anionic polyelectrolyte Praestol 2515 was purchased from Evonik - Degussa and was used without further purification. The cationic surfactant HTAB with molecular weight equal to 340 g/mol was produced by Aldrich Chemical Co. Polymer stock solution was prepared at room temperature by dissolving Praestol 2515 in powder form in distillate water and by gentle stirring for a period of

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3–5 days and was stored also at the room temperature. Polymer–surfactant solutions were prepared by adding appropriate amounts of HTAB into mixtures of distillate water and polymer stock solutions by gentle stirring for at least 8 h.

The association between Praestol 2515 and HTAB in aqueous solution has been studied experimentally by the changes in the physical properties of the mixture solutions such as the superficial tension and the viscosity. The superficial tension and viscosity measurements were performed on a glass stalagnometer, respectively on an Oswald viscosimeter with a distillate water flow time of about 100 sec at 20°C.

The rheological behaviours of the solutions are experimentally studied with a Rheotest RV rheoviscosimeter manufactured by VEB MLW Prüfgerätewerk Medingen, Dresden, Germany.

## Results and discussion

The study of complexes formation between an anionic weak anionic polymer and a moderate cationic tensioactive substance was started with the determination of critical micellar concentrations,  $c_{cm}$  of the surfactant and polyelectrolyte in aqueous solutions. The knowledge of values of these concentrations is necessary because the study is focused on the complex formed between the polymer which is non-associated to the micelles and the tensioactive substance associated as micelles.

The experimental results of surface tension for the Praestol 2515 and HTAB solutions are presented comparatively in figure 1. One may notice that  $c_{cm}$  for the HTAB solution is equal to  $3 \cdot 10^{-4}$  %, while the polymer solution has this concentration of  $2 \cdot 10^{-3}$  %. This fact is useful to determine the conditions in which the both substances associate in the aqueous solution according to their concentrations.

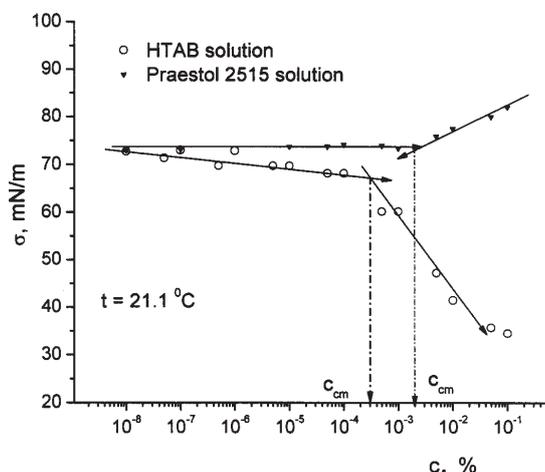
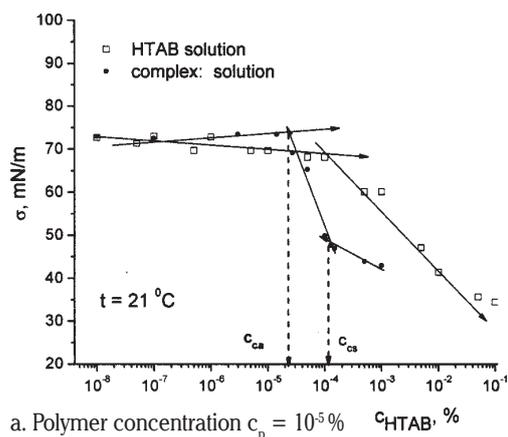


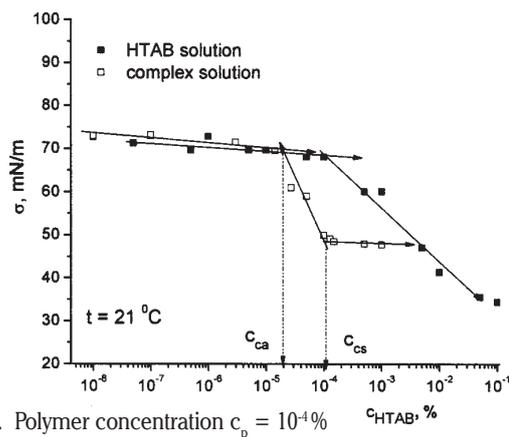
Fig. 1. Critical micellar concentration calculation of HTAB, respectively of Praestol 2515 solutions

Figures 2a – 2d present comparatively the computation procedure for the critical concentrations of saturation  $c_{cs}$  for HTAB and Praestol 2515 solutions keeping three polymer concentrations at values:  $c_p = 1 \cdot 10^{-5}$  % (2a),  $c_p = 1 \cdot 10^{-4}$  % (2b),  $c_p = 1 \cdot 10^{-3}$  % (2c),  $c_p = 1 \cdot 10^{-2}$  % (2d).

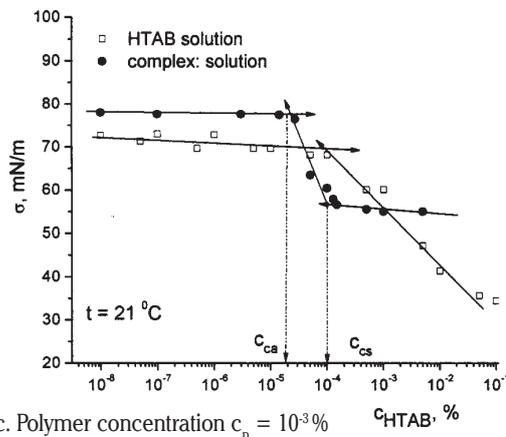
In the system of fixed polymer concentration with increasing amount of surfactant two critical concentrations of surfactant are defined: critical aggregation concentration,  $c_{ca}$  and critical saturation,  $c_{cs}$ . The  $c_{ca}$  is a surfactant concentration at which an interaction between polymer and surfactant takes place and a complex starts to form. No interaction between the polymer and surfactant



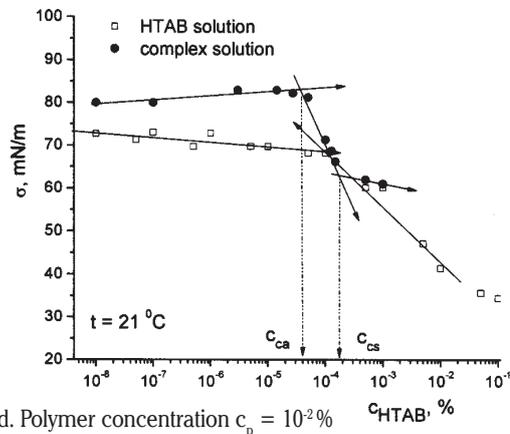
a. Polymer concentration  $c_p = 10^{-5}$  %  $c_{HTAB}$ , %



b. Polymer concentration  $c_p = 10^{-4}$  %  $c_{HTAB}$ , %



c. Polymer concentration  $c_p = 10^{-3}$  %  $c_{HTAB}$ , %



d. Polymer concentration  $c_p = 10^{-2}$  %  $c_{HTAB}$ , %

Fig. 2. Determination of the critical aggregation concentrations  $c_{ca}$  and of the critical saturation concentrations  $c_{cs}$  for the polymer solutions with concentrations  $c = 1 \cdot 10^{-5}$  % (a),  $c = 1 \cdot 10^{-4}$  % (b),  $c = 1 \cdot 10^{-3}$  % (c),  $c = 1 \cdot 10^{-2}$  % (d)

is detected until  $c_{ac}$  is reached. Generally, it appears that an ionic surfactant interacts with the polymer chain at a  $c_{ac}$ , which is substantially lower than the critical micelle concentration,  $c_{mc}$  of the pure surfactant solution [6, 8].  $c_{ac}$  is the surfactant concentration for which the polymer is saturated in surfactant. The two concentrations are essential for understanding and studying the polymer – surfactant interactions and are determined from the superficial tension – surfactant curve presented in Figures 2a – 2d. Analysing the diagrams, one may see that in all cases the complexes between Praestol 2515 and HTAB are definite because the  $c_{ac}$  marks the onset of association of surfactant to the polymer. Since  $c_{ac}$  is lower than the  $c_{mc}$  of HTAB solution, aggregation of HTAB with polymer is more favourable than normal micellization of the surfactant. Generally, ionic surfactants form micellar complexes with the polymer chain, when  $c_{ac}$  is lower than the  $c_{mc}$  of the pure surfactant solution and the polymer concentration is lower than the  $c_{mc}$  of pure polymer solution. For higher polymer concentrations than the  $c_{mc}$ , the values of the  $c_{ac}$  and  $c_{cs}$  become modified, suggesting that another association take place between the polymer micelles and tensioactive substances [1, 9]. In this case, the superficial tension of the formed complex is greater than that of the surfactant solution and comparable with that of the polymer solution as shows the diagram presented in figure 2d.

The values of  $c_{ca}$  and  $c_{cs}$  of the Praestol 2515 and HTAB mixture for various polymer concentrations,  $c_p$ , presented in table 1 evidence the modifier values for  $c_{ca}$  and  $c_{cs}$  when the polymer concentration was greater than  $c_{cm}$ . The results presented in figure 2 demonstrate the importance of the initial degree of association of the polymer in solutions, and respectively, of the tensioactive substance concentration upon the complex formed by their mixture.

**Table 1**  
 $c_{ca}$  AND  $c_{cs}$  OF THE PRAESTOL 2515 AND HTAB MIXTURE FOR VARIOUS POLYMER CONCENTRATION,  $c_p$

$c_p$ , %	$c_{ca}$ , %	$c_{cs}$ , %
$1 \cdot 10^{-5}$	$2 \cdot 10^{-5}$	$1 \cdot 10^{-4}$
$1 \cdot 10^{-4}$	$2 \cdot 10^{-5}$	$1 \cdot 10^{-4}$
$1 \cdot 10^{-3}$	$2 \cdot 10^{-5}$	$1 \cdot 10^{-4}$
$1 \cdot 10^{-2}$	$4 \cdot 10^{-5}$	$2 \cdot 10^{-4}$

The aggregation between polyelectrolyte and surfactant leads to an increase in viscosity of the solution, and in other rheological characteristics – hence the use of these associative thickeners as rheology modifiers [1, 6]. At higher surfactant content, the viscosity effect is lost. As explained in [6], in order to have cross-linking and thus a viscosity effect, there must be a sufficiently high number of hydrophobes macromolecules per micelle. At higher surfactant concentrations, there will be only one hydrophobe macromolecule in a micelle and all cross-linking effects are lost. These viscosity effects produced by adding surfactant to a solution of hydrophobically modified water-soluble polymer are general. There are other interactions, like electrostatic interactions, that influence this effect. For example, addition of oppositely charged surfactant to a hydrophobically modified polyelectrolyte gives much larger viscosity effect than for non-ionic surfactant [6]. Figure 3 shows the Praestol 2515 - HTAB solution apparent viscosity as a function of surfactant concentration at  $5 \cdot 10^{-4}$  % polymer concentration. The general trend emphasized in figure 3 is that the apparent

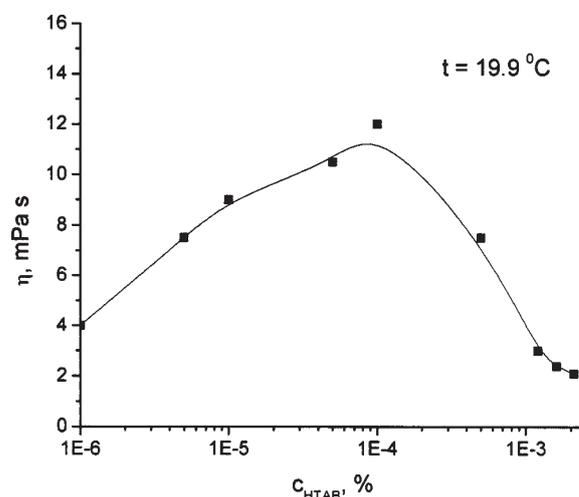


Fig. 3. The dependence of apparent viscosity on surfactant concentration for  $c_p = 5 \cdot 10^{-4}$  %

viscosity increases initially at small HTAB concentrations to a maximum value, beyond which, at higher surfactant concentrations, there is a gradual decrease. The initial effect can be attributed to the increase in Praestol coil size due to the surfactant molecules and micelles bound to the polymer chain. The coil expansion continues until the number of bound micelles reaches its maximum value, which is assumed that occurs where the specific viscosity also exhibits a maximum. The subsequent reduction in the solution viscosity as more micelles were added can be attributed to electrostatic screening due to the excess bromide ions [6, 8, 9].

The rheological study aimed to give more insights into the flow behaviour of Praestol 2515 – HTAB complex solutions. Primarily, the polymer solution was characterized by determining their rheogram, which is a graph that displayed the shear stress, force per unit area creating or produced by the flow, and the shear rate, gradient of the velocity perpendicular to the flow direction [10-13]. Then, measurements were made to study the influence of HTAB concentration,  $c_{HTAB}$ , on rheological properties of the complex solutions in two cases: for  $c_{HTAB}$  greater than  $c_{cs}$  and for  $c_{HTAB}$  less as  $c_{cs}$ .

The rheograms of the Praestol 2515 polymer solutions are presented in figures 4. As one can notice the solution is of Bingham pseudoplastic type, without a rheological characteristic dependence on time or viscoelastic properties.

The rheograms presented in figures 5 show that the formed complex solution is also of Bingham pseudoplastic type and the solution has not a rheological characteristic depending on time or viscoelastic properties. As one may see, the solutions maintain their rheological character when HTAB is added.

The effect of the concentration of the tensioactive substance in the complex solution is depicted in rheograms presented in figures 6 – 7. First, it was investigated the case corresponding to  $c_{HTAB}$  greater than  $c_{cs}$ . As expected, the viscosity of the complex solutions gradually decreases when the  $c_{HTAB}$  increases as show diagrams from Figure 6. Contrary, when  $c_{HTAB}$  was less than  $c_{cs}$  and the  $c_{HTAB}$  increases, the viscosity of the complex solutions increases too as show the diagrams from figure 7.

The experimental data has been fitted by nonlinear regression applied to Herschel-Bulkley rheological model associated to the following equation [10]:

$$\tau = \tau_0 + a \cdot \dot{\gamma}^n \quad (1)$$

where:

$\tau$  is the shear stress,  
 $\dot{\gamma}$  - the shear rate,  
 $\tau_0$  - threshold flow,  $n$  the index flow and  $a$  the apparent viscosity.

$\tau_0$ ,  $n$  and  $a$  are constants of the model. All values of the model constants are presented in tables 2 and 3.

Note that the addition of HTAB decreases the value of the flow threshold constant,  $\tau_0$  and the apparent viscosity,  $a$ , as long as  $c_{HTAB}$  is greater than  $c_{cs}$  and increase the values of these constants, when  $c_{HTAB}$  is less than  $c_{cs}$ . For all cases, the flow index value,  $n$  remains practically constant.

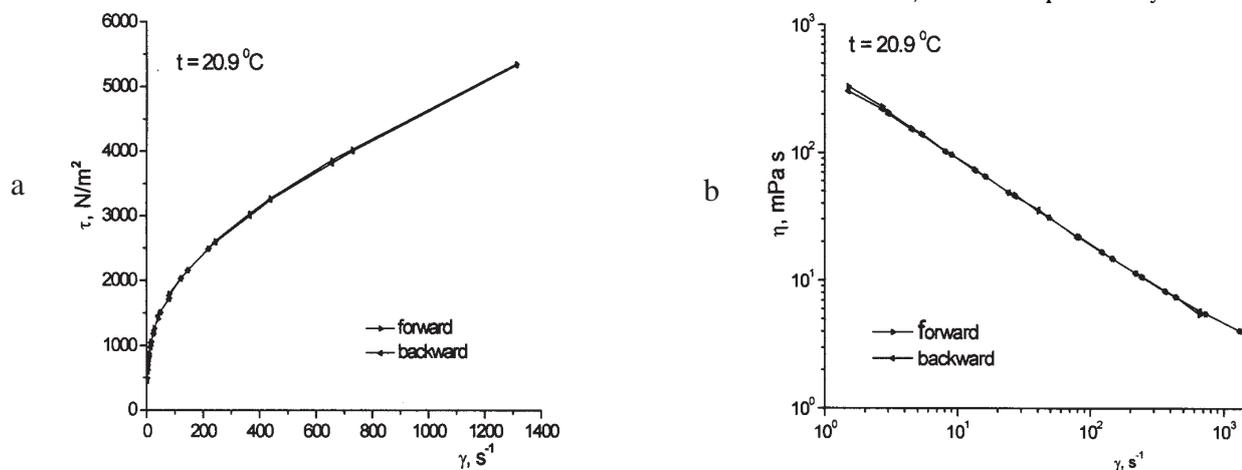


Fig. 4. Rheogram of the Praestol 2515 solution of  $c = 0.1\%$  in coordinates  $\tau = f(\dot{\gamma})$  (a) and  $\eta = f(\dot{\gamma})$  (b)

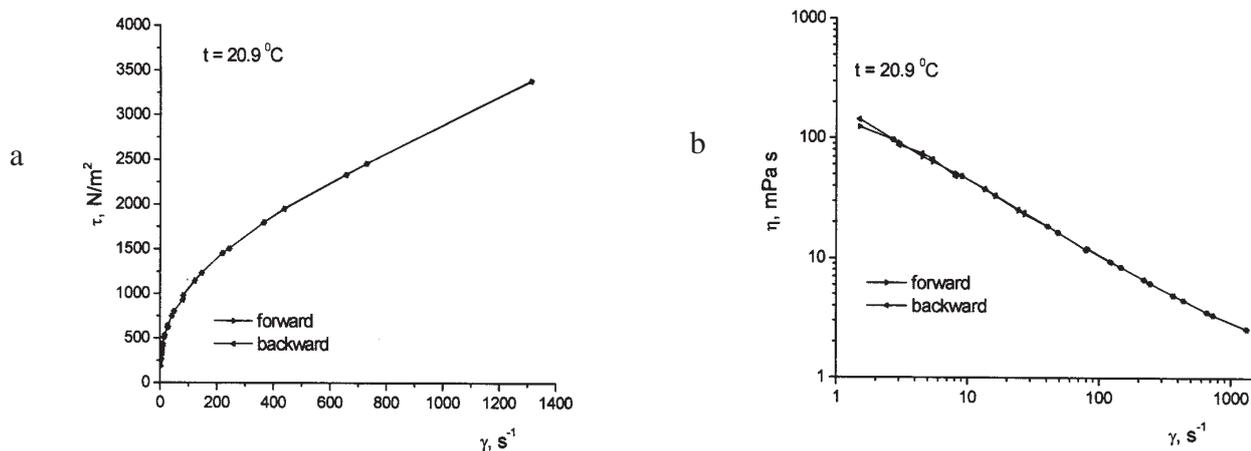


Fig. 5. Rheogram of the complex solution with  $c_p = 0.1\%$  and  $c_{HTAB} = 1.2 \cdot 10^{-3}\%$ , in coordinates  $\tau = f(\dot{\gamma})$  (a) and  $\eta = f(\dot{\gamma})$  (b)

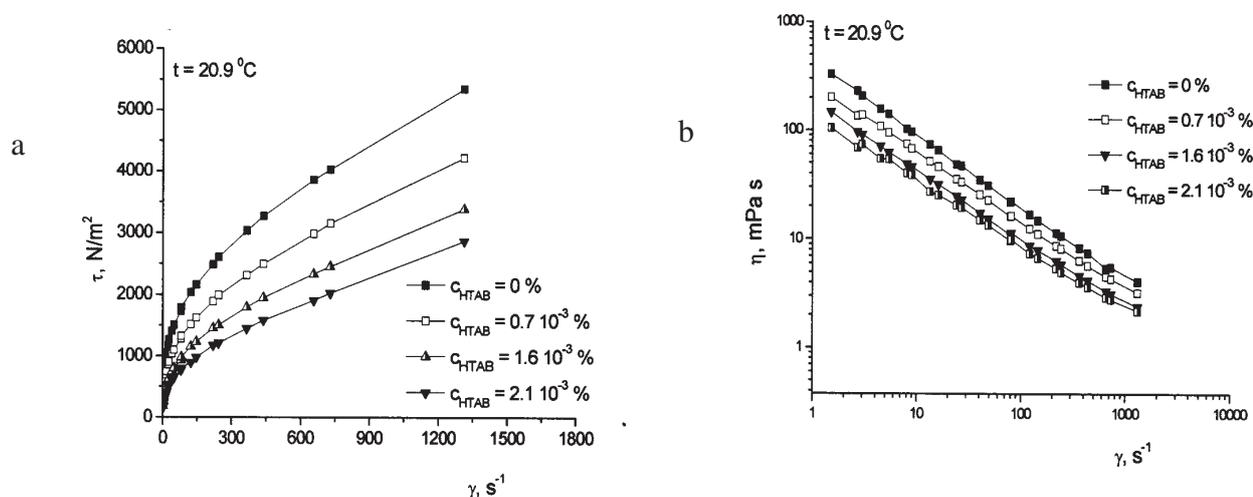


Fig. 6. Rheograms of the complex solution with  $c_p = 0.1\%$  and  $c_{HTAB} > c_{cs}$  in coordinates  $\tau = f(\dot{\gamma})$  (a) and  $\eta = f(\dot{\gamma})$  (b)

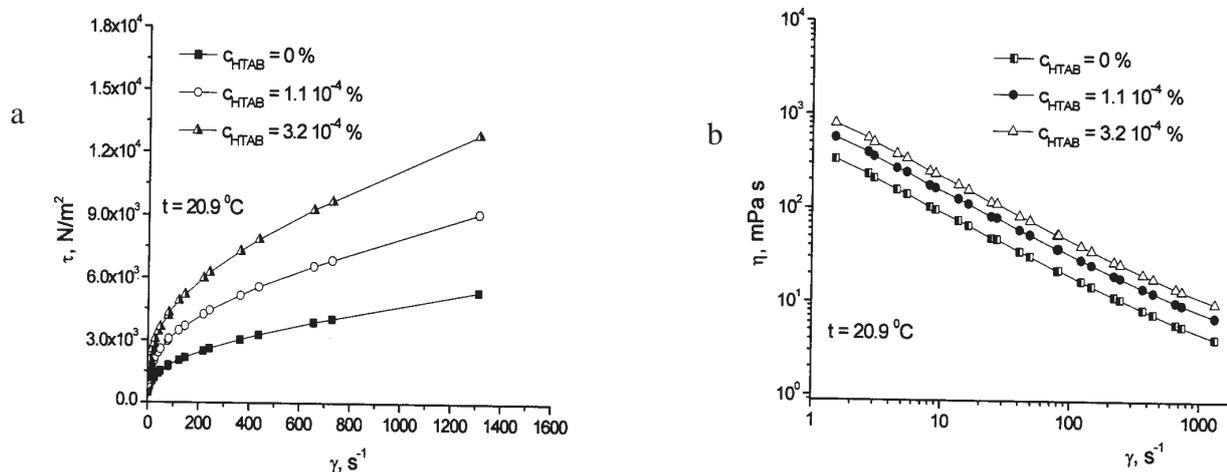


Fig. 7. Rheograms of the complex solution with  $c_p = 0.1\%$  and  $c_{HTAB} < c_{cs}$  in coordinates  $\tau = f(\gamma)$  (a) and  $\eta = f(\gamma)$  (b)

$c_{HTAB}$	$\tau_0$	a	n
0	558.72	189.5	0.43
$7.0 \cdot 10^{-5}$	334.65	140.4	0.45
$1.0 \cdot 10^{-4}$	224.07	101.6	0.46
$1.6 \cdot 10^{-3}$	241.53	84.4	0.48
$2.1 \cdot 10^{-3}$	171.69	78.2	0.47

$c_{HTAB}$	$\tau_0$	a	n
0	558.72	189.5	0.43
$1.1 \cdot 10^{-4}$	695.61	324.3	0.45
$3.2 \cdot 10^{-4}$	840.10	458.3	0.45

**Table 2**  
THE MODEL CONSTANTS IN EQUATION (1) FOR THE COMPLEX PRAESTOL 2515 – HTAB WITH  $c_p = 0.1\%$  AND  $c_{HTAB} > c_{cs}$

**Table 3**  
THE MODEL CONSTANTS IN EQUATION (1) FOR THE COMPLEX PRAESTOL 2515 – HTAB WITH  $c_p = 0.1\%$  AND  $c_{HTAB} < c_{cs}$

## Conclusion

By mixing Praestol 2515 polymer solutions with HTAB one may definitely notice the formation of complex with a superficial tension lower than that of the initial polymer solution and that of the HTAB solution. This complex is formed between the HTAB micelles and polymer chains. In solutions of  $c_p < c_{cm}$ , by mixing the polymer with HTAB some complexes are formed that have the same values of  $c_{ca}$  and  $c_{cs}$ , and in the solutions of  $c_p > c_{cm}$ , other complexes are formed that have different values of the  $c_{ca}$  and  $c_{cs}$ , as compared to the situation when the polymer macromolecules are not associated.

The Praestol 2515 polymer solution is Bingham pseudoplastic type, without a rheological characteristic dependent on time or viscoelastic properties. By adding HTAB surfactant some complexes are formed with apparent viscosity and flow threshold lower than those of the pure polymer solution as long as  $c_{HTAB}$  is greater than  $c_{cs}$  and greater than those of the pure polymer solution when  $c_{HTAB}$  is less than  $c_{cs}$ . For all cases, the flow index remains practically constant. The rheograms uniform increase indicates that the formed complexes are stable and resistant to a medium shear stress. For the solid – liquid interface processes are recommended the complexes formed between polymers solution with  $c_p < c_{cm}$  and surfactants solution with  $c > c_{cs}$ .

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