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# **pH INFLUENCE ON ADSORPTION BEHAVIOR, SURFACE DILATIONAL RHEOLOGY AND FOAM STABILITY OF MIXED SODIUM HUMATES / CETYLTRIMETHYLAMMONIUM BROMIDE SOLUTIONS**

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*The results of the ring and the oscillating drop shape methods investigation of adsorption and surface rheological characteristics of natural polyelectrolytes–sodium humates solutions with additives of cetyltrimethylammonium bromide (CTAB) at a liquid–gas interface at different pH values are presented. The main features of concentration dependences of surface tension and visco-elasticity modulus for mixed sodium humates / CTAB solutions may be connected with the aggregate formation in the adsorption layer at appropriate CTAB concentrations. The possibility of foam formation from sodium humates / CTAB mixed solutions is studied. It was shown that pH reduction leads to an increase of foam stability.*

## **INTRODUCTION**

Mixtures of polyelectrolytes and oppositely charged surfactants are of increasing interest due to their importance in different branches of industry. Understanding interfacial rheology of adsorbed layers of such systems is very important for foam and emulsion stabilization. Indeed, destabilization of these systems can be due to several mechanisms such as drainage and thin-liquid film rupture both of which are known to be linked to the interfacial rheology of the dispersion interface [1].

Mixed polyelectrolyte / surfactant solutions show drastic changes of the surface properties with increasing surfactant concentration [2–4]. Even small additives of surfactant to polyelectrolyte solution lead to strong decrease of surface tension. This strong synergistic effect was known for many decades and explained by the formation of relatively hydrophobic polyelectrolyte / surfactant complexes.

Goddard proposed a simple model of the surface structure of dilute polyelectrolyte/surfactant solutions: the surfactant ions form a monolayer at the liquid surface and attract electrostatically the elongated charged macromolecules [5]. The charged groups of the polymer play the role of counterions. In [6] was shown that Goddard's model has some disadvantages: it does not take

into account the chemical nature of the polyelectrolyte backbone chains, insufficient to explain the high surface elasticity at extremely dilute solutions. Authors of [6] proposed a modification of this classic model by taking into account hydrophobic interactions in the adsorption layer leading to the formation of almost two-dimensional nano- or micro-aggregates. These conclusions were corroborated by ellipsometry measurements [6]. Moreover, application of the neutron reflectivity [7] has shown that the surface structure of polyelectrolyte/surfactant solutions can be divided into two main types. In the first case, as shown by neutron reflectivity, the adsorption layers are relatively thick and cannot be described in terms of a surfactant layer with some extended polymer (type 1). In the second case the adsorption layer thickness approaches the typical values of surfactant layers (type 2). The adsorption layers of these two kinds lead to different patterns of the surface tension dependency on surfactant concentration [7].

Humic acids (HA) are natural weak-acid polyelectrolytes. They contain hydrophilic functional groups (mainly carboxylic and hydroxyl) and hydrophobic aromatic and aliphatic moieties giving to the HA characteristics of an amphiphile [8, 9]. Thus, HA exhibit surface activity in aqueous solution [10–12] and the ability

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to associate with different molecules by electrostatic and/or hydrophobic interactions [13–18]. In [19] soluble and insoluble complexes, which are formed due to the interactions between the sodium humates and cetyltrimethylammonium bromide, were analyzed by small-angle X-ray scattering technics, and the possible structures of these complexes were proposed. In [15, 16, 18] for mixtures of humic acids with cationic dye and cationic surfactants (dodecyl- and cetylpyridinium chloride) it was shown that the binding capacity of HA increases with pH (increasing degree of ionization of a polyelectrolyte) and the length of the surfactant hydrocarbon radical.

The effect of alkyltrimethylammonium bromides additives on surface tension of sodium humates solutions was studied in [20]. It was shown that the effectiveness of reducing the surface tension increases with increasing surfactant chain length.

In this paper we aim to measure interfacial rheological properties of oppositely charged surfactant/polyelectrolyte layers at different pH values, composed of anionic polyelectrolyte, sodium humates, and a cationic surfactant, CTAB, with interfacial dilatational rheological measurement techniques. Furthermore, we attempt to correlate the surface rheology data to the foamability (e.g., the propensity of a system to generate foam) and the foam stability of the corresponding solutions.

## EXPERIMENTAL

Humic acids and their sodium salts were received from brown coal of Alexandrian deposit (Ukraine). The procedure for producing HA samples and the results of their elemental and functional analyses are presented in [21]. Sodium humates (SH) solutions to be examined were obtained by dissolving dry HA in a 0.1 N NaOH solution. The pH of the SH solutions was 11.5. The cationic surfactant, cetyltrimethylammonium bromide, was from Sigma. The solutions were prepared in bidistilled water. All the measurements in this work were performed at two SH concentrations of  $C_{SH} = 0.6; 7.6$  g/l and various CTAB concentrations and at three pH values 4.0; 7.0; 11.5.

Regularities of the precipitation of humic substances from mixed with CTAB solutions were studied by photocolormetry. The sediment

precipitated after 1 day was separated by centrifugation at 1500 revolutions per minute during 15 minutes, and the optical density of the supernatant liquid was measured with an KF-11 colorimeter at  $\lambda = 430$  nm. The measurement results were presented in the form of relationship between the ratio of the optical density of the sodium humates solution at a given concentration of the added CTAB,  $D$ , to that of the initial sodium humates solution,  $D_0$ .

The dynamic surface properties at the liquid/air interface of mixed solutions of sodium humates with CTAB were measured as a function of surface age, concentration of components, pH. The experiments were performed by the Du Noüy ring method (TE-1, Lauda, Germany) and drop profile analysis tensiometry (PAT-2P, SINTERFACE Technologies, Germany) at 25 °C. To study the dilatational elasticity, the drop, after having reached the adsorption equilibrium, was subjected to harmonic oscillations with an amplitude of 7–8 % and frequencies in the range between 0.005 and 0.2 Hz.

Dilatation modulus ( $E$ , mN/m) characterizes the viscoelastic properties of surfactant surface layers and takes into account all relaxation processes that affect surface tension  $\gamma$ . At a small amplitude  $\Delta S$  of harmonic oscillations of a surface with an angular frequency of  $\Omega = 2\pi\nu$ ,  $\Delta S = \Delta \bar{S} \exp(i\Omega t)$  and the following expression can be derived for the dilatation viscoelastic modulus [22, 23]:

$$E = \frac{\Delta\gamma}{\Delta S/S_0} = \frac{d\gamma}{d \ln S}.$$

The visco-elastic modulus  $E$  is a complex number, with a real part  $E_r$  (the storage modulus) equal to the elasticity and the imaginary part  $E_i$  (the loss modulus) given by the product of the viscosity,  $\eta_a$ , and the imposed angular frequency,  $\Omega$ , of the area variations:  $E = E_r + iE_i$

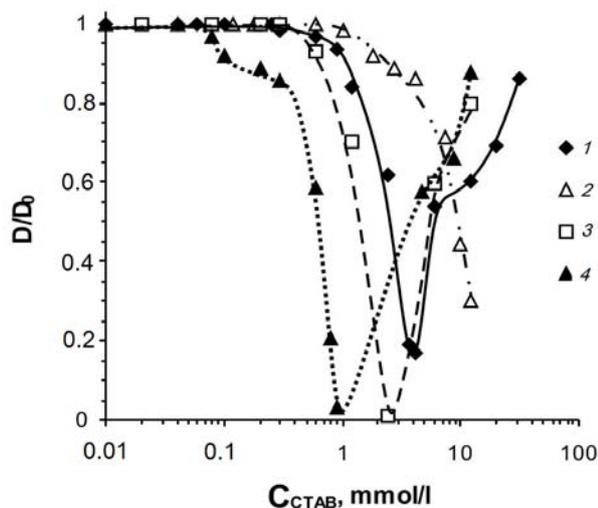
$$|E| = \sqrt{E_r^2 + E_i^2}.$$

The foam was formed due to air barbotage at a rate of 50–60 mm<sup>3</sup>/s. Foam stability was evaluated as the ratio of the volume of foam remaining after 10 minutes,  $V_t$ , to the initial volume of foam,  $V_0$ .

## RESULTS AND DISCUSSION

**Phase behavior.** Before discussing the adsorption behavior of polyelectrolyte/surfactant mixtures, it is useful to give a brief description of the bulk phase behavior typical of these systems. Phase behavior of sodium humates solutions in the presence of CTAB additives is similar to that for other mixed oppositely charged polyelectrolyte/ionic surfactant solutions. When the concentration of CTAB is close to the concentration of oppositely charged groups of humic substances, macroscopic aggregates in solution are formed and phase separation or precipitation is observed [19, 24, 25]. With further increase in the CTAB concentration complexes may again become soluble due to their hydrophilization by interactions between the hydrophobic regions of HA chains and CTAB hydrocarbon radicals [19, 25].

The effects of CTAB additives on the solubility of humic substances according to the present work are shown in Fig. 1.



**Fig. 1.** Dependences of the ratios of optical densities of mixed SH/CTAB solutions,  $D$ , to that of SH solution,  $D_0$ , on CTAB concentration and pH:

pH = 11.5 (1, 2); pH = 7.0 (3); pH = 4.0 (4);  
 $C_{SH} = 0.6$  g/l (1, 3, 4), 7.6 g/l (2)

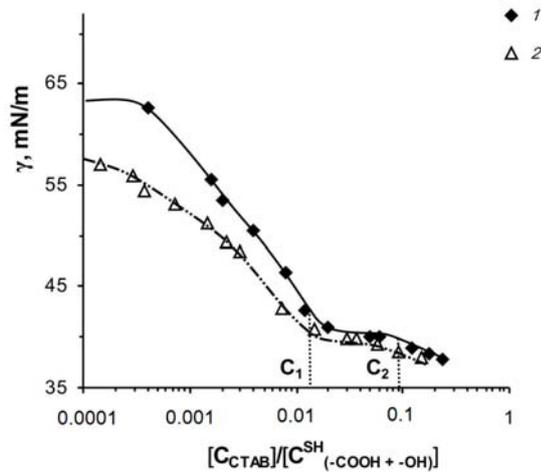
At very dilute CTAB concentrations, the mixtures are clear and transparent and it is assumed that any surfactant/polyelectrolyte complex is completely soluble. As the CTAB concentration is increased the optical density of solutions decreases, solutions tend to become increasingly turbid or cloudy owing to the

decrease in solubility of the complex. There is a minimum of solubility on the dependences of change in optical density of SH/CTAB solutions on CTAB concentration, after which further increase in the CTAB concentration leads to an increase in the optical density of the mixed solutions and the solutions become clear again. So, the complexes can be resolubilized with the surfactant concentration increase owing to the excess charge that accumulates on the complexes.

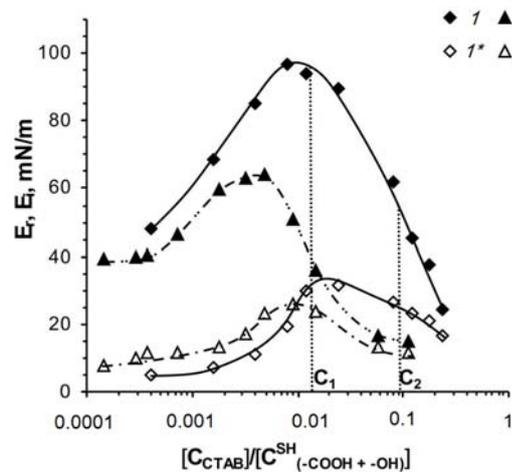
pH reduction shifts solubility minimum to lower CTAB concentrations, and the SH concentration increase – toward higher CTAB concentrations. This behavior is probably due to a change in the number of dissociated functional groups of HA macromolecules available for interactions with CTAB when pH and the SH concentration in the solution are changed [21].

**Adsorption behavior and surface dilational rheology.** Fig. 2 shows equilibrium surface tension isotherms for mixed sodium humates/CTAB solutions. There are two CTAB concentration ranges on the surface tension isotherms of SH/CTAB mixtures which are characterized by various slope angles of tangent line to these dependences. The surface tension of mixed SH/CTAB solutions is sharply reduced in the CTAB concentration range below  $C_1$  and reaches a plateau. In this case the region of sharp change in the slope angle of the surface tension isotherm ( $C_1$ ) can be associated with the beginning of ionic surfactant aggregates formation at some points of the polymer chains and is designated as a critical concentration of aggregation. The presence of a plateau in the surface tension isotherm in the range of  $C_1 < C_{CTAB} < C_2$  may be the result of aggregation in the bulk solution leading to a nearly constant activity of the monomer. Further surface tension reduction of mixed solutions at CTAB concentrations above  $C_2$  indicates the saturation of the polyelectrolyte molecules by ionic surfactant and the beginning of CTAB monomer concentration growth, which replace SH/CTAB complexes in the adsorption layer. The solubility of SH/CTAB complexes starts to decrease at CTAB concentrations above  $C_2$ .

Surface viscoelasticity increases and reaches a maximum at CTAB concentrations below  $C_1$  (Fig. 3), adsorption layers are elastic.



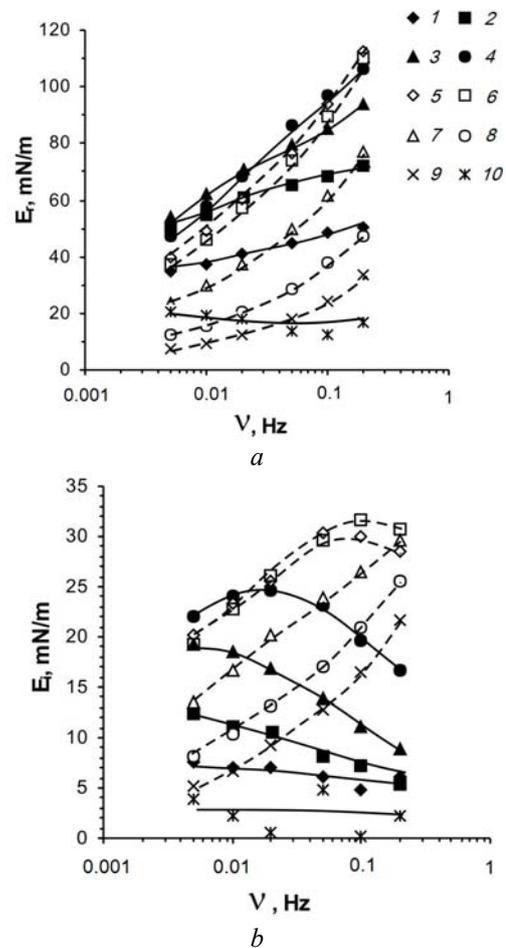
**Fig. 2.** Dependences of equilibrium surface tension ( $\gamma$ ) of SH/CTAB mixtures (pH = 11.5) on the ratio of CTAB concentration to the concentration of SH functional groups,  $[C_{CTAB}]/[C_{SH}^{(-COOH + -OH)}]$ . Sodium humates concentration in the solution, g/l: 0.6 (1); 7.6 (2)



**Fig. 3.** Dependences of surface elasticity  $E_r$  (1, 2) and viscosity  $E_i$  ( $1^*$ ,  $2^*$ ) moduli of SH/CTAB mixtures (pH = 11.5) on the ratio of CTAB concentration to the concentration of SH functional groups,  $[C_{CTAB}]/[C_{SH}^{(-COOH + -OH)}]$ . Sodium humates concentration in the solution, g/l: 0.6 (1); 7.6 (2). Oscillation frequency 0.1 Hz

High elasticity modulus values of SH/CTAB solutions (up to  $\sim 97$  and  $65$  mN/m for the  $C_{SH} = 0.6$  and  $C_{SH} = 7.6$  g/l, respectively) indicate that the rigid structure of the adsorption layer is formed, probably both through electrostatic and hydrophobic interactions between the hydrophobic parts of the SH chains or hydrocarbon radicals of CTAB and hydrophobic regions of the SH chains.

Further increase of the CTAB concentration leads to the beginning of viscoelastic modulus decrease and increase of the  $E_i/E_r$  ratio in the  $C_1$  concentration range (Fig. 3). Adsorption layers become viscoelastic. Such changes of surface rheological characteristics demonstrate the appearance of a new mechanism of surface stress relaxations which may be related to exchange processes in consequence of the aggregates formation and disintegration in the adsorption layer. Reduction of surface viscoelasticity is accompanied by a change of the  $E_r$  and  $E_i$  frequency dependences character (Fig. 4).



**Fig. 4.** Dependences of surface elasticity  $E_r$  (a) and viscosity  $E_i$  (b) moduli of SH/CTAB mixtures (pH = 11.5) on the oscillation frequency. Ratios of SH functional groups to the concentration of CTAB concentration,  $[C_{CTAB}]/[C_{SH}^{(-COOH + -OH)}]$ : 0.0004 (1), 0.0016 (2), 0.004 (3), 0.008 (4), 0.012 (5), 0.024 (6), 0.08 (7), 0.18 (8), 0.24 (9), 0 (10). Sodium humates concentration in the solution 0.6 g/l

Thus, in the range of CTAB concentrations below values corresponding to the maximum  $E_r$  values slope angle of the elasticity modulus on the oscillation frequency dependence increases, and after reaching a maximum surface elasticity begins to decrease (Fig. 4, *a*). Viscosity modulus decreases with increasing of oscillation frequency at CTAB concentrations below the values corresponding to a maximum  $E_i$ . At higher CTAB concentrations  $E_i$  increases with increasing of oscillation frequency (Fig. 4, *b*). At CTAB concentrations corresponding to the maximum values of the surface viscosity  $E_i = f(\nu)$  dependences pass through a maximum.

The above results indicate a change in the structure of the adsorption layer of mixed SH/CTAB solutions in CTAB concentration range corresponding to the first kink in the surface tension isotherm, and may be due to the formation of aggregates.

In spite of different chemical nature and extent of hydrophobicity of molecules obtained in this study for the SH/CTAB mixtures concentration dependences of equilibrium surface tension, elasticity and viscosity moduli are qualitatively similar to those of a number of mixtures of synthetic polyelectrolytes with oppositely charged surfactants: polyethylenimine / sodium dodecylsulfate (PEI / SDS) [26], polyvinylpyridinium chloride / sodium dodecyl sulfate / NaCl (PVP chloride / SDS / NaCl) [27], polyacrylic acid / alkyltrimethylammonium bromide (PAA / CnTAB) [28], polystyrene sulfonate / dodecyltrimethylammonium bromide (PSS / DTAB) [6] and for mixtures of natural polyelectrolyte  $\lambda$ -carrageenan with DTAB [29]. All of the surface tension concentration dependencies for the systems described above are characterized by at least two concentration ranges with abrupt changes of the slope of the surface tension isotherm and the plateau region between them. At low surfactant concentrations adsorption layers are elastic and characterized by high values of the elasticity modulus. At ionic surfactant concentrations corresponding to the first kink in the surface tension isotherm elasticity modulus sharply decreases and the contribution of the imaginary components to the surface viscoelasticity increases. Such changes in the surface properties of synthetic polyelectrolyte / ionic surfactant mixtures are connected with the formation of three-dimensional aggregates in the adsorption layer.

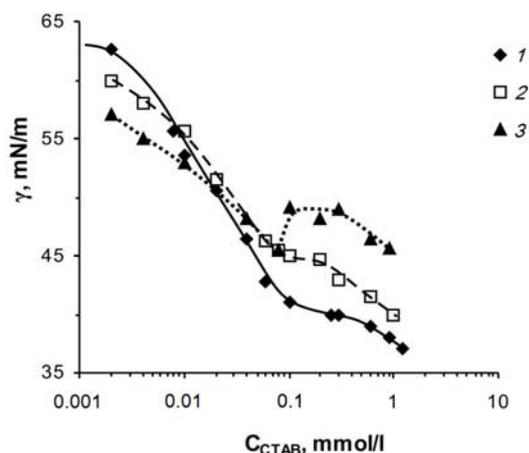
Formation of the latter for PSS / DTAB solutions is confirmed by a strong increase in ellipsometric signal [6]. For the listed above synthetic polyelectrolyte / surfactant mixtures neutron reflection measurements indicate the formation of the multilayer structure of the adsorption layer [7] at surfactant concentrations higher than the first kink in the surface tension isotherm.

Adsorption and surface rheological properties of protein solutions mixed with ionic surfactant, as well as for other polyelectrolyte / ionic surfactant mixtures determined by complex formation between the components. Dependences of the equilibrium surface tension of protein / surfactant solutions on surfactant concentration are similar to the described above [2, 30]. The character of the concentration dependences of surface viscoelasticity for such systems is more complex and depends on the nature of the protein [3, 31, 32], the nature of surfactant – cationic or anionic [33]. As a result, with increasing surfactant concentration viscoelasticity modulus for such mixtures may go up, passing through a maximum [2, 3, 31], and may decrease from values which are character for individual protein solutions to the values which are character for surfactant [32].

The complexity of the studied in this work SH/CTAB systems does not permit to do a reliable conclusions about the behavior of the adsorption layer. The similarity between the concentration dependencies of the surface tension, dilational elasticity and viscosity moduli measured in this work (Figs. 2, 3) and the results for synthetic polyelectrolyte / surfactant mixed solutions [6, 26–28] indicate that the same changes in the adsorption layers structure of these systems occur at increasing surfactant concentration. Considering the similarity in the adsorption and rheological characteristics of mixed SH/CTAB solutions with mixtures of synthetic polyelectrolyte / surfactant, and a high degree of hydrophobicity of humic acid macromolecules, we can assume that the structure of SH/CTAB adsorption layers could be close to a model for the absorption layer of polyelectrolyte / surfactant mixtures [6], which takes into account the hydrophobic interactions in the surface layer, leading to the formation of two-dimensional nano- and micro-aggregates at low surfactant concentrations. The destruction of the rigid structure of the SH/CTAB adsorption

layer with increasing CTAB concentration by analogy with mixtures of synthetic polyelectrolyte / surfactant may occur due to the formation of three-dimensional aggregates in the surface layer.

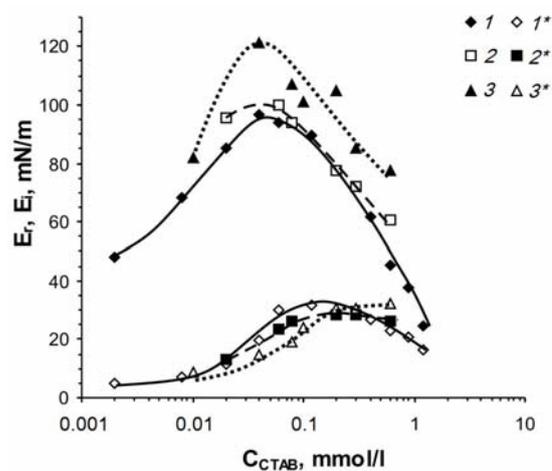
The ionization degree of weak polyelectrolytes, which is a function of pH, affects the nature of their interactions with oppositely charged surfactant and on the adsorption behavior of such mixtures.



**Fig. 5.** Dependences of equilibrium surface tension of SH/CTAB mixed solutions on CTAB concentration at different pH values: 11.5 (1), 7.0 (2), 4.0 (3).  $C_{SH} = 0.6$  g/l

pH decrease leads to an increase in the values of equilibrium surface tension of mixed SH / CTAB solutions (Fig. 5). At low CTAB concentrations the surface tension value of mixture at pH 4.0 and 7.0 is slightly lower than at pH 11.5. This may be due to the higher surface activity of SH in the neutral and acidic pH. There is a maximum in the plateau region of surface tension isotherm of mixed SH / CTAB solutions at pH 4.0 (Fig. 5). The abrupt surface tension increase may be connected with the desorption of SH / CTAB complexes and their transition to the bulk phase due to the formation of macroscopic aggregates. So, the optical density of SH / CTAB mixtures at pH 4.0 decreases in the same CTAB concentration range (0.1–0.4 mmol/l) in which the maximum on surface tension isotherm is observed.

Character of the elasticity and the viscosity moduli dependences of the SH / CTAB mixtures on CTAB concentration in the neutral and acidic conditions is similar to those in the alkaline pH range (Fig. 6). pH reduction results in dilational elasticity increase and  $E_i/E_r$  decrease.



**Fig. 6.** Dependences of surface elasticity  $E_r$  (1, 2, 3) and viscosity  $E_i$  ( $1^*$ ,  $2^*$ ,  $3^*$ ) moduli of SH/CTAB mixed solutions on CTAB concentration at different pH values: 11.5 (1), 7.0 (2), 4.0 (3).  $C_{SH} = 0.6$  g/l. Oscillation frequency 0.1 Hz

It is interesting to compare results obtained in this work with results for other weak polyelectrolytes. In [7] it was shown that controlling the degree of charge on weak polyelectrolytes by varying the pH of the system effects the adsorption behavior of mixed polyacrylic acid / dodecyltrimethylammonium bromide (PAA / DTAB) and branched polyethylenimine / sodium dodecylsulfate (PEI / SDS) solutions. PAA is anionic at high pH but neutral at low pH whereas PEI is cationic at low pH owing to protonation of the nitrogens but neutral at high pH.

For mixtures of PAA / DTAB were obtained similar to our results of the pH effect on the equilibrium surface tension value: the  $\gamma$  values in the range of ionic surfactant concentration below CMC in alkaline pH region is lower than in the acidic.

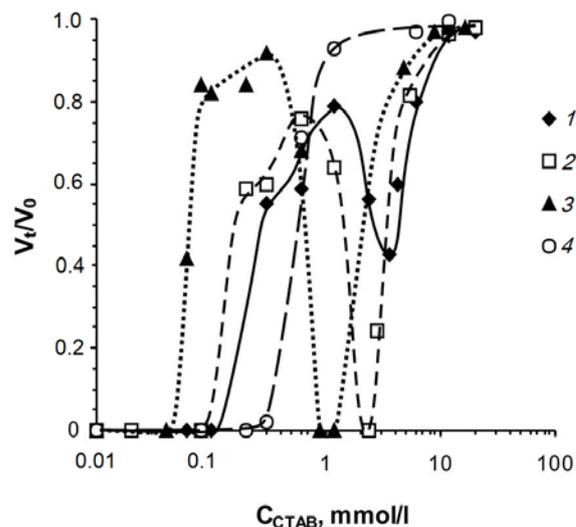
For mixtures of branched PEI with SDS the variation in adsorption behavior with pH is the opposite of what would be expected if the interactions in the system were predominantly electrostatic. There should be more pronounced adsorption behavior at low pH where the polymer is strongly cationic, whereas it appears that the strongest interactions in this system occur at pH 10 ( $\gamma$  values at pH 7 and 10 lower than at pH 3) when the polymer is essentially neutral. It seems likely, therefore, that the main driving force for interaction in this system is hydrophobic forces between the surfactant

chains and the polymer backbones rather than electrostatic attractions between the oppositely charged headgroups and the protonated nitrogens on the polymer.

Probably, the effect of pH on the adsorption behavior of SH/CTAB mixtures as well as PAA/DTAB is associated with a strong interactions at high pH due to the greater degree of ionization of the polyanion and controlled mainly by electrostatic interactions between oppositely charged groups of ionic surfactant and polyelectrolyte leading to the formation of surface-active complexes SH/CTAB. At low pH, when the number of ionized groups in the SH molecules lower, the interactions between polyelectrolyte and ionic surfactant have to be predominantly hydrophobic. This assumption is also consistent with an increase in the surface elasticity at lower pH. The contributions of the different types of interactions in the binding of HA with ionic surfactants depending on the pH, the length of the ionic surfactant hydrocarbon radical are shown in [13–19].

**Foam stability of mixed SH/CTAB solutions.** Fig. 7 represents the dependences of foam stability for mixed SH/CTAB solutions at different pH and individual CTAB solutions as a function of CTAB concentration. For pure surfactant solutions, the foam stability increases monotonically from zero to 1 when the concentration of surfactant is raised from 0.01 to 10 mmol/l. For SH/CTAB mixtures there exist two CTAB concentration ranges where stable foam is formed.

There is a clear relationship between the dependences of foam stability (Fig. 7) and optical density (Fig. 1) of mixed SH/CTAB solutions on CTAB concentration at different pH values. The foam stability of mixtures increases with increasing of CTAB concentration and reaches a maximum at the limit of SH/CTAB complexes solubility. Reduction of the optical density of the mixed solutions is accompanied by a decrease of foam stability. At full deposition of precipitates from mixed solutions foam does not formed, while the foam stability for pure CTAB attains the maximum (Fig. 7). Further increase of CTAB concentration in the mixture leads to increase of the solubility and foam stability of SH/CTAB mixtures to values characteristic for the individual solutions of CTAB.



**Fig. 7.** Dependences of ratios of foam volume remaining after 10 minutes,  $V_t$ , to the initial foam volume  $V_0$ , of CTAB solutions (4) and SH/CTAB mixtures (1–3) on CTAB concentration at different pH: 11.5 (1), 7.0 (2), 4.0 (3).  $C_{SH} = 0.6$  g/l

In [1] the foam formation and foam stability for mixtures of polystyrenesulfonate sodium salt (PSS) with dodecyltrimethylammonium bromide (DTAB) were studied. Dependences of foam stability of PSS/DTAB mixtures are similar to those obtained in the present work for SH/CTAB. Such dependences are characterized by two zones of surfactant concentrations where the foam stability measured with mixed solutions is higher than the foam stability for pure surfactant (or pure polyelectrolyte) solutions and a precipitation range between them, in which the foam is absent. It was shown that the first maximum of foam stability occurs when the polyelectrolyte/surfactant complexes are on the limit of their solubility. The foam stability of PSS/DTAB mixtures is strongly correlated to shear surface moduli. The authors [1] believe that two phenomena are likely responsible for the absence of foam in a PSS/DTAB mixture in the precipitation region: (1) most of the surfactant is bound to the polymer complexes that have precipitated out of solution leaving insufficient amounts for high foam stability; (2) the polymer-surfactant precipitates act as hydrophobic antifoam particles which can provoke foam collapse. The foam absence at full deposition of precipitates from SH/CTAB mixture can probably be attributed to the same reasons.

We also note that the protein solutions [34] and a mixtures of polyelectrolyte / ionic surfactant [35] are capable to form a stable foam at pH values close to the isoelectric point (IEP), with a minimum of foam films stability for polyelectrolyte / surfactant found in the IEP.

As can be seen from Fig. 7, foam stability of SH/CTAB mixtures increases with a pH decrease. This may be connected with increase in elasticity of mixed adsorbed layers on conversion from base to acid pH. The first maximum of foam stability shifts to lower CTAB concentrations with a pH decrease. Thus, we can obtain more stable foams from mixed solutions than from pure surfactant (or pure polyelectrolyte) solutions by regulating the pH and proportion of components in the mixture.

### CONCLUSIONS

The investigation of adsorption and surface rheological properties of mixed sodium humates / CTAB solutions at the liquid–gas interface is presented and the possible mechanism of mixed adsorption layers formation is proposed.

The main features of concentration dependences of surface tension, elasticity, viscosity moduli and of frequency dependences of rheological properties for mixed sodium humates / CTAB solutions give evidence on the change of adsorption layer structure and may be connected with the aggregate formation in the adsorption layers at appropriate CTAB concentrations.

The foam stability of mixed sodium humates / CTAB solutions is determined by the proportion of components in the mixture and increases with pH decrease that leads to increase of elasticity modulus of SH / CTAB adsorption layers. The intervals of CTAB concentrations and pH values which characterized by formation of stable foams are determined.

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**Вплив рН середовища на адсорбційну поведінку,  
поверхневу дилатаційну реологію та стійкість пін розчинів сумішей  
гумати натрію / цетилтриметиламоній бромід**

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*Представлені результати дослідження адсорбційних і поверхневих реологічних характеристик розчинів природних поліелектролітів – гуматів натрію з добавками цетилтриметиламоній броміду (ЦТАБ) на межі поділу рідина–газ методами кільця і форми осцилюючої краплі. Виявлено, що основні особливості концентраційних залежностей поверхневого натягу і модуля в'язкопружності розчинів сумішей гумати натрію / ЦТАБ можуть бути пов'язані з утворенням агрегатів в адсорбційному шарі при відповідних концентраціях ЦТАБ. Досліджена можливість утворення пін з розчинів гумати натрію / ЦТАБ, і показано, що зниження рН середовища приводить до збільшення стабільності піни.*

**Влияние рН среды на адсорбционное поведение,  
поверхностную дилатационную реологию и устойчивость пен растворов смесей  
гуматы натрия / цетилтриметиламмоний бромид**

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*Представлены результаты исследования адсорбционных и поверхностно-реологических характеристик растворов природных полиэлектролитов – гуматов натрия с добавками цетилтриметиламмоний бромида (ЦТАБ) при различных значениях рН среды на границе раздела жидкость–газ методами кольца и формы осциллирующей капли. Выведено, что основные особенности концентрационных зависимостей поверхностного натяжения и модуля вязкоупругости растворов гуматы натрия / ЦТАБ могут быть связаны с образованием агрегатов в адсорбционном слое при соответствующих концентрациях ЦТАБ. Исследована возможность образования пен из растворов смесей гуматы натрия / ЦТАБ, и показано, что снижение рН среды приводит к увеличению стабильности пены.*