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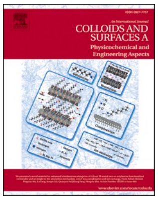

Effect of head-group of cationic surfactants and structure of ionic groups of anionic polyelectrolyte in oppositely charged polymer-surfactant complexes

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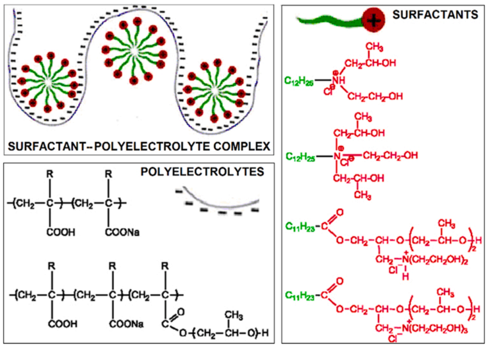
GRAPHICAL ABSTRACT



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Dedicated to Professor Ziyafaddin H. Asadov on the Occasion of his 70th Birthday.

Keywords:
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ABSTRACT

In this study, a detailed assessment of interactional conduct between different head-groups of cationic surfactants and different monomer fragments of anionic polyelectrolyte of aqueous media is reported. Tensiometry, conductometry, viscosimetry, dynamic light scattering have been employed to get insight into interactions among cationic surfactant and polyelectrolyte in interfacial region critical aggregation and micellization concentration, surface excess concentration, surface pressure at interface, minimum area occupied with the aid of one molecule of cationic surfactant at air-solvent interface, adsorption efficiency, surface tension at critical micelle concentration and the positive degree of counterion binding had been calculated. Thermodynamic parameters, i.e., standard Gibbs free energy of micellization and adsorption processes had been evaluated. Polyelectrolyte-surfactant interaction used to be studied in dependence on nature of head-group of cationic surfactant and polyelectrolyte chain and their influence on colloidal-chemical parameters of polyelectrolyte-surfactant complexes has been compared. Petrocollecting ability of these complexes in the waters of various mineralization degree was investigated.

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1. Introduction

Application areas of surfactants are very broad and they have more probability for implementation in industry. Surfactants are frequently used in manufacturing of detergents [1,2] and emulsifiers [3,4], in cleaning of industrial waste waters [5]. Addition of polymers to surfactants leads to enhancement of their properties. Thus, there is much information about an impact of the added polymers on micellization capacity, surfactivity, phase transitions, reological and other properties of surfactants. This particularity is especially manifested in oppositely-charged polyelectrolyte-surfactant complexes. So, application possibilities of such polymer-surfactant complexes are still more widened in preparation of cosmetics [6], perfumes [7,8], production of biofuels, purification of oils and fuels by extraction [9], petroleum production [10,11] and other areas [12]. Petkova and co-authors [13] studied the foaming ability and surface activity properties of mixtures polyvinylamine with surfactants have different head groups - sodium dodecyl sulphate and sodium dodecyl oxyethylene sulphate. It was found that in a mixture with a strong polymer-surfactant interaction, the stability of the foam is higher. E. Vasilieva and co-authors [14] obtained the complexes of polyacrylic acid with hexylene-1,6-bis (hexadecyldimethylammonium bromide) and hydroxyethylated analog-hexylene-1,6-bis(hexadecylmethylethylolammonium bromide). In the complexes study of polyacrylic acid with surfactants, which form gemini at concentrations of 1, 3 and 5 mM, it was found that the CAC value of the surfactant, with the hydroxy group is lower. M.S. Bakshi and I. Kaur [15] explored interactive electrostatic effect beetwen surfactants with the different head groups (benzyldimethylhexadecylammonium chloride, hexadecylpyridinium bromide, hexadecylpyridinium chloride), and polyelectrolytes (carboxymethylcellulose sodium salt and polystyrene sulfonate sodium salt). It was found that the steric nature of the head group of surfactants weakens its interaction with the polyelectrolyte.

It is regarded from the scientific literature that anionic polymer-cationic surfactant and cationic polymer-anionic surfactant systems had been studied. Sometimes, anionic polymer-anionic surfactant structures are also met [16]. In the structures such as oppositely charged polymer and surfactant, a reaction occurs between a counter-ion in the surfactant hydrophilic group and a counter-ion of the polymer. Thereby, the latter ion becomes replaced through a voluminous counter-ion of the surfactant, i.e., a polymer-surfactant complex is formed. Obtainment and study of oppositely-charged surfactant-polymer complexes have been carried out for the recent 50 years [17–22]. According to nature of polyelectrolyte, the following classes of the indicated complexes have been commonly extra studied [22]: carboxymethylcellulose-surfactant, polydiallyldimethylammonium chloride-surfactant, polystyrene sulfonate-surfactant, vinyl monomer-based polyelectrolyte-surfactant complexes. With regard to polymer, properties of these complexes depend on nature, structure, average molecular mass of polymer, nature and polarity degree of its polar groups as properly as some different factors. Regarding surfactant, these properties are dependent on hydrophilic-lipophilic balance, structure, length of alkyl chain, nature of polar group and counter-ion of the surfactant and some other factors.

One of the most studied representatives of polyelectrolytes forming complexes with surfactants are these acquired on the basis of vinyl monomers, for example, sodium salt of polyacrylic (PAA) and polymethacrylic acids (PMAA) [23,24].

Anghel and coauthors [25] studied an impact of nature of a counterion in decylammonium salts on properties of their complexes with PAA and PMAA. It was established that, in the systems with organic counterions, an interaction is stronger, surface tension and relative viscosity values being maximum in such cases. In the complexes obtained with PMAA, the interaction is weaker as compared with that in PAA-based complexes. The acetate ion interacts more strougly than the thiocyanate ion [25]. In the complexes of PAA with alkyltrimethylammonium bromides (C_nTAB, n = 8,10,12,14,16), with lengthening of the surfactant alkyl chain, an extend of surface elasticity is observed as a result of formation of more rigid structure in adsorption layer [26]. At high values of pH in such kind complexes, the interaction will become stronger [27].

E.A.Vasilyeva and coauthors [28] studied a complex of N-(2-hydroxyethyl)-N-hexadecylpyrrolidinium bromide with PAA through a range of physico-chemical methods. Formation of such complex causes a decrease of the generated nanoparticles concentration by approximately one order. The polymer exerts absolutely no impact on the surfactant solubilization capacity [20]. Neutralization degree of PAA seriously influences the properties of the complexes formed on its basis. So, as COOH-groups of PAA bind with a surfactant (dodecylpyridinium and cetylpyridinium chloride), a neutralization degree rises [29,30]. By investigation of oppositely charged polymer-surfactant complexes of various classes, it was established that a degree of a surfactant binding with a polymer is linearly dependent on the charge density [31]. An interaction of tetradecyldimethylaminooxide zwitter-ionic surfactant with PAA and PMAA in aqueous solution has been studied [32]. When studying physico-chemical properties of polymer-surfactant complexes by different methods, it was established that, in a small pH interval, when rod-like micelles are formed, changes in physico-chemical properties of the polymer-surfactant system are observed. Herewith, hydrogen bonding and hydrophobic forces play an important role in appearance of polymer-surfactant interaction in such complexes.

In polymer-surfactant complexes, polymer-surfactant interaction is different depending on the nature of surfactant [33]. Thus, in researches performed with PAA, it was discovered that, with a nonionic surfactant ($C_{12}E_6$), PAA interacts at the expense of hydrogen bonding, with anionic surfactant (sodium dodecylsulphate - SDS) – due to weak hydrophobic forces and with cationic surfactant (dodecyltrimethylammonium chloride) –via electrostatic forces [33].

As is seen from the literature reports, the interaction force between surfactant and polymer in the surfactant-polymer systems depends on nature and average molecular mass of polymer, nature of polar groups, pH value, ionic forces strength, length of the surfactant alkyl chain, nature of the surfactant hydrophilic group and other factors. When surfactants are mixed with poly(meth)acrylate type polyelectrolytes, their petroleum-collecting capacity increases [23,34]. In this regard, it is interesting to study the interactive effect of surfactants and polyelectrolytes from their nature, which contain different head groups.

Investigation of the complexes of PAA and PMAA as well as their propoxylated derivatives with the surfactants containing C_{12} alkyl chain and different hydrophilic groups for studying an influence of nature of ionic groups of both surfactant and polymer is the main essence of the presented paper.

2. Materials and methods

2.1. Reagents

PAA and PMAA were synthesized by the method of radical polymerization of acrylic (AA) and methacrylic acid (MAA) under an action of ammonium persulfate - $(NH_4)_2S_2O_8$ initiator in the mixture water - 2-propanol. Kinematic viscosity of the obtained polyacids was determined using Stabinger Viscometer SVM 3000 (Anton Paar GmbH, Austria). Based on the obtained results, characteristic viscosities [η] of PAA and PMAA had been calculated - [η] for PAA is 0.20 dl/g (dioxan 303 K), for PMAA - 0.16 dl/g (0.002 N HCl solution, 303 K). Using Mark-Houwink equation (for PAA $[\eta] = 7.6 \cdot 10^{-4} \cdot M^{0.5}$and for PMAA $[\eta] = 6.6 \cdot 10^{-4} \cdot M^{0.5}$), average molecular mass was calculated as 69 000 for PAA and 59 000 for PMAA.

Both of the polyacids were neutralized by NaOH at the level 50 % mol. Acid number of PAA is 750 mg KOH/g. After 50 % neutralization, its acid number decreased down to 362 mg KOH/g. Acid number of PMAA decreased after 50 % neutralization from 644 down to 312 mg KOH/g. As a result, neutralized PAA (NPAA) and neutralized PMAA

(NPMAA) were obtained with neutralization degree α = 0.5 for both products.

The formulas of the polyelectrolytes used in this work are given in Table 1.

As dodecyl-chain containing cationic surfactants, four ammonium-type salts were used whose obtainment and study were desribed earlier [35–37]. The purity of the surfactants $C_{12}PEt$ – 97 %, $C_{12}P_2Et$ – 96 %, $C_{12}EP_2D$ –96 % and $C_{12}EP_2T$ – 95 %. Their formulas are also included into Table 1.

2.2. Propoxylation of NPAA and NPMAA

5 % wt.aqueous solutions of NPAA and NPMAA having α = 0.5 had been prepared. Each of these solutions was placed into a tightly closed glass flask (resistant to a pressure 3−5 atm) and propylene oxide (PO) was added at the quantity equal to molar fraction of free carboxylic groups. The reaction was conducted at room temperature in the nitrogen atmosphere for 8−10 h. To remove unreacted PO and water from the reaction medium, the final mixture was evaporated under 5−6 mm Hg vacuum in rotary evaporator (Ratovapor R-210, BUCHİ, Switzerland) till reaching a constant mass. In the IR-spectra of the synthesized propoxylated NPAA (NPPAA) and propoxylated NPMAA (NPPMAA), intensity of the 1700 cm^{-1} peak intrinsic for free carboxylic groups decreases and the peaks at 1720 cm^{-1} characteristic for ester group appear.

2.3. Surface tension measurements

Surface tension was determined by a DuNouy ring KSV Sigma 702 tensiometer (Finland). The sample under study was placed into the glass cell (with a double jacket) and water bath was used for thermostating. A Pt wire ring was put into the sample solution and then slowly pulled through the liquid-air border. An average value of surface tension was determined based on 3 readings with interval of 3 min. The Pt ring was rinsed the usage of water and flamed with Bunsen burner between measuments. The deviations of the surface tension values for distilled water from 72.0 (25 °C) were not larger than ±0.2 mN/m.

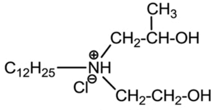
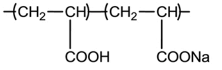
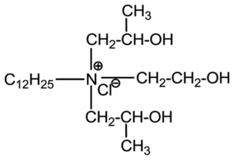
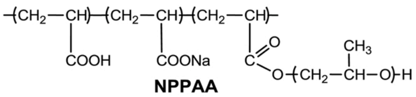
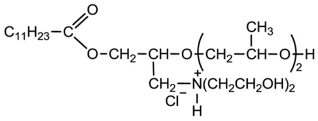
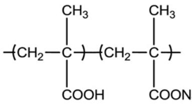
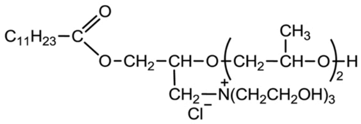
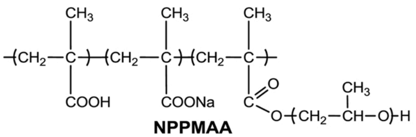
2.4. Electroconductometric measurements

Specific electroconductivity (κ) of the polymer-surfactant complexes were measured using "Anion 4120" conductometer (Russion Federation). During these measurements, the interval of determination of κ was (10^{-4}–10) S/m. The temperature range for these measurements was 0–100 °C and the acceptable relative error was ± 2%. First, the electrodes were added into 25 mL of the polyelectrolyte solution to measure its specific electroconductivity. To reach the necessary temperature and equilibrium, the samples were kept under the desired conditions for 1 h. After creation of the equilibrium, the surfactant solution was dropwise added to the polyelectrolyte solution the usage of a microsyringe and kept for 5 min for reaching equilibrium. When the equilibrium was achieved, the value of κ was recorded. It is known that, with an addition of surfactant solution to polymer solution, concentration of the polymer gradually decreases. To keep concentration of the polymer solution constant, after each addition of the surfactant solution, the calculated amount of the concentrated polymer solution was added. In this way, it was possible to keep the polymer concentration in the system constant. After completion of each titration, the electrode was rinsed with distilled water and dried. Specific electroconductivity of the used distilled water must be in the interval 2–3 μS/cm.

2.5. Study of petroleum-collecting and dispersing properties

Investigations of petroleum-collecting and dispersing properties of the obtained surfactants have been performed in parallel for pure-state reagents and their 0.1 % wt. aqueous solutions. As an example of crude oil, Pirallahy petroleum (from the oil field near Baku, Azerbaijan) was used. Its density was 0.9244 g cm^{-3} (20 °C), kinematic viscosity equaled 1.05 cm^2 s^{-1} (30 °C) 0.02 g of the surfactant (or its solution) was added to a thin film (of 0.17 mm thickness) of the taken crude oil on the

Table 1
Formulas of the cationic surfactants and polyelectrolytes used in this work.

Cationic surfactants	Polyelectrolytes
 **$C_{12}PEt$**	 **NPAA**
 **$C_{12}P_2Et$**	 **NPPAA**
 **$C_{12}EP_2D$**	 **NPMAA**
 **$C_{12}EP_2T$**	 **NPPMAA**

surface of three waters (Caspian Sea, fresh and distilled) in separate Petri dishes. Petrocollecting coefficient-K was determined by the formula $K = S_0/S$, where S_0 is the initial area of the crude oil surface, and S is a current area of the surface of petroleum in the form of thickened spot. In the course of the test, the surface area of the spot was measured at definite time intervals (τ) and corresponding values of petrocollecting coefficient were computed. Petroleum-dispersing effect was estimated by a degree of cleaning of polluted water surface from petroleum – K_D which was calculated as a ratio of the area of the cleaned water surface and the initial surface area of the polluted water.

Characteristics of fresh water: density 996.0 kg/m^3 (20 °C), pH = 7–8. Chemical composition (100 g, gram-ekv): Ca^{2+} 0.0052; Mg^{2+} 0.0023; Cl^- 0.0007; SO_4^{2-} 0.0044; $HCO\text{-}_3$ 0.0273; $CO^{2-}{}_3$ 0.0009; total hardness 4.5 mg-ekv/g; electroconductivity - 613.0 μS/cm; NaCl-210.2 mg/l.

Characteristics of Caspian Sea water: density 1009.8 kg/m^3 (20 °C), pH = 7.7. Chemical composition (mg/1 *l* water); Na^+ 2650; K^+ 20; Ca^{2+} -250; Mg^{2+} -900; NH_4^+ 0.15; Cl^- 500; SO_4^{2-} 2800; $NO\text{-}_3$ 0.1; $PO^{3-}{}_4$ 0.35; SiO_2 0.5; NaCl-9.900 g/l (20−22 °C); total hardness 69 mg-ekv/g; electroconductivity - 17.86 μS/cm.

3. Results and discussion

3.1. Synthesis polymer-surfactants complexes

According to [38,39], when PAA and PMAA are neutralized, i.e., with a rise of pH of their aqueous solutions, surface tension at their border with air increases. But, when propoxylating PAA and PMAA, lowering of surface tension values of their aqueous solutions of the same concentration at the border with air is observed. Table 2 includes the values of pH and surface tension of 0.01 % wt. aqueous solutions of NPAA, NPPAA, NPMAA and NPPMAA. As is clear from the table, at the taken concentrations, the mentioned polymers slightly impact surface tension at the water-air border.

Investigations on pH change were carried out when the surfactants containing different head-groups (at the amount of 0.2 % wt.) were added to 0.01 % wt. aqueous solutions of the indicated polymers. Therefore, the pH increases from 6.6 to 6.7. Such a little decrease of pH slightly impacts surface tension of the polymer and it may be disregarded. If the solution's pH is higher than 6–6.5, the surface tension value stabilizes and approaches the water-air boundary surface tension value. The value of pH of the studied NPAA is higher than 6.5 and it has no surface activity.

As is clear from Fig. 1, the obtained cationic surfactants lower surface tension at the water-air border. Figs. 2–5 shows the surface tension isotherms of polyelectrolyte-surfactant complexes.There are three identifiable points in the surface tension of the mixture which are conventionally designated T_1, T_2 and T_3, as shown in the figure. T_1 (or CAC) is critical aggregation concentration. T_2 (or CSC) is critical saturation concentration. T_3 (or CMC) is critical micellization concentration. Some authors [40] indicate existence of four characteristic concentrations in certain polyelectrolyte-surfactant systems.

With an increase of surfactant concentration in the solution, a complex starts to form between the surfactant molecules and polar groups of the polyelectrolyte. Herewith, the surface tension value abruptly diminishes. In the concentration interval of partial stabilization, an exchange reaction between the surfactant molecules and polar groups of polyelectrolytes come to completion. The counterion of the surfactant becomes substituted by the ion of the polyelectrolyte. When this process completely finishes, i.e., after saturation of the monomer units of the polyelectrolyte chain with the surfactant ions, the newly added surfactant molecules are consumed in the process of free micelles formation. It is accompanied with surface tension lowering. After CMC, formation of micelles comes to completion. Sometimes, at T_2 concentration, precipitation is observed [34]. This is explained by a decrease of hydrophilicity of the final complex resulting from replacement of the counter-ions in the polar groups of polyelectrolyte by bulky counter-ions of the surfactant.

Table 2
Some physico-chemical indices of the polyelectrolytes 0.01 % wt.aqueous solutions at 298 K.[a]

Polyelectrolyte	γ, mN/m	pH	Dynamic viscosity (η), mPa·s	Kinematic viscosity (ν), mm^2/s	Density (ρ_0), g/cm^3
NPAA	70.4	6.6	1.1686	1.1742	0.9952
NPPAA	70.4	6.7	1.0274	1.0302	0.9973
NPMAA	70.1	6.7	0.93976	0.94427	0.9952
NPPMAA	70.2	6.7	0.94594	0.95046	0.9952

[a] The uncertainties in tensiometry and pH-metry measurements were within 2 %, while those in viscosity measurements were less than 3 %.

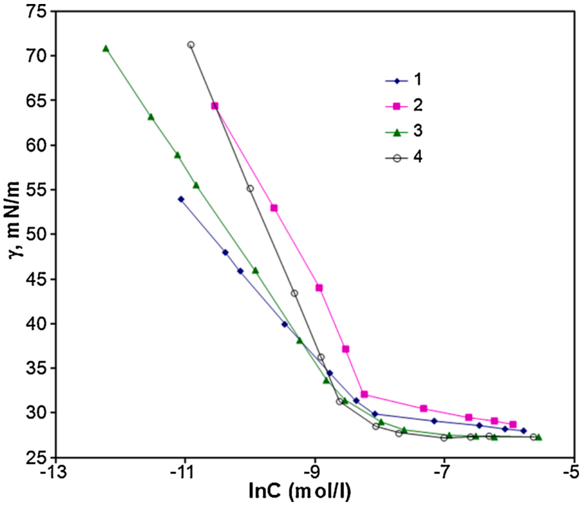


Fig. 1. Surface tension isotherms of $C_{12}Pet$ (1), $C_{12}P_2Et$ (2),$C_{12}EP_2D$ (3) and $C_{12}EP_2T$ (4) surfactants at water-air border (t = 25 °C).

3.2. Critical micellization concentration and critical aggregation concentration

According to the surface tension isotherms in Figs. 2–5, the CMC value of the cationic surfactants, T_1, T_2 and T_3 values of the polyelectrolyte-surfactant systems were determined (Table 4). As is seen from this table, for the polyelectrolyte-surfactant complexes, excepting

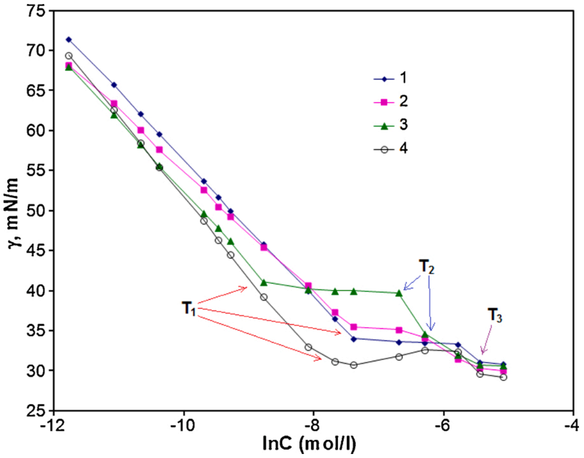


Fig. 2. Dependence of surface tension at water-air border in the presence of $C_{12}PEt$-polyelectrolyte complex on concentration of the surfactant (t = 25 °C). Polyelectrolyte (0.01 % wt.): 1-NPAA; 2-NPPAA; 3-NPMAA; 4-NPPMAA.

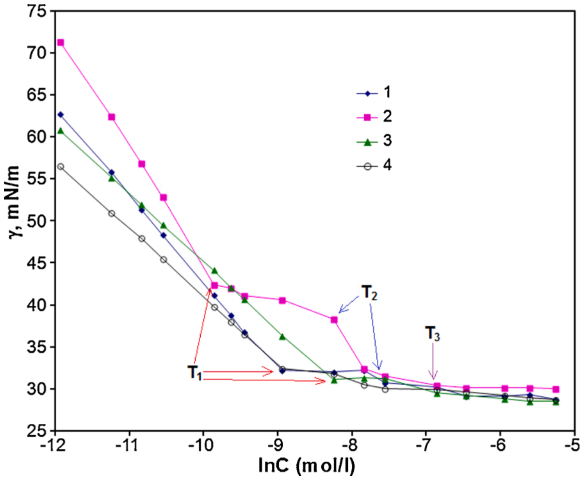


Fig. 3. Dependence of surface tension at water-air border in the presence of $C_{12}P_2Et$- polyelectrolyte complex on concentration of the surfactant (t = 25 °C). Polyelectrolyte (0.01 % wt.): 1-NPAA; 2-NPPAA; 3-NPMAA; 4-NPPMAA.

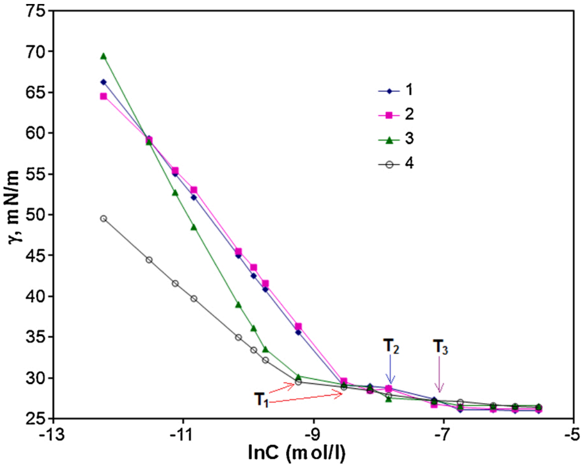


Fig. 4. Dependence of surface tension at water-air border in the presence of $C_{12}EP_2D$-polyelectrolyte complex on concentration of the surfactant (t = 25 °C). Polyelectrolyte (0.01 % wt.): 1-NPAA; 2-NPPAA; 3-NPMAA; 4-NPPMAA.

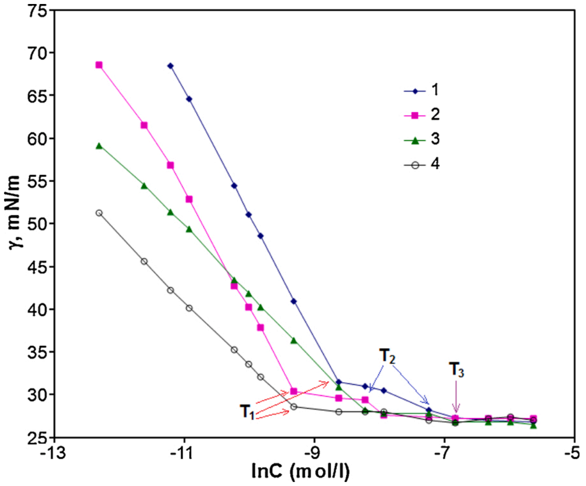


Fig. 5. Dependence of surface tension at water-air border in the presence of $C_{12}EP_2T$- polyelectrolyte complex on concentration of the surfactant (t = 25 °C). Polyelectrolyte (0.01 % wt.): 1-NPAA; 2-NPPAA; 3-NPMAA; 4-NPPMAA.

the complexes of $C_{12}PEt$ surfactant, aggregation concentrations are considerably low. In $C_{12}PEt$-polyelectrolyte complex, when replacing NPAA with NPPAA, the value of T_3 decreases. Substitution of NPMAA by NPPMAA causes an increase of T_3. From the comparison of T_3 values of the polyelectrolyte complexes formed by $C_{12}P_2Et$ and $C_{12}EP_2T$, it is noticeable that propoxylation of both polyelectrolytes lowers the values of T_3. It is seen from Table 3 that CMC of the surfactants rises when the number of the isopropylol and ethylol groups in them increases. A similar regularity is observed in $C_{12}PEt$-polyelectrolyte and $C_{12}P_2Et$-polyelectrolyte complexes (Table 4), too. Thus, for the systems where the number of isopropylol groups in the head-group of the surfactant is larger, the T_3 value is smaller. Among the complexes of $C_{12}EP_2D$ and $C_{12}EP_2T$ with PAA-based polyelectrolytes, with an increase of the number of ethylol groups in the surfactant head-group, T_3 becomes lowered (as in the surfactants without polyelectrolyte). Analogical regularity is recorded among the complexes formed by monoethylol-, diethylol- and triethylolnonylammonium bromide surfactants with NPPAA [23]. In the case of the surfactant complexes with PMAA-based polyelectrolytes, vice versa, T_3 value rises as the number of ethylol groups in the surfactant head-group increases.

3.3. *Maximum adsorption (Γ_{max}) and minimal cross-section area of polar group (A_{min})*

Comparison of Γ_{max} and A_{min} values for the surfactants (Table 3) and their complexes with PAA-based polyelectrolytes (Table 4) gives a rise to state the following.

When passing from $C_{12}PEt$ surfactant to its complex with NPAA, Γ_{max} increases from 1.69 to 1.73 μmol· m^2. If the same surfactant is compared with its NPPAA-based complex, it may be seen that Γ_{max} diminishes from 1.69 to 1.52 μmol· m^2. When the same surfactant contains not one but two propoxy units (i.e., in the case of $C_{12}P_2Et$ surfactant), Γ_{max} becomes larger as compared with that of $C_{12}PEt$ surfactant correspondingly 2.77 and 1.69 μmol· m^2. Transition from $C_{12}P_2Et$ surfactant to its complex with NPAA brings about lowering of Γ_{max} from 2.77 to 2.11 μmol· m^2. On passing from the same surfactant to its complex with NPPAA, Γ_{max} slightly increases from 2.77 to 2.80 μmol· m^2.

The above-considered cases cover the ionic surfactants obtained using ethylene chlorohydrin. The situation with the ionic surfactants synthesized using di- and triethanolamine is different. Transition from $C_{12}EP_2D$ surfactant to its complex both with NPAA and NPPAA causes a decrease of Γ_{max} from 2.20 down to 2.05 and 1.95 μmol· m^2. Comparison of $C_{12}EP_2T$ surfactant and its two complexes with NPAA and NPPAA shows that, in both transitions to a complex with polyelectrolyte, diminution of Γ_{max} from 3.50 down to 2.90 and 2.62 μmol· m^2. Comparing two ethanolamine-based surfactants, i.e., $C_{12}EP_2D$ and $C_{12}EP_2T$ surfactants is of interest, too. According to Table 3, in the case of diethanolamine-based surfactant, Γ_{max} is smaller (2.20 μmol· m^2) than that of triethanolamine-based surfactant (3.50 μmol· m^{-2}).

Comparison of the polyelectrolyte-surfactant complexes based on PMAA-derived polyelectrolytes and 4 above-described surfactants enables to come to the following conclusions. Transition from $C_{12}PEt$ surfactant to its complex with NPMAA and NPPMAA leads to augmentation of Γ_{max} from 1.69 to 1.79 and 2.01 μmol· m^2.

When passing from $C_{12}P_2Et$ surfactant to its complex with NPMAA and NPPMAA Γ_{max} diminishes from 2.77 down to 1.64 and 1.63 μmol· m^2.

When $C_{12}EP_2D$ surfactant is converted to its complex with NPMAA, Γ_{max} increases from 2.20 to 2.90 μmol· m^2. However, when the same surfactant becomes complexed with NPPMAA, Γ_{max} is lowered from 2.20 down to 1.40 μmol· m^2. Transformation of $C_{12}EP_2T$ surfactant into its complex with both NPMAA and NPPMAA turns Γ_{max} to be lowered from 3.50 down to 1.57 and 1.52 μmol· m^2.

Table 3
Surface properties of the cationic surfactants with different head-groups in aqueous solution at 298 K [35–37].

Surfactant	β	CMC×10^4, mol· dm^{-3}		Γ_{max}×10^{10}, mol· cm^{-2}	A_{min}×10^2, nm^2	γ_{CMC}, mN· m^{-1}	π_{CMC}, mN· m^{-1}	pC_{20}	ΔG_{mic}, kJ· mol^{-1}	ΔG_{ad}, kJ· mol^{-1}
$C_{12}PEt$	0.42	2.93[a]	2.94[b]	1.69	98.5	28.2	43.8	4.71	–28.60	–31.21
$C_{12}P_2Et$	0.48	2.56	2.60	2.77	59.9	32.1	39.9	4.28	–30.27	–31.71
$C_{12}EP_2D$	0.69	2.90	2.80	2.20	75.5	27.3	44.7	4.56	–34.25	–36.29
$C_{12}EP_2T$	0.81	2.50	2.40	3.50	47.4	27.2	44.8	4.26	–37.38	–38.66

[a] The CMC value determined by electroconductivity method.
[b] The CMC value determined by surface tension method.

Table 4
Surface properties of the (0.01 %) polyelectrolyte -surfactant complexes in aqueous solution at 298 K.

Complexes	β_1	β_2	T_1×10^4, mol· dm^{-3}		T_2×10^3, mol· dm^{-3}	T_3×10^3, mol· dm^{-3}		CAC/CMC[b] (or T_1/T_3)	Γ_{max}×10^{10}, mol· cm^{-2}	A_{min}×10^2, nm^2	π_{CMC}, mN· m^{-1}
NPAA-$C_{12}PEt$	0.10	0.30	6.20[a]	6.17[b]	3.08	3.90[a]	4.32[b]	0.143	1.73	96.2	41.3
NPPAA-$C_{12}PEt$	0.14	0.31	1.55	6.17	1.23	3.09	3.08	0.200	1.52	109.2	41.7
NPMAA- $C_{12}PEt$	0.17	0.44	1.05	1.54	1.23	1.85	1.87	0.08	1.79	92.5	41.3
NPPMAA- $C_{12}PEt$	0.14	0.30	1.50	4.63	3.09	3.05	4.32	0.107	2.01	82.6	42.4
NPAA-$C_{12}P_2Et$	0.05	0.25	0.58[a]	0.52[b]	0.39	0.55[a]	0.52[b]	0.100	2.11	78.6	41.3
NPPAA-$C_{12}P_2Et$	0.29	0.36	1.55	0.52	0.26	0.39	0.40	0.130	2.80	59.3	39.6
NPMAA-$C_{12}P_2Et$	0.24	0.26	1.05	2.62	0.52	1.85	1.00	0.262	1.64	101.2	42.5
NPPMAA-$C_{12}P_2Et$	0.12	0.15	1.30	1.31	0.26	0.42	0.39	0.336	1.63	102.1	42.0
NPAA-$C_{12}EP_2D$	0.03	0.19	2.90[a]	1.95[b]	0.78	1.15[a]	1.17[b]	0.167	2.05	80.8	45.9
NPPAA-$C_{12}EP_2D$	0.29	0.30	1.90	1.95	0.39	1.08	0.78	0.250	1.95	85.1	45.6
NPMAA-$C_{12}EP_2D$	0.44	0.50	0.97	0.97	0.29	0.40	0.39	0.250	2.90	57.2	44.5
NPPMAA-$C_{12}EP_2D$	0.27	0.38	0.92	0.97	0.29	0.37	0.39	0.250	1.40	118.4	44.8
NPAA-$C_{12}EP_2T$	0.22	0.31	0.89[a]	1.80[b]	0.36	0.74[a]	0.72[b]	0.250	2.90	57.2	43.8
NPPAA-$C_{12}EP_2T$	0.32	0.39	0.54	0.89	0.27	0.39	0.36	0.247	2.62	63.4	44.4
NPMAA-$C_{12}EP_2T$	0.50	0.52	0.45	2.70	0.36	1.85	1.00	0.270	1.57	105.9	45.2
NPPMAA-$C_{12}EP_2T$	0.34	0.41	0.45	0.89	0.36	1.00	0.72	0.124	1.52	109.3	45.0

[a] Measured by electroconductometry method.
[b] Measured by tensiometry method.

3.4. *Surface pressure (π_{CMC})*

As is seen from Table 3, with an increase of the number of isopropylol groups, the surface pressure value decreases but, when number of ethylol groups augments the surface pressure rises a little. From Table 3, it is also noticeable that the surface pressure of $C_{12}PEt$ surfactant is 43.8 mN/m whereas, for its complexes with the studied polyelectrolytes, the surface pressure value varies in the range 41.3–42.4 mN/m (Table 4). Therefore, when $C_{12}PEt$ surfactant gets complexed, the value of surface pressure declines a little. Surface pressure of $C_{12}P_2Et$ surfactant equals 39.9 mN/m. When passing to its complexes with the indicated polyelectrolytes, surface pressure rises excluding the complex NPPAA-$C_{12}P_2Et$. Surface pressure of $C_{12}EP_2D$ is equal to 44.7 mN/m. When this surfactant becomes complexed with mentioned polyelectrolytes, in all cases, the value of π_{CMC} increases excepting the complex NPMAA-$C_{12}EP_2D$.

Among the all used surfactants, $C_{12}EP_2T$ surfactant has the highest value of π_{CMC} (44.8 mN/m). When it forms complexes with the acrylic acid-derived polyelectrolytes, the surface pressure value is lowered. But when $C_{12}EP_2T$ gets complexed with methacrylic acid-based polyelectrolytes, the situation is vice versa, i.e., π_{CMC} rises.

A comparative analysis of these data enables to conclude that the variation of the π_{CMC} value when polyelectrolyte-surfactant complexes is formed depends on the nature of the surfactant head-group and the type of polyelectrolyte.

3.5. *Conductometric measurements and binding degree (β) of surfactant counter-ion*

Conductometric measurements are mainly used to determine CMC of ionic surfactants. In these measurements, with an increase of ionic surfactants concentration, their specific electroconductivity rises (Fig. 6). In κ-C plot, two straight lines are observed. The point of their intersection corresponds to the CMC value. The ratio of the slopes after and before CMC is equal to a dissociation degree (α) of the counter-ion. A binding degree (β) of the counter-ion is calculated by the formula:

$$\beta = 1 - \alpha \quad (1)$$

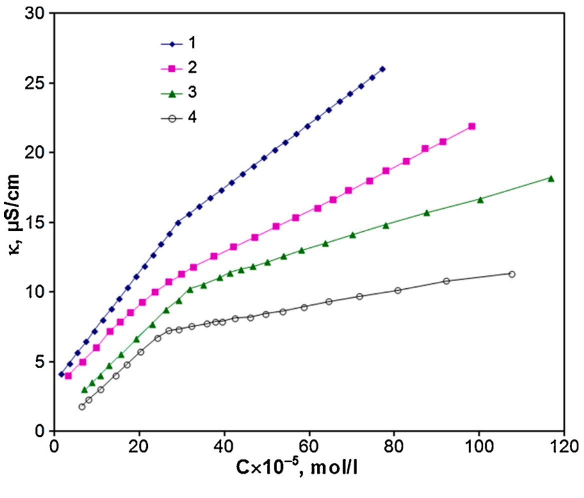


Fig. 6. Dependence of specific electrical conductivity of aqueous solutions of $C_{12}PEt$ (1), $C_{12}P_2Et$ (2), $C_{12}EP_2D$ (3) and $C_{12}EP_2T$ (4) on their concentration (t = 25 °C).

The calculated values of β for the synthesized surfactants are given in Table 3. As is noticed from the table, the value of β rises as the number of isopropylol and ethylol groups in the surfactant increases.

As the concentration of polyelectrolytes is raised, specific electroconductivity rises linearly [38]. It shows that, in the polymer chain, no aggregation process occurs in the studied concentration range.

In polyelectrolyte-surfactant systems, κ-f(C) plots mainly exhibit three distinctive critical concentrations [41–43]. The first of them is critical aggregation concentration (T_1), the second is the concentration of saturation of the polymer chain (T_2) and the third is T_3. In the studied polyelectrolyte-surfactant complexes, only two different critical concentrations are observed: T_1 and T_3. In Fig. 7 (see Figs. S1–S15 in Supporting Information), the graphs of κ vs. surfactant concentration dependence for the investigated polyelectrolyte-surfactant complexes are illustrated. As was just mentioned, for these systems, two critical concentrations are noticed. So, two binding degrees (β_1 and β_2) will be valid. β_1 is the binding degree of the surfactant counter-ion at the critical concentration of aggregation, β_2 is the counter-ion binding degree at T_3. Their values are included into Table 4. As is noticeable from this table, the values of β_1 are smaller than those of β_2. Moreover, in some cases, β_1 has smaller values as compared with β_2 (i.e., T_3). This circumstance points out that, at low concentrations of surfactant, the counter-ion is mainly in dissociated state. Its reason is transition of the surfactants counter-ion to a common phase as a result of its interaction with the counter-ion of polyelectrolyte. A smaller value of β_1 than β_2 shows that, in complexes with polyelectrolytes, the surfactant counter-ion dissociates to a larger extent. Therefore, polar groups of the polyelectrolytes enhance dissociation of the surfactant counter-ion. This fact indicates that polyelectrolyte-surfactant complexes are formed at the expense of incompletely strong electrostatic forces.

As a number of isopropylol and ethylol groups in the surfactant headgroup rises, the value of β increases. Therefore, these groups adversely impact a dissociation of the surfactant counter-ion. When comparing the β (β_1 and β_2) values for unpropoxylated and propoxylated polyelectrolytes complexes, it may be marked that, in the case of AA-based polyelectrolyte, propoxylation brings about a rise of β. But, for MAA-based polyelectrolyte, the situation is opposite. These regularities are observed for the polyelectrolyte complexes with the studied 4 ionic-liquid surfactants. Thus, propoxy groups added to PAA negatively influence a dissociation of the surfactant counter-ion. However, when added to PMAA, these groups favour a dissociation of the counter-ion of the surfactant.

3.6. Viscosimetric measurements of the obtained polyelectrolyte-surfactant complexes

Viscosimetric researches enable to attain additional information on interaction taking place between polyelectrolyte and surfactant. It is known that relative viscosity - η_r is the ratio of time of polymer-surfactant complex flowing from capillary - t_{ps} and that time for solvent - t_s:

$$\eta_r = t_{ps}/t_s \qquad (2)$$

In Figs. 8–11, the graphs for dependence of η_r of the synthesized polyelectrolyte-surfactant complexes on the surfactant concentration are described. As is seen from these figures, relative viscosity of NPAA is higher than that of NPMAA. Its reason may be existence of NPMAA macromolecules in water in a spiral form and hindrance created by methyl group for interaction between polar groups. Meanwhile, it is noticeable from the graphs that, after propoxylation of the polyelectrolytes, their relative viscosities are lowered. When free carboxylic groups are propoxylated, ionic groups in the polymer backbone are transformed into nonionic groups. The number of the interacting polar groups diminishes which results in a decrease of relative viscosity. As may be seen from Fig. 8, in the case of NPAA-surfactant complexes, relative viscosity is lowered when concentration of the surfactant rises. Herewith, Na^+ cations from the COONa group become replaced by the bulky cation of the surfactant. Therefore, interaction forces between the polyelectrolyte chains are weakened. So, conformation of the polymer chain changes and its relative viscosity decreases. After the replacement of all cations of the polyelectrolyte, stabilization of relative viscosity occurs. This corresponds to T_1 concentration. The surfactant molecules added after this concentration are accumulated at the polymer chain. At this concentration range, the value of both surface tension and relative viscosity remain constant. Further increasing of concentration favours formation of micelles that causes a rise of relative viscosity. This corresponds to T_3 concentration. But, in the case of the complexes of the propoxylated polyelectrolytes with surfactants, this process takes place insignificantly and relative viscosity changes slightly. That is why observation of surfactant-polyelectrolyte interaction in the surfactant complexes of the propoxylated polyelectrolytes is difficult.

3.7. Thermodynamics of micellization and aggregation processes

The values of free Gibbs energies for micellization and aggregation

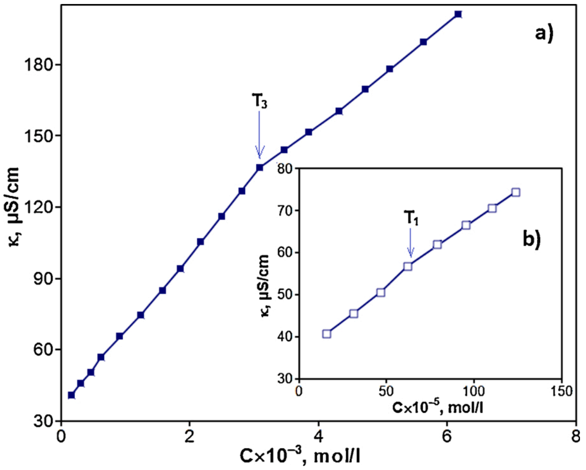


Fig. 7. Dependence of specific electrical conductivity of aqueous solutions of C_{12}PEt-(0.01 %)NPAA complex on concentration of the surfactant (t = 25 °C): a) at high concentrations; b) at low concentrations.

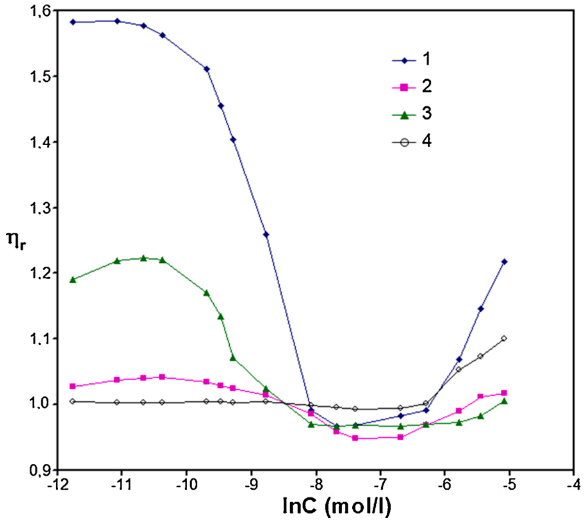


Fig. 8. Dependence of relative viscosity of C_{12}PEt- polyelectrolyte complex on concentration of the surfactant (t = 25 °C). Polyelectrolyte (0.01 % wt.): 1-NPAA; 2-NPPAA; 3-NPMAA; 4-NPPMAA.

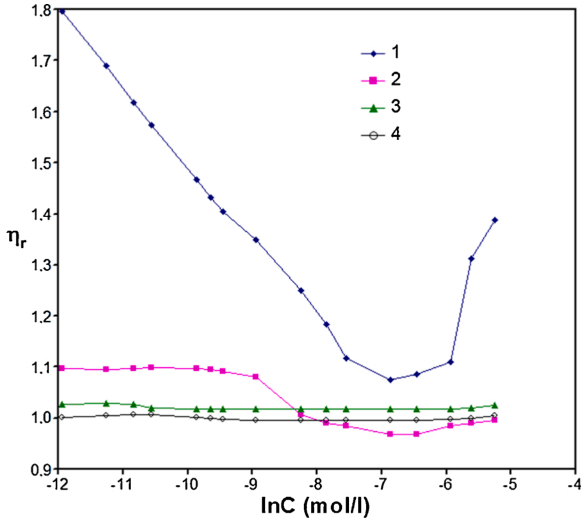


Fig. 9. Dependence of relative viscosity of $C_{12}P_2Et$- polyelectrolyte complex on concentration of the surfactant (t = 25 °C). Polyelectrolyte (0.01 % wt.): 1-NPAA; 2-NPPAA; 3-NPMAA; 4-NPPMAA.

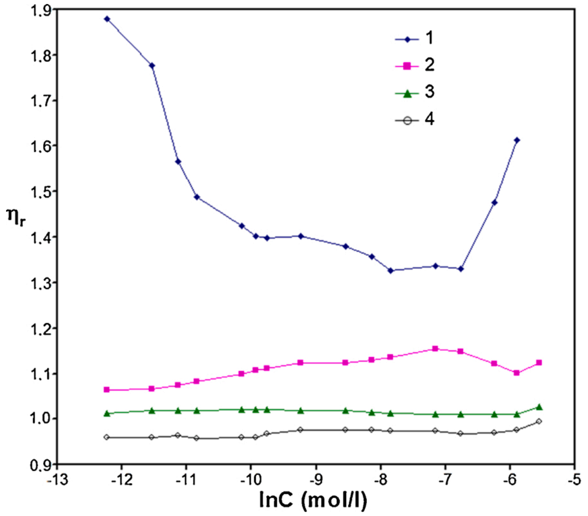


Fig. 10. Dependence of relative viscosity of $C_{12}EP_2D$- polyelectrolyte complex on concentration of the surfactant (t = 25 °C). Polyelectrolyte (0.01 % wt.): 1-NPAA; 2-NPPAA; 3-NPMAA; 4-NPPMAA.

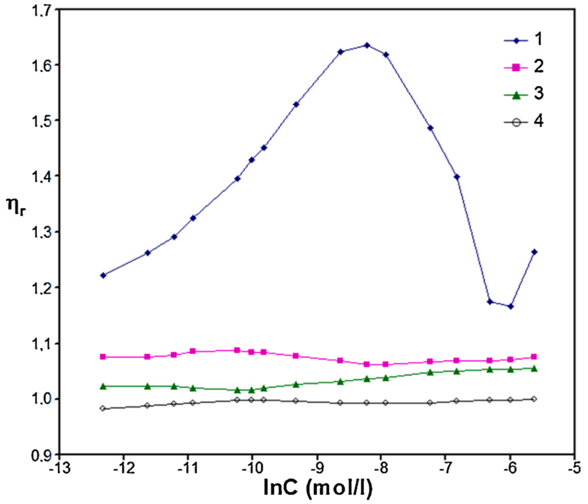


Fig. 11. Dependence of relative viscosity of $C_{12}EP_2T$- polyelectrolyte complex on concentration of the surfactant (t = 25 °C). Polyelectrolyte (0.01 % wt.): 1-NPAA; 2-NPPAA; 3-NPMAA; 4-NPPMAA.

Table 5
Free Gibbs energy of aggregation, micellization and (0.01 %) polyelectrolyte-surfactant interaction in the polyelectrolyte-surfactant systems (298 K).

Complexes	ΔG^o_{agg}, kJ· mol^{-1}	ΔG^o_{mic}, kJ· mol^{-1}	ΔG^o_{ps}, kJ· mol^{-1}
NPAA-C_{12}PEt	−31.08	−30.47	−0.61
NPPAA-C_{12}PEt	−32.25	−31.88	−0.37
NPMAA-C_{12}PEt	−37.08	−36.87	−0.21
NPPMAA-C_{12}PEt	−33.04	−30.48	−2.56
NPAA-$C_{12}P_2$Et	−36.11	−35.85	−0.26
NPPAA-$C_{12}P_2$Et	−44.36	−39.89	−4.47
NPMAA-$C_{12}P_2$Et	−39.82	−34.10	−5.72
NPPMAA-$C_{12}P_2$Et	−35.97	−33.80	−2.17
NPAA-$C_{12}EP_2$D	−32.04	−31.74	−0.30
NPPAA-$C_{12}EP_2$D	−40.13	−35.98	−4.15
NPMAA-$C_{12}EP_2$D	−47.29	−44.09	−3.20
NPPMAA-$C_{12}EP_2$D	−41.71	−40.56	−1.15
NPAA-$C_{12}EP_2$T	−38.20	−36.52	−1.68
NPPAA-$C_{12}EP_2$T	−43.63	−41.13	−2.50
NPMAA-$C_{12}EP_2$T	−45.46	−41.13	−4.33
NPPMAA-$C_{12}EP_2$T	−44.29	−39.30	−4.99

processes for ionic polyelectrolyte-surfactant complexes in aqueous solutions were calculated using the following formulas [44,45]:

$$\Delta G_{mic} = (1+\beta_2)RT\ln CMC \qquad (3)$$

$$\Delta G_{agg} = (1+\beta_1)RT\ln CAC \qquad (4)$$

The values computed on the basis of these formulas are presented in Table 5. From this table, it is evident that Gibbs free energy changes are negative for both micellization and adsorption processes. It means that both processes are spontaneous. This tendency can be seen from the table that, for all complexes, ΔG_{agg} is smaller than ΔG_{mic}. It shows that, in these complexes, aggregation process occurs more readily than micellization. Comparison of ΔG_{agg} and ΔG_{mic} values also indicates that, after propoxylation of NPAA, for respective NPPAA-surfactant complexes, the values of ΔG_{agg} and ΔG_{mic} decreases. But, for NPPMAA-surfactant complexes, those values increase as compared with the ones for NPMAA-surfactant complexes. Therefore, propoxylation of NPAA positively affect aggregation and micellization processes of the corresponding polyelectrolyte-surfactant complexes. In the case of NPMAA propoxylation, the contrary situation is observed.

The change of Gibbs free energy for interaction of polyelectrolyte and surfactant – ΔG^o_{ps} may be calculated using the following formula [46]:

$$\Delta G^o_{ps} = \Delta G^o_{agg} - \Delta G^o_{mic} = (1+\beta_1)RT\ln T_1 - (1+\beta_2)RT\ln T_3 \qquad (5)$$

This parameter is the Gibbs free energy change per mole of surfactant molecules transitioning from free surfactant micelle phase to combined surfactant–polymer aggregates. Evidently, the more negative the ΔG^o_{ps}, means more favorable the surfactant cation transition to the polyelectrolyte-induced aggregates. The calculated ΔG^o_{ps} values are listed in Table 5. As is seen, these values vary in the range from −0.21 to –5.72 kJ/mol. By magnitude, they correspond to the ΔG^o_{ps} values for interaction of nonpolyelectrolytes with ionic-liquid surfactants (–3 … −4 kJ/mol) [47]. From the obtained values, it may be concluded that, in the considered polyelectrolyte-surfactant complexes, in distinction to sodium polyacrylate-dodecyl trimethylammonium bromide system [27], not electrostatic interaction forces but other interaction forces are dominant. Its reason is existence of such functional fragments as isopropylol and ethylol groups in the head-group of these surfactants. Bulky structure of surfactant head-group hinders its approach to polyelectrolyte functional groups. In such cases, creation of hydrogen bonding may be observed instead of electrostatic interaction forces.

When studying complexes formed by NPAA with the surfactants of alkyltrimethyl ammonium and alkylpyridinium bromide-type surfactants which have the same length of the alkyl chain, it was established that hydrophobicity and steric effect of the surfactant head-group adversely affects approaching of the surfactant to active groups of the polymer [48]. The reason of low-magnitude values of ΔG^{o}_{ps} for the studied complexes consists on high values of β for the surfactants resulting in relative weakening of polyelectrolyte-surfactant interaction.

3.8. Measurement of dynamic light scattering (DLS)

In Figs. 12 and 13, size-distribution graphs of the aggregates formed by polyelectrolyte-C_{12}PEt and polyelectrolyte-$C_{12}EP_2T$ complexes in aqueous medium using DLS method are given.

Diameter of particles in 0.1 % aqueous solution of polyelectrolyte-C_{12}PEt complex is in the range 50.7–445.1 nm (Fig. 12). Distribution is unimodal and symmetric. The particles of diameter 150.3 nm are dominant by mass (12.5 %).

From the comparison of the C_{12}PEt surfactant and NPMAA-C_{12}PEt complex, it is seen, when passing from the surfactant to its complex with NPMAA, the unimodal peak is replaced with the bi-modal peaks. The reason for the formation of the bi-modal peak is the strong interaction of surfactant molecules with carboxyl groups of polyelectrolite, which neutralizes the anion groups well. In this case the larger aggregates suggest a spontaneous organization in vesicles. The coexistence of small micelles with large vesicles was already reported for other surfactants [49]. The diameter of the particles which are deminant by mass also diminishes.

In 0.1 % aqueous solution of NPAA-$C_{12}EP_2T$ complex, the diameter of the particles varies in the range 58.1–388.6 nm (Fig. 13). The distribution is unimodal. The particles having 150.3 nm diameter are dominant by mass (13.9 %).

The comparison of the DLS histograms of $C_{12}EP_2T$ surfactant and NPAA-$C_{12}EP_2T$ complex shows that transition from the indicated surfactant to its complex with NPAA leads to a decrease of the aggregates diameter. At the same time, the range of diameter gets considerably narrower.

3.9. Petrocollecting and petrodispersing properties of the obtained polyelectrolyte-surfactant complexes

Petrocollecting and dispersing properties of the synthesized polyelectrolyte-surfactant complexes were studied under laboratory conditions using 0.1 % wt. aqueous dispersed solution of the complex on the example of thin (thickness 0.17 mm) film of Pirallahy crude oil on the surface of three waters (the Caspian Sea, fresh and distilled).

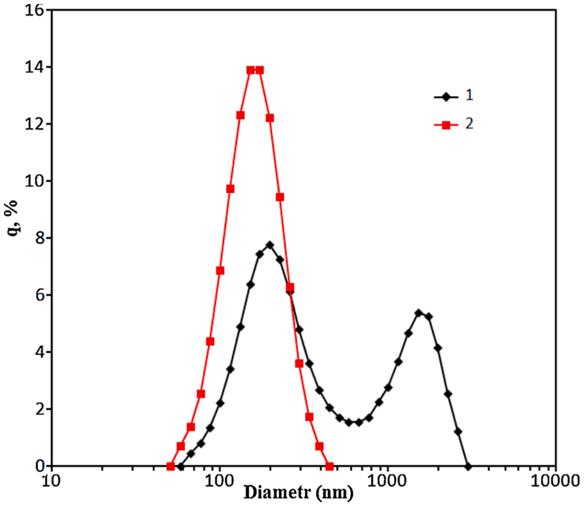


Fig. 12. The results of DLS measurements (25 °C) for 0.1 % wt.aqueous solutions of NPMAA(0.01 %)-C_{12}PEt complex (1) and C_{12}PEt (2).

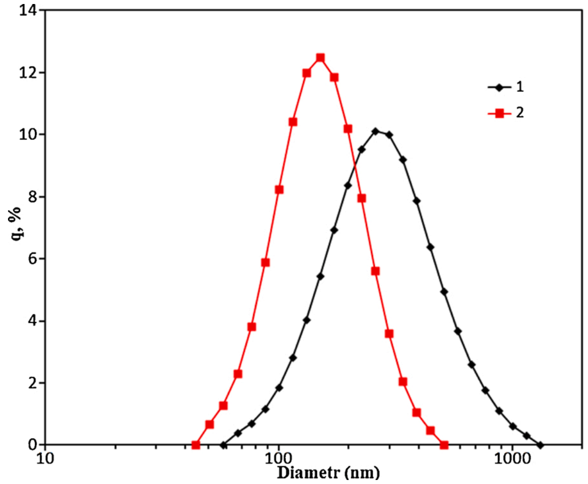


Fig. 13. The results of DLS measurements (25 °C) for 0.1 % wt.aqueous solutions of NPAA(0.01 %) -$C_{12}EP_2T$ complex (1) and $C_{12}EP_2T$ (2).

The results of these studies are the following. Among the polyelectrolyte-C_{12}PEt complexes, in the sea water, the most effective petrocollectors are NPMAA-C_{12}PEt and NPPMAA-C_{12}PEt complexes (for both of them $K_{max} = 30.4$, $\tau \sim 3$ days). In the sea water, the strongest petrodispersant is NPAA-C_{12}PEt complex ($K_D = 99.2$ %, $\tau > 3$ days). On the surface of fresh water, the most effective petrocollector is NPMAA-C_{12}PEt complex. On the distilled water surface, the best petrocollecting capability is exhibited by NPPMAA-C_{12}PEt complex ($K_{max} = 77.4$, $\tau > 3$ days).

From the polyelectrolyte-$C_{12}P_2$Et complexes, in the sea water, NPPMAA-$C_{12}P_2$Et is the most distinctive as petrocollector ($K_{max} = 125.0$, $\tau \sim 3$ days) and NPPAA-$C_{12}P_2$Et – as petrodispersant ($K_D = 97.8$ %, $\tau \sim 1$ day), On the surface of fresh and distilled waters, NPPMAA-$C_{12}P_2$Et complex is the best petrocollecting agent (K_{max} is respectively 30.4 and 23.9, $\tau \sim 3$ days).

Among the polyelectrolyte-$C_{12}EP_2D$ complexes, in the medium of the sea water, NPMAA-$C_{12}EP_2D$ complex is the most noticeable petrocollector ($K_{max} = 20.3$, $\tau \sim 3$ days). NPPAA-$C_{12}EP_2D$ complex excels the other complexes by petrodispersing capability ($K_D = 97.8$ %, $\tau \sim 1$ day). In the fresh water, for NPMAA-$C_{12}EP_2D$ complex $K_{max} = 11.5$ and $\tau \sim 1$ day results are observed. In the case of distilled water, the comparatively high collecting capacity is recorded for NPPMAA/$C_{12}EP_2D$ complex ($K_{max} = 19.4$, $\tau \sim 3$ days).

From the polyelectrolyte-$C_{12}EP_2T$ complexes, on the surface of the sea water, the highest effectiveness as petrocollector is shown by NPAA-$C_{12}EP_2T$ complex ($K_{max} = 30.4$, $\tau > 3$ days). In the same water, NPPAA-$C_{12}EP_2T$ and NPPMAA-$C_{12}EP_2T$ complexes are the strongest dispersants (for both of them, $K_D = 98.9$ %, τ is respectively 1 and 3 days). In fresh water, NPMAA-$C_{12}EP_2T$ may be marked ($K_{max} = 19.4$, $\tau \sim 3$ days) as a collector, in distilled water - NPPAA-$C_{12}EP_2T$ and NPMAA-$C_{12}EP_2T$ complexes (for both of them $K_{max} = 16.0$, τ is correspondingly 1 and 3 days) exert a petrocollecting action.

On the whole, the synthesized complexes are strong petrocollecting and petrodispersing agents. In the sea water, very strong petrocollecting properties are displayed by NPPMAA-$C_{12}P_2$Et complex ($K_{max} = 125$, $\tau >$ 3 days) and a very high petrodispersing capacity is revealed for NPAA-C_{12}PEt complex ($K_D = 99.2$ %, $\tau > 3$ days).

4. Conclusion

Polyelectrolyte-surfactant complexes were prepared by mixing aqueous solutions of modificates of PAA or PMAA obtained via their neutralization by NaOH at 50 % mol level and subsequent propoxylation with PO and surfactant (4 cationics with dodecyl chain) water solutions of respective concentration. Colloidal-chemical and specific electroconductivity parameters of polyelectrolyte-surfactant complexes and surfactant itself, viscosity parameters of the mentioned complexes and polyelectrolytes themselves were comparatively studied and it was established that these indices depend on the nature of both surfactant head-group and polyelectrolyte. These complexes exhibit high petrocollecting and petrodispersing effect in the sea water.

CRediT authorship contribution statement

Gulnara A. Ahmadova: Investigation, Resources, Writing - original draft. **Ravan A. Rahimov:** Writing - review & editing, Supervision, Methodology. **Aygul Z. Abilova:** Investigation, Resources, Writing - original draft. **Khuraman A. Huseynova:** Investigation, Data curation. **Elmar Imanov:** Writing - original draft. **Fedor I. Zubkov:** Validation, Formal analysis.

Declaration of Competing Interest

The authors declare with certain confidence that no financial interests, personal relationships or anything of similar nature that can have any kind of influence on the work presented in the current paper are known to them.

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Appendix A. Supplementary data

Supplementary material related to this article can be found, in the online version, at doi:https://doi.org/10.1016/j.colsurfa.2020.126075.

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