Molecular structure of mixed adsorption layers surfactant—polymer at a liquid—liquid interface

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Isotherms of the binding of dodecyl sulfate anions (DDS^-) and Na^+ counterions during their coadsorption with a nonionic polymer, proxanol (PR), at the interface of dodecane—water emulsions have been measured by conductometry and Na-selective potentiometry. The adsorption of DDS^- and PR is concurrent. The affinity constant of PR to the interface determined by the Langmuir model decreases as the concentration of PR increases, and the surface concentration of DDS^- tends to a nonzero limiting value at high concentrations of PR. The surface (ϕ_0) and electrokinetic (ζ) potentials at the interface have been determined at various polymer concentrations by the spin probe and electrophoresis methods. The average dielectric permeability and density of polymer segments in the adsorption layer have been determined by ESR. The lower boundary of the hydrodynamic thickness of the polymer adsorption layer at the interface has been estimated from the dependences of ϕ_0 and ζ on the ionic strength.

Key words: liquid—liquid interfaces, ESR, spin probe, polymer adsorption, sodium dodecyl sulfate, surface potential, electrokinetic potential.

Polymer adsorption plays a key role in the stabilization of colloidal particles and in the formation of organized structures in Langmuir—Blodgett (LB) films (see, *e.g.*, Ref. 1, 2). The most efficient stabilization of emulsions by polymers is achieved by the combination of steric and Coulomb repulsions of dispersed particles, which takes place during the coadsorption of polymer and low-molecular ionic surfactants. Similar two-component systems are also used for the formation of LB layers.[1] The thickness of the polymer adsorption layer, the character of the lateral distribution of components in the surface layer, and the surface and electrokinetic potentials of the particles are important structural parameters determining the interaction between the dispersed particles and the functional properties of LB layers.[2]

To determine the thicknesses of polymer adsorption layers and solid dispersed particles, various physical methods are used presently: dynamic light scattering, small-angle neutron scattering, sedimentation, and measurements of rheological and electrokinetic parameters (see, *e.g.*, Refs. 2—7). However, methods based on measurements of average sizes of dispersed particles are inappropriate for emulsions characterized by considerable polydispersity.

In this work, the coadsorption of an anionic surfactant (sodium dodecyl sulfate) and the nonionic polymer proxanol (block-copolymer of poly(ethylene glycol) and poly(propylene glycol)) at interfaces in dodecane—water emulsions was studied. Proxanol is an efficient stabilizing agent, in particular, for emulsions of perfluoranes used for the preparation of blood substitutes.[8] The spin probe method is used here for the first time to determine the surface potential of emulsions and the lateral distribution of the adsorbed polymer. To determine the thickness of the polymer adsorption layer, the electrophoretic mobility of the emulsion particles was measured. Conductometry and potentiometry was used for studying the adsorption isotherms of dodecyl sulfate (DDS^-) anions and Na^+ counterions.

Experimental

Sodium dodecyl sulfate (DDSNa) (Sigma), dodecane (reagent grade) distilled *in vacuo*, and proxanol (PR) (trade mark 268, molecular weight 12000) were used.

Emulsions were prepared by ultrasonic dispergation on a UZDN-2 instrument according to the procedure described in Refs. 9 and 10 at standard concentrations of the components (DDSNa in a range from 1 to 10 mmol L^{-1}, dodecane, 4.5 vol. %, and water). Then the emulsions were diluted to the final concentrations with aqueous solutions of DDSNa, NaCl, and PR. For electrophoretic measurements, the emulsions were prepared by the injection of the organic phase into an aqueous solution containing NaCl and DDSNa according to the procedure described in Ref. 11. Aqueous solutions were prepared using bidistilled water with a specific conductivity of $1.1 \cdot 10^{-6}$ Ohm^{-1} cm^{-1}.

A surface-active radical cation, *N*-heptyl-*N,N*-dimethyl-*N*-(2,2,6,6-tetramethylpiperidyl-4-oxyl)ammonium bromide (**1**) (Fig. 1), was used for determining the surface potentials of the emulsions, and the 2,2,6,6-tetramethylpiperidyl-1-oxyl-

Translated from *Izvestiya Akademii Nauk. Seriya Khimicheskaya*, No. 7, pp. 1653—1661, July, 1996.

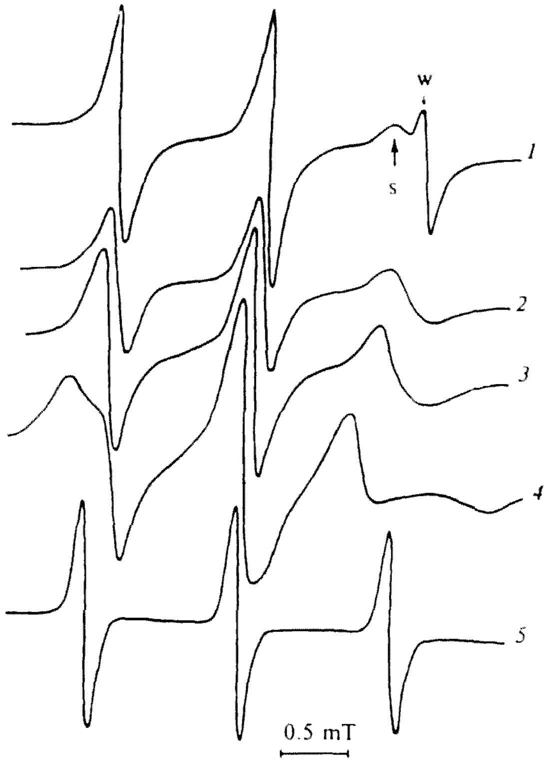
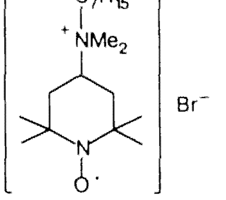


Fig. 1. ESR spectrum of probe **1** in dodecane—DDSNa—water emulsions with various concentrations of proxanol (C_{PR}). C_{PR}, mmol L^{-1}: 0.16 (*1*, *5*), 0.08 (*3*); and 0 (*4*), c_{DDSNa}, mmol L^{-1}: 0.5 (*1*—*4*), and 0 (*5*). Curve *2* was obtained by subtracting the aqueous component from curve *1*. s and w are HFS components with $m = -1$ for probes localized at the interface and in water, respectively. Spectrum of probe **1** in water is identical to curve *5*.

4-phosphonic acid (**2**), radical (Fig. 2), existing as a monocharged anion at neutral pH, was used for determining the local dielectric permeability in the adsorption layer.



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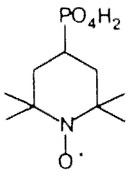

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Probe **1** was introduced into the prepared emulsions as alcohol solutions in which the final ethanol concentration did not exceed 0.5 %. Probe **2** was added to aqueous solutions before dispergation.

ESR spectra were recorded on a Bruker ER-200 D instrument at 20 °C. For subsequent mathematical processing, the spectra were stored in the memory of an Aspect-2000 computer interfaced to an ESR-spectrometer.

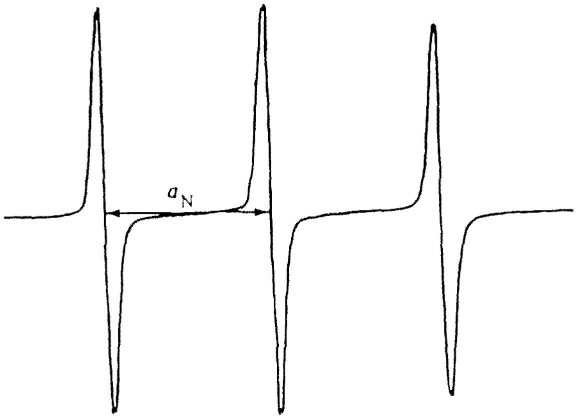

Fig. 2. ESR spectrum of radical **2** in the polymer adsorption layer of dodecane—water emulsions (20 °C).

Electrophoretic and conductometric measurements were carried out on previously described installations.[9,11] The concentration of Na^+ in the emulsion was measured in a thermocontrolled cell at 25±0.1 °C on an I-135MI ionometer and by an ESL-51-07 Na^+-selective glass electrode; the error for the measurement of the electrode potential using a nonlinear smoothing procedure was ±0.3 mV. Since PR could affect indications of the measuring electrode, calibrating curves were obtained in solutions containing DDSNa and PR. The steepnesses of these curves were lower than the theoretical steepness and varied as the concentration of PR increased, which is likely caused by the interaction of PR with the electrode glass and the formation of complexes of PR with DDSNa.[12] The adsorption of polymer and DDSNa on the dodecane—water surface was studied at surfactant concentrations considerably lower than the critical constant of micelle formation ([DDSNa] < 3 mmol L^{-1}) and at [PR] < 1 % when the effect of complex formation in solution can be neglected.[12]

Results and Discussion

The dependences of the concentration of free Na^+ ions (c_{Na}) and specific conductivity (λ) in dodecane—water emulsions on the concentration of DDSNa (c) in the absence of PR are presented in Fig. 3. The $\lambda(c)$ dependences are similar to those obtained previously[9] for another volume fraction of the organic phase; the break points on both curves in Fig. 3 at the DDSNa concentration of ~12.8 mmol L^{-1} correspond to the formation of micelles. Since the affinity of DDS^- anions for the dodecane—water boundary is substantially higher than that for micelles,[11] micelles are formed after the emulsion surface is completely covered. Then the DDSNa concentration corresponding to the complete coverage of the emulsion surface can be determined as the difference between the value equal to 12.8 mmol L^{-1} and the value of CMC in the absence of emulsions (8 mmol L^{-1})[9]: $c_s^* = 4.8$ mmol L^{-1}.

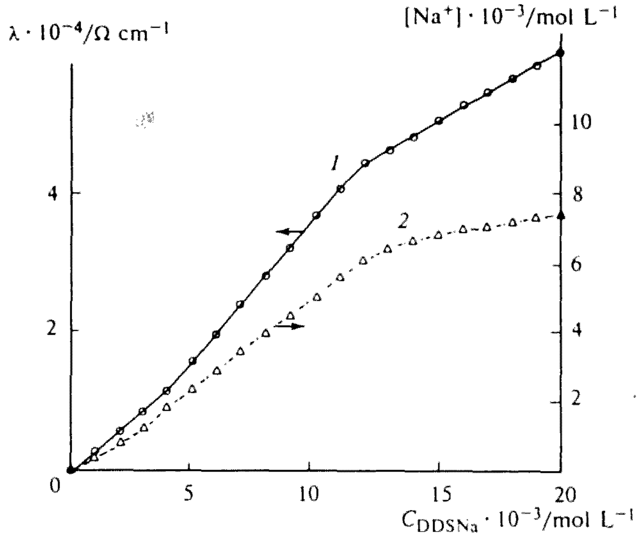

Fig. 3. Dependences of specific conductivity (*1*) and concentration of free Na^+ ions (*2*) on the concentration of DDSNa in dodecane—water emulsions. Volume fraction of the organic phase is 2.25 %, 20 °C.

The measured specific conductivity of a solution of DDSNa (below CMC) is determined by the equation

$$\lambda = c_{Na^+}\mu_{Na^+} + c_{DDS^-}\mu_{DDS^-}, \qquad (1)$$

where μ_{Na^+} and μ_{DDS^-} are the mobilities of the ions. The μ_{DDS^-} value can be determined from Eq. (1) using the c_{Na^+} (and c_{DDS^-}) values from the potentiometric measurements (Fig. 3) and μ_{Na^+} from the published data:[13] μ_{DDS^-} = 20 Ohm^{-1} cm^2 mol^{-1}.

The dependences of λ and [Na^+] in dodecane emulsions on the concentration of PR in the presence of 1 mmol L^{-1} DDSNa are presented in Fig. 4. The main contribution to the λ value is caused by free Na^+ and DDS^- ions in the solution and in the diffusion regions of the double electric layer. In fact, the conductivity of the emulsion under conditions when almost all DDSNa is adsorbed on the interface (*i.e.*, in the absence of PR, at a high fraction of the organic phase (5 %) and at a DDSNa concentration of 1 mmol L^{-1}) coincides with the calculated value of λ with an accuracy up to 3 % due to the free Na^+ ions. Therefore, the concentrations of DDS^- in the solution at various concentrations of PR were calculated by Eq. (1) from the dependences presented in Fig. 4 and the values of μ_{Na^+} and μ_{DDS^-}. The obtained values (they are not shown in Fig. 4) as well as λ and c_{Na^+} increase as the concentration of PR increases, which is evidence for the displacement of DDS^- and Na^+ ions from the surface by PR molecules, *i.e.*, the adsorptions of DDS^- and PR compete with one another.

A simple Langmuir model was used for the quantitative analysis of the competing adsorption of DDS^- and PR. This model has been successfully applied previously to low-molecular adsorbates,[14] in particular, DDS^- anions at the oil—water interface.[11] More detailed statistical theories have been developed to describe polymer adsorption on solids.[14,15]

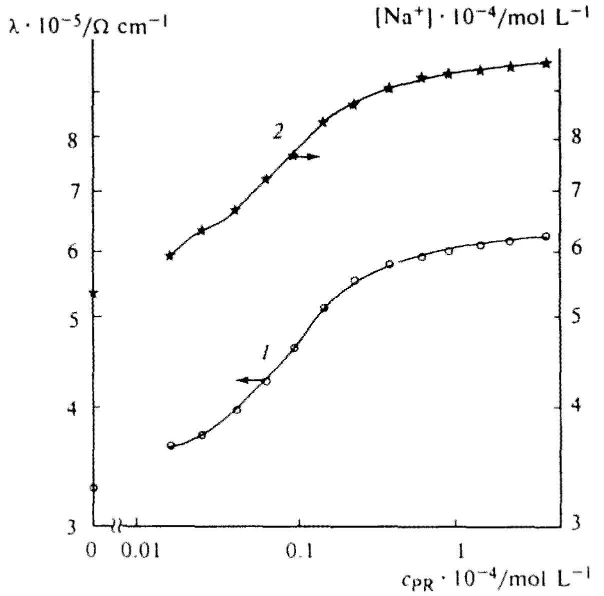

Fig. 4. Dependences of specific conductivity (*1*) and concentration of free Na^+ ions (*2*) on the concentration of proxanol in dodecane—water emulsions. Volume fraction of the organic phase is 1.25 %, concentration of DDSNa is 1 mmol L^{-1}, 20 °C.

For the competitive adsorption of two components, the equation for the degree of coverage of the surface with DDS^- anions (ϑ_A), as can be easily shown, takes the form

$$\vartheta_A = \frac{K_A c_A}{1 + K_A c_A + K_{PR} c_{PR}}, \qquad (2)$$

where K_A and K_{PR} are the binding constants for DDS^- and PR with the surface and c_A and c_{PR} are the concentrations of these compounds in solution. The K_A value depends on the surface potential:[11]

$$K_A = K_A^\circ \exp(-F\phi_o/RT), \qquad (3)$$

where F is the Faraday's number and R is the universal gas constant. The values of ϕ_o were estimated in terms of the Gouy—Chapman theory for each point of the binding isotherm from the values of the surface concentrations of DDS^- and the fraction of bound Na^+ counterions relative to the bound DDS^- ions (β) using the equations:

$$\vartheta_A = \frac{c_s}{c_s^*}, \quad \sigma_A = \frac{e\vartheta_A}{s_A}, \qquad (4)$$

$$\sigma = \sigma_A(1 - \beta), \qquad (5)$$

$$\sigma = -2(2\varepsilon_o\varepsilon c_i RT)^{1/2}\mathrm{sh}(F\phi_o/2RT), \qquad (6)$$

where c_s is the volume concentration of adsorbed DDS^- ions relative to the solution volume, c_s^* is the value of c_s

for the limiting coverage of the surface, σ_A is the surface charge density due to the adsorbed DDS^- anions in the absence of bound Na^+ counterions, σ is the total charge density, s_A is the surface per DDS^- ion, c_i is the concentration of the uni-uni-valent electrolyte (NaCl), ε is the dielectric permeability of a medium, ε_o is the dielectric permeability of vacuum in the International System of Units, and e is the charge on an electron.

The values of $K_A{}^\circ$ at various ionic strengths were taken from Ref. 11, and the values of s_A for the water—air interface were taken from Ref. 16.

The c_i and ε values in the surface layer at high concentrations of the adsorbed polymer should differ, in general case, from their values in an aqueous medium.[17,18] The estimation of local ε values in the surface layer performed by the use of the spin probe (see below) showed that the difference between ε and ε_{H_2O} does not exceed 10 to 15 % at the concentrations of PR used in the solution. We also assume that the C_i values are equal to their values in the aqueous phase; $c_s{}^* = 4.8$ mmol L^{-1}.

The values of K_{PR} at various concentrations of proxanol were calculated from Eq. (2) at relatively high concentrations of PR ($c_{PR}{}^\circ > 4\cdot10^{-5}$ mol L^{-1}, $c_{PR} \sim c_{PR}{}^\circ$, where $c_{PR}{}^\circ$ is the initial concentration and c_{PR} is the current concentration of PR) (Fig. 5). As can be seen from Fig. 5, the K_{PR} value is not constant. It decreases by almost an order of magnitude as c_{PR} increases from $2\cdot10^{-5}$ to $3\cdot10^{-4}$ mol L^{-1}. This result testifies that the Langmuir model does not adequately describe proxanol adsorption.

Another specific feature of the coadsorption isotherms of DDSNa and PR is the following. At concentrations of DDS^- ions higher than $c_s{}^*$, their displacement from the surface by polymer molecules is not complete even at high concentrations of PR, and the surface concentration of DDS^- tends to a nonzero limiting value. This is distinctly seen from the dependences of the surface and electrokinetic potentials on the concentration of PR (Table 1 and Fig. 6). The characters of these dependences also contradict the Langmuir model (see Eq. (2)).

Table 1. Values of the surface charge density (σ), surface potential (ϕ_o), ζ potential, and distance to the slipping plane d_ε (thickness of the polymer adsorption layer) in the adsorption layer of dodecane—water emulsions containing DDSNa and proxanol

$c_{PR}\cdot10^4$ /mol L^{-1}	$\sigma\cdot10^2$ /C m^{-2}	Ionic strength	ϕ_o /mV	ζ /mV	d_ε/Å
2.1	2.23	3	84.2	25.9	55.6
		10	69.0	16.0	40.5
		30	49.9	8.7	29.4
		50	40.4	5.7	26.0
4.2	2.17	3	86.4	25.2	58.0
		10	70.4	15.2	42.4
		30	49.4	8.8	29.0
		50	39.6	5.7	25.7
8.4	2.13	3	78.9	26.0	54.0
		10	72.0	15.4	42.6
		30	48.2	9.4	27.5
		50	41.8	5.9	25.9

The use of charged surface-active probes for the determination of ϕ_o is based on the fact that the parti-

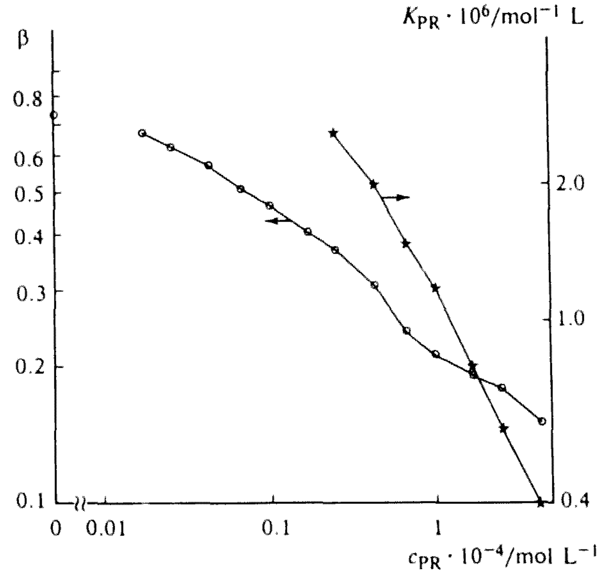

Fig. 5. Dependences of the binding constant of proxanol with the dodecane—water surface (K_P) and fraction of bound counterions (β) on the concentration of proxanol (c_{PR}). Volume fraction of dodecane is 1.25 %, concentration of DDSNa is 1 mmol L^{-1}.

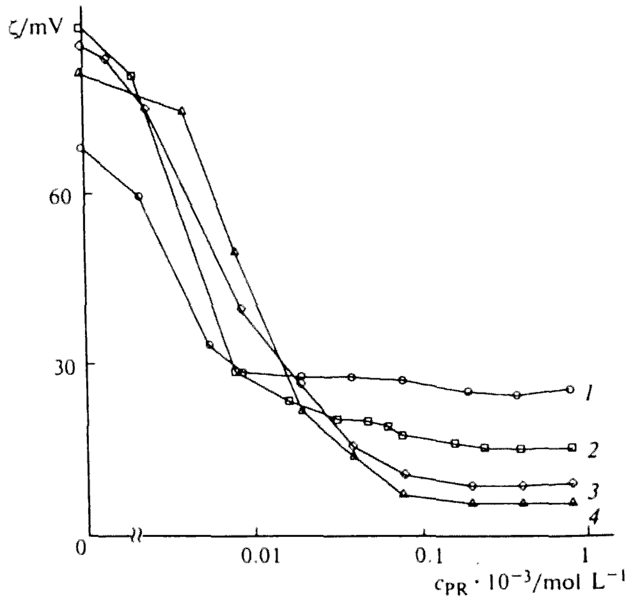

Fig. 6. Dependences of the ζ potential on the concentration of proxanol in the aqueous phase at various ionic strengths of solution, mol L^{-1}: 0.003 (*1*), 0.01 (*2*), 0.03 (*3*), and 0.05 (*4*). Concentration of DDSNa is 3 mmol L^{-1}.

tion coefficient of the probe between the aqueous phase and the surface is determined by the equation

$$K = K_h \exp(-F\phi_o/kT), \qquad (7)$$

where K_h characterizes binding due to nonelectrostatic interactions. The K value can be determined from the ratio of the intensities of the ESR signals of the probes in the aqueous phase and on the surface. This ratio depends on the ratio of the volumes of the aqueous phase and the near-surface layer, which can be included in the K_h value. The K_h value is usually determined by measurements at high ionic strengths (when $\phi_o \to 0$) or on uncharged surfaces with similar chemical compositions.[19,20]

This method has been used previously for the determination of ϕ_o in liposomes and cells.[19,20] It should be modified when applied to emulsions, because the ionic surfactant and polymer are in dynamic equilibrium between the aqueous phase and the interface; in addition, measurements at high ionic strengths are impossible for emulsions (unlike liposomes and cells) due to their irreversible coagulation. The approach used in this work for the determination of ϕ_o in emulsions is presented below.

The ESR spectra of probe **1** at various concentrations of PR are given in Fig. 1. The ratio of the integral intensities of the signals from the probe bound to the surface (s) and located in water (w) was determined by a computer subtracting of the reference signal of the aqueous solution of probe **1** with different statistical weights from the total spectrum until the complete disappearance of the "water" signal in it. The integral intensity of the differential signal was calculated by double integration.

It can be seen from Fig. 1 (spectrum *2*) that the "surface" ESR spectrum for emulsions containing DDSNa and PR differs substantially from the spectrum of the probe in emulsions stabilized only by DDSNa (spectrum *4*) or only by PR (spectrum *5*). In the latter case, the spectrum is identical to that of probe **1** in water, *i.e.*, at the value of the interface area existing in the studied samples, and in the absence of a negative charge, probe **1** almost does not adsorb on the interface. When the concentration of PR increases, the "surface" signal monotonically changes its form from that typical of the rotation in an anisotropic "liquid-crystalline" medium (spectrum *4*)[9] to the form corresponding to fast isotropic (or weakly anisotropic) rotation (see intermediate spectrum *3* at the PR concentration of 0.08 mmol L^{-1}). These spectral changes show that the probe environment on the surface consists not only of DDSNa (or PR) molecules, but is likely an almost homogeneous mixture of these components.

The "water" signal was almost absent in the ESR spectra of the probe in the absence of PR and at low ionic strengths (c_i < 50 mmol L^{-1}). Fast coagulation occurred at high concentrations of the electrolyte in the absence of PR. Therefore, the ionic strength dependences of the partition coefficient necessary for the determination of ϕ_o were obtained only in the presence of adsorbed PR. These dependences for the DDSNa concentration of 0.5 mmol L^{-1}, which is considerably lower than the concentration of the complete coverage of the surface (4.8 mmol L^{-1} at the volume fraction of the organic phase of 2.5 %), are presented in Fig. 7.

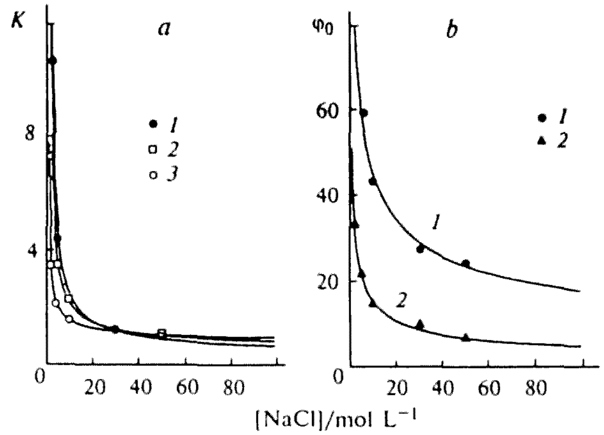

Fig. 7. *a*. Dependences of the distribution coefficient of probe **1** between the aqueous phase and the interface at various concentrations of proxanol, mmol L^{-1}: 0.08 (*1*), 0.42 (*2*), and 0.83 (*3*). Concentration of DDSNa is 0.5 mmol L^{-1}, concentration of the organic phase is 2.5 vol. %, 20 °C. *b*. Modeling dependences of ln$K$ on the ionic strength in terms of the Gouy—Chapman theory by Eq. (8). Values of b obtained by modeling were added to ln$K$ values, so that ordinates in the figure directly correspond to ϕ_o values in mV. Points are experimental values for proxanol: 0.08 (*1*) and 0.83 mmol L^{-1} (*2*); solid lines are results of modeling using the nonlinear least-squares method.

For the quantitative description of these dependences, we express the potential ϕ_o in Eq. (6) by the partition coefficient of the probe K (Eq. (7)). Then the relationship between ϕ_o and the concentration of the electrolyte (c_i) takes the following form:

$$y = (2kT/e)\ln(ax^{-1/2} + (a^2/x + 1)^{1/2}) - b, \qquad (8)$$

where $y = (kT/e)\ln K$, $b = -(kT/e)\ln K_h$, $a = \sigma(8\varepsilon\varepsilon_o kT)^{-1/2}$, $x = c_i$, $\phi_o(\mathrm{mV}) = y + b$.

The experimental data in Fig. 7 fit to the dependences calculated from Eq. (8) by varying the parameters a and K_h using the nonlinear least-squares method (PSI-PLOT program). The examples of this description are presented in Fig. 7, *a*, *b*. It can be seen that the appropriate choice makes it possible to achieve good agreement between the calculated and experimental curves. This approach made it possible to simultaneously determine the values of ϕ_o (Fig. 7, *b*) and the values of the surface charge density (σ) from the parameter a.

As can be seen from Eq. (8), the dielectric permeability (ε) in the adsorption layer must be known in order to determine σ. To estimate the ε values, we applied the spin probe method, using the fact that the value of the isotropic hyperfine splitting on the nitrogen nucleus (a_N) in the ESR spectrum of the probe is sensitive to the polarity of its surroundings. It should be mentioned first of all that the value of a_N for probe **1** bound to the surface (15.8 G) was independent of the PR concentration in the range from 0 to 1.8 mmol L^{-1} within the experimental error (0.1 G). Radical **2** (Fig. 2) was used along with probe **1**. Radical **2** should not sorb on the interface due to its negative charge at pH > 7 and the absence of hydrophobic residues. In order to measure the a_N values directly in the adsorption layer, an aqueous emulsion containing 5 % dodecane, 5 mmol L^{-1} DDSNa, and 2 mmol L^{-1} PR, and a solution of probe **2** (10^{-4} mol L^{-1}) were centrifuged for 30 min at g ~3000. The cream-like mass that formed on the solution surface consisted of the emulsion drops surrounded by polymer shells, because no separation into aqueous and oil phases was observed, and it reversibly transformed to the initial emulsion upon dilution with water. The mass was carefully transported from the surface of the tube to an ESR-cell. The value of a_N for probe **2** in this phase turned out to be equal to 17.05±0.02 G; in water, a_N = 17.11 G; and in dioxane, a_N = 15.95 G.

To determine local ε values in the adsorption layer, the calibration dependences of a_N were measured in aqueous solutions of dioxane, whose chemical structure models oxyethylene fragments of PR. The value a_N = 17.05 G was obtained for an ~10 % solution of dioxane in water. The dielectric permeability ε ~72,[21] which is 10 % lower than that of pure water, corresponds to this mixture.

The calibrating dependences of a_N on the concentration of dioxane make it possible to simultaneously obtain a rough estimation of the weight fraction of oxyethylene fragments in the adsorption layer, which is ~0.1. Another method for estimating the fraction of oxyethylene segments is the measurement of a_N values in solutions of polyoxyethylene, in which the ratio of the number of free OH groups to the number of oxyethylene groups is approximately the same as in polyoxyethylene fragments of proxanol 268. The fraction of oxyethylene fragments estimated in this way is 0.05 to 0.1.

The values of ϕ_0 and σ at various concentrations of PR and at an ionic strength of 10 mmol L^{-1} are presented in Table 2. It can be seen that the σ values decrease as the concentration of PR increases, which is likely caused by the displacement of DDS^- by PR molecules according to the adsorption isotherms presented above. In addition, the absolute values of σ are considerably lower than the maximum values corresponding to coverage of the surface only with DDSNa molecules ($\sigma_{max} \simeq 0.4$ C m^{-2} for the surface area per DDSNa molecule $\simeq 45$ Å^2).[16] The method for determining ϕ_0 by charged spin probes is sensitive to the local surface charge density and not to that averaged over the whole surface. Therefore, if DDS^- anions form separate microphases on the surface, the σ value would be close to σ_{max} and would weakly depend on the concentration of PR. Thus, it follows from the data of Table 2 that DDS^- and PR are distributed over the surface rather uniformly, which agrees with the changes in the ESR line shape of probe **1** as the concentration of PR increases (see Fig. 1).

Table 2. Values of the surface charge density (σ) and surface potential (ϕ_0) during concurrent adsorption of DDSNa and proxanol

$c_{PR} \cdot 10^4$ /mol L^{-1}	$\sigma \cdot 10^3$/C m^{-2}	ϕ_0/mV (10 mmol L^{-1} NaCl)
0.42	12.5	51.5
0.83	12.3	44.7
1.67	9.8	41.1
4.2	7.4	30.0
8.3	3.7	14.5

In order to estimate the thickness of the adsorption layer formed by the adsorbed polymer, we carried out simultaneous measurements of the surface and electrokinetic potentials at equal ratios of DDSNa and PR in solution and at their absolute concentrations, which are much higher than those corresponding to the complete coverage of the surface (in the absence of the second component). The latter condition always is fulfilled for electrophoresis, and in ESR experiments it occurs at very low volume fractions of an organic phase (0.5 %) and high concentrations of DDSNa ([DDSNa] > 4 mmol L^{-1}). At these ratios of the concentrations of the adsorbates and the total surface area of emulsions, the surface concentrations of DDS^- and PR should be equal in both experiments.

Electrokinetic potentials (ζ) were calculated from the measured electrophoretic mobilities (u) by the Smoluchowki formula

$$u = \frac{\varepsilon\zeta}{6\pi\eta}, \qquad (9)$$

where η is the viscosity of the solution. The conditions in which Eq. (9) can be applied to the studied emulsions (in the absence of PR) were discussed in Ref. 11. The dependences of the ζ potential on the concentration of PR at various ionic strengths are presented in Fig. 6. When the ζ values were calculated, a value of ε different from that in water (ε = 72) was used only for high concentrations of PR (>0.1 mmol L^{-1}). The concentration dependences of the ζ potential (unlike adsorption isotherms) are caused by an increase in the distance from the slipping plane to the interface due to the formation of the polymer adsorption layer as well as by the displacement of DDS^- ions.

It can be seen from Fig. 7 that at [PR] > 0.1 mmol L^{-1} the ζ values depend rather weakly on [PR], which is not described by the Langmuir theory (Eq. (2)). The partition coefficient of the probe also depends weakly on the concentration of PR in the range of [PR] > 0.2 mmol L^{-1} (see below). The incomplete displacement of DDS$^-$ anions even at high concentrations is likely caused by the fact that DDS$^-$ ions and PR molecules interact on the surface to form complexes, due to which DDS$^-$ ions are retained on the surface. The existence of this interaction in solution at high concentrations of both components is evidenced by the aforementioned changes in λ of solutions of DDSNa in the presence of PR and by the published data.[12]

We derived equations of the adsorption isotherms of DDS$^-$ and PR that take into account the formation of complexes between DDS$^-$ and PR on the surface (they are not presented here because of their awkward character) and explain the incomplete displacement of DDS$^-$ ions at high concentrations of PR. It also follows from these equations that at high concentrations of PR the extent of coverage of the surface with DDS$^-$ ions is independent of K_A and, hence, of the ionic strength and potential ϕ_o. This gives grounds to use simple Eq. (6), in which the surface charge density is independent of the ionic strength and ϕ_o.

The dependences of the partition coefficients of the probe on the ionic strength at DDSNa concentration of 4 mmol L^{-1} and at various concentrations of PR (Fig. 8, *a*) are qualitatively similar to the curves in Fig. 7. Modelling these dependences (examples are presented in Fig. 8, *b*) show good agreement with the Gouy—Chapman theory as for low concentrations of DDS. The values of ϕ_o and σ (see Table 2), obtained as well as experimental values of partition coefficients *K*, are almost independent of the concentration of PR at [PR] > 0.2 mmol L^{-1} (0.25 %).

Knowing ϕ_o and ζ measured at equal surface concentrations of DDS and PR, it is possible to determine the distance from the interface surface, where the negative charges of the adsorbed DDS$^-$ ions are localized, to the slipping plane by the known Gouy—Chapman formula for uni-uni-valent electrolytes:[22]

$$\mathrm{th}(e\zeta/4kT) = \mathrm{th}(e\phi_o/4kT)\exp(-\varkappa d_e), \qquad (10)$$

where $\varkappa^{-1}$ is the Debye length and d_e is the distance from the adsorbed DDS$^-$ anions to the effective slipping plane.

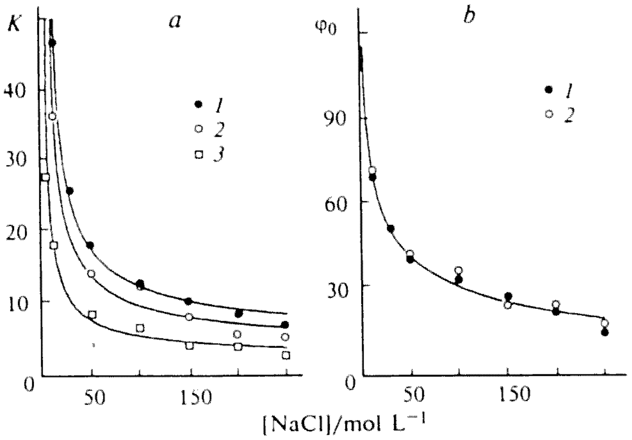

Fig. 8. *a*. Dependences of distribution coefficients of spin probe **1** on the ionic strength at the concentration of DDSNa of 4 mmol L^{-1} and fraction of the organic phase of 0.5 %. Concentration of proxanol, mmol L^{-1}: 0.08 (*1*), 0.21 (*2*), and 1.05 (*3*). *b*. Examples of modeling the dependences in Fig. 8, *a* in terms of the Gouy—Chapman theory by Eq. (8); see captions for Fig. 7.

When there is a polymer adsorption layer partially permeable to ions and water, the notion of the slipping plane has a conventional character, and the value of d_e (the so-called electrokinetic thickness of the layer) depends on the radial distribution of polymer segments and on ionic strength.[23,24] It also should be kept in mind that polymer adsorption can change the static parameters of the double electric layer (surface charge, dielectric permeability).[18,25]

In this work, potentials ϕ_o and ζ were measured at equal surface charges; therefore, the possible effect of the adsorption of PR on σ was insignificant. The value of ε, as follows from the experiments described above, is close to ε_{H_2O}. It is difficult to experimentally measure the possible change in the concentration of the electrolyte in the adsorption layer; therefore, this effect was not taken into account. However, it should be mentioned that the effects of dielectric exclusion[26,27] are probably insignificant in this case due to the insignificant difference between ε and ε_{H_2O}. The values of potentials ϕ_o and ζ and the values of d_e determined from Eq. (10) for various ionic strengths and concentrations of PR are presented in Table 1. The values of d_e increase as the ionic strength decreases in accordance with the predictions of the theory;[23,24] in addition, they are almost independent of the concentration of PR in the concentration range from $8 \cdot 10^{-5}$ to $8 \cdot 10^{-4}$ mol L^{-1}.

As far as we know, there are no published data on direct measurements of the electric surface potential in emulsions (the potential measured by the vibrating electrode method contains a dipole component, which is difficult to exclude unambiguously in the determination of ϕ_o,[28,29] while the ζ potential is measured in the slipping plane, which does not coincide with the plane of the location of the potential-determining ions).

The present measurements of ϕ_o, surface charge density, and the ζ potential and isotherms of adsorption of the surfactant and counterions make it possible to draw several conclusions about the structural organization of the surfactant molecules and the nonionogenic polymer proxanol adsorbed at the interface. First, it is shown that the adsorption of DDS$^-$ and proxanol is competitive. The data on the adsorption of DDS$^-$ ions in the presence of proxanol were used for studying the affinity of PR molecules for the interface in terms of the generalized Langmuir model, in which the constant of the binding of DDS$^-$ ions to the surface depends on the value of the surface potential. It turned out that in terms of this model the value of the affinity of PR molecules for the surface (binding constant K_{PR}) decreases as the concentration of PR increases. This result can be explained by the change in the conformation of the adsorbed polymer: at low degrees of coverage of the surface not only polyoxypropylene, but also polyoxyethylene fragments of PR are probably localized at the interface; at high degrees of coverage, polyoxyethylene fragments are probably extruded to the aqueous phase.

Second, it follows from the dependences of ϕ_0 and of the ESR line shapes of probe **1** bound to the surface on the concentration of PR (Fig. 1 and Table 2) that DDSNa and PR molecules do not form separate microphases on the surface, but are rather uniformly distributed over the surface. This conclusion agrees with the aforementioned explanation of the incomplete displacement of DDS$^-$ ions by PR molecules due to the formation of complexes on the surface.

As is known, binding of counterions plays a substantial role in the structure of micelles, determining, in particular, the degree of aggregation and the transition from spherical to cylindrical micelles.[30] There are no direct studies of interactions with counterions for oil—water emulsions. Indirect data have been obtained by electrophoretic measurements.[11,29] The results of this work (Fig. 3) show that the fraction of bound counterions (β) in dodecane—water emulsions at complete coverage of the surface with DDSNa molecules is higher than that in DDSNa micelles (0.7 and 0.6, respectively), which agrees with denser packing of DDSNa molecules in emulsions. The β value decreases to 0.15—0.17 as the concentration of PR on the surface increases. This means that the amount of bound counterions at complete coverage of the surface is mainly determined by the electrostatic potential on the surface rather than by the interaction of individual ions.

Previously, good agreement with the Gouy—Chapman—Stern theory was obtained in the study of the electrostatic properties of phospholipid liposomes and cells.[19,20,31] The absolute values of ϕ_0 determined in these works did not exceed 80 mV. The results of our work show that the physical approximations accepted in this theory, *i.e.* neglecting the discrete character of the charge distribution over the surface and the dependence of the dielectric permeability on the electric field at the interface, are also valid for oil—water emulsions.

The thickness of the polymer adsorption layer at the interface is one of the main parameters directly characterizing the efficiency of the stabilizing effect of polymer;[2] it is also important to know this parameter for constructing LB layers.[1] The thicknesses of adsorption layers are mainly determined by dynamic light scattering, small-angle neutron scattering, and measurements of rheological and ellipsometric parameters.[2—7] However, dynamic scattering and other hydrodynamic methods measuring average sizes of particles are inappropriate or should result in high errors in the case of polydispersed emulsions.

The approach used in this work is based on the introduction of charged surfactant molecules at the interface and the simultaneous measurements of the surface and electrokinetic potentials. Its advantage is its independence from the degree of polydispersity peculiar to the emulsion. However, the measured so-called electrokinetic thickness d_e differs from the hydrodynamic thickness d_h due to the permeability of the polymer adsorption layer to water and ions. According to the theory,[23,24] d_e increases, tending to d_h as the ionic strength decreases.

The data of Table 1 show that d_e increases in accordance with the theory as the ionic strength decreases from 50 to 3 mmol L^{-1}; however, it does not reach a plateau in the studied range of ionic strengths. Therefore, only a lower estimation of the hydrodynamic thickness (d_h) can be given, which is ~57 Å. Nevertheless, it is of interest to compare this value with the geometric sizes of the free polymer in solution.

Proxanol 268 is an "amphipatic" block-copolymer of the A—B—A type containing an anchor (adsorbing on the surface) site B, polyoxypropylene (POP) with molecular weight 2600, and two polyhydroxyethylene (POE) fragments A comprising 80 % of the molecular weight of the whole polymer. According to modern views,[2] the role of POE fragments is to provide steric stabilization for the dispersed particles.

Since d_e is independent of the concentration of PR when it changes by an order of magnitude, it can be assumed that PR is probably adsorbed as a monolayer (and not as a polymolecular layer). It is reasonable to compare d_e with the geometric sizes of POE fragments exposed to the aqueous phase. If these fragments are identical with the average molecular weight of 4700, which corresponds to a degree of polymerization of ~107 and the total number of C—C and C—O bonds in the chain is equal to 320. It has been shown theoretically and experimentally[32] for POE that the mean square end-to-end distance is equal to double the end-to-end distance in the model of a free-linked Gaussian chain: $(r_0^2)^{1/2} = 2n^{1/2}l$ (n is the number of bonds and l is the average bond length), $(r_0^2)^{1/2} \simeq 54$ Å. Therefore, double the value of the inertia radius $2R_g = 2(r_0^2/6)^{1/2} \sim 43$ Å.[32]

As can be seen from Table 1, the values of d_e (55—57 Å) at the minimum ionic strength of 3 mmol L^{-1} that can be achieved in our experiments, are close to the value of $(r_0^2)^{1/2}$ and higher than $2R_g$ for POE fragments of proxanol. Since these d_e values are only the lower estimation of the hydrodynamic thickness (d_h), it can be assumed that POE chains in proxanol at the dodecane—water interface probably exist in the state of a stretched statistical coil.

As far as we know, there are no published data on the thicknesses of adsorption layers of nonionogenic polymers at liquid—liquid interfaces; therefore, a comparison with the results obtained for solid surfaces is of interest. The hydrodynamic thicknesses for POE—POP—POE block-copolymers, which are similar to proxanol and adsorb on quartz particles and polystyrene latexes, have been studied by dynamic light scattering.[5] In the case of quartz, POP and POE chains adsorbed to form thin adsorption layers with constant thicknesses (~20 Å). In the case of latexes, only POP chains adsorbed, and the thickness of the layer increased to 100 Å as the molecular weight of POE increased. Similar results for latexes have been recently obtained in Ref. 7. In both works, the values of d_h were greater than the sizes of statistical coils ($2R_g$) for POE chains, which agrees with the results of this work.

This work was financially supported by the Russian Foundation for Basic Research (Project No. 93-03-18470) and the International Science Foundation (Grant NEH 000).

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Received May 3, 1995;
in revised form February 9, 1996