Physical Chemistry

Hydrodynamic thickness and deformational properties of adsorption layers of poly(ethyleneoxides)

*I. P. Sergeeva**, *V. D. Sobolev, and N. V. Churaev*

Institute of Physical Chemistry, Russian Academy of Sciences,
31 Leninsky prosp., 117915 Moscow, Russian Federation.
Fax: +7 (095) 952 7514

From the measurements of surface potentials of quartz capillaries before and after adsorption of poly(ethylene oxides) (PEO) of various molecular mass, an assessment of the equilibrium hydrodynamic thickness δ of the adsorption layers has been obtained. The results have been compared with those of independent measurements of δ. The flow of the polymer solution under increasing pressure drops at the ends of a capillary, which causes the corresponding shear stress (τ) on the surface of adsorbed PEO layers, results in the deformation of the latter, which manifests itself in decreasing δ. The δ values decrease by several times when the shear stress τ rises to 2×10^2 N m^{-2}. Such values of τ have been obtained using thin capillaries (r = 5÷6 mm) and by application of the capillary electrokinetic method with pressure drops up to 5÷6 MPa.

Key words: adsorption of polymers; electrokinetic potential of adsorbed layers; deformation of adsorbed polymer layers; hydrodynamic thickness of adsorbed polymer layers.

Adsorption of nonionic water soluble polymers is often used for the stabilization of colloid systems by the repulsive forces that appear due to overlapping of the peripheral parts of the saturated adsorption layers (AL) of the approaching moieties. This steric protection can provide stability to the dispersion even in the absence of electrostatic repulsion forces.[1,2]

Direct measurements of the steric repulsion forces of polymer adsorption layers by the crossed cylinders method have shown[3–8] that exponentially increasing repulsion forces appear when the distance between the surfaces is less than twice the thickness of a single adsorption layer. However these are not equilibrium forces and their value depends on the rate at which the surfaces approach one another. This is a result of the rheological properties of adsorption layers and their slow reconstruction after disturbance caused by contact deformation. Times of fast relaxation can be up to ten minutes. The establishment of complete equilibrium accompanied by desorbtion of the polymer, requires a considerably longer period. In this case, repulsive forces can change to attractive ones,[9] and both the properties of the single adsorption layers and the structural effects in the overlapping zone caused by reciprocal penetration

---

Translated from *Izvestiya Akademii Nauk. Seriya Khimicheskaya,* No. 1, pp. 31—37, January, 1994.

1066-5285/94/4301-0022 $12.50 © 1994 Plenum Publishing Corporation

of "tails" and "loops" are significant.

Steric interaction has been investigated theoretically[1,9] and experimentally[3—8] using model systems and by experiments with colloidal systems.[1,2,10—17] Nevertheless, the deformational properties of a single AL have not been studied much, mainly due to the difficulty in creating high tangential shear stresses necessary to observe deformation.

Experimental

We managed to obtain the target results by the capillary electrokinetic method.[18,19] The use of thin capillaries (r = 5÷10 μm, l = 7÷8 cm) and considerable pressure drops Δp (up to 5 MPa) makes it possible to obtain up to 200 $\mathrm{N \cdot m^{-2}}$ shear stresses ($\tau = r\Delta p/2l$) on the surface of a capillary with solution flow. The arising deformation of the adsorption layer is seen in a change in its thickness, which is reflected in a corresponding change in the position of the slip plane and in the value of the electrokinetic ζ-potential. Since r is much greater than the Debay radius ($1/\kappa$), the ζ-potential value can be calculated by the Helmholtz—Smoluchowski equation:

$$\Delta E/\Delta p = \varepsilon\zeta/4\pi\eta K, \qquad (1)$$

where ΔE is the streaming potential; ε — dielectric permittivity; η — viscosity, and K — specific electroconductivity of the solution in the capillary.

To find the hydrodynamic thickness (δ) of adsorbed polyethylene oxide layers, which defines the position of the borders of the tails of the macromolecules,[20—23] the Gouy equation for a 1—1 electrolyte was used

$$\delta\kappa = \ln[\mathrm{th}(e\varphi_l/4kT)/\mathrm{th}(e\zeta/4kT)], \qquad (2)$$

where φ_l is the potential of a quartz surface, e — the charge of an electron, k — Boltzmann constant.

Measurements of the ζ-potential at various pressure drops Δp and at various τ, respectively, make it possible to obtain the deformation characteristics of single layers — δ(τ). The thickness of an adsorbed layer is measured beginning when $\zeta = \varphi_l$ and $\delta = 0$. When the thickness of the adsorbed layer is much more than $1/\kappa$, the values of ζ decrease, and it becomes difficult to measure δ. In this case, the possibility of measuring δ depends upon the accuracy of the measurement of the flow potentials.

To determine the dependence δ(τ) using Eq. (2), two assumptions were made. The first one implies that the potential of a solid quartz surface is not changed after adsorption of PEO. In a series of works,[12,17—19,24] it was shown that this assumption is unsuitable for PEO. In this case, the φ_{lo} potentials of the surface under the PEO layer, which have a lower absolute value than φ_l, should be used in Eq. (2).[17—19]

According to the second assumption, an adsorption layer of PEO does not affect the distribution of ions and potentials near the solid charged surface. This allows one to apply the constant values of ε and $1/\kappa$ of the bulk solution to the zone of the adsorption layer. Theoretical consideration of this question[25] led us to the conclusion that the corresponding corrections in Eq. (2) are only essential at a high volume fraction of polymer ($m \geq 0.1$) in the AL. PEO have low values of m at 10^{-3}—10^{-4} mol $\mathrm{L^{-1}}$ concentrations of the KCl background solution and at pH 6.5.[16,17] On the other hand, when the electrolyte concentration is increased to 10^{-2} mol $\mathrm{L^{-1}}$, the values of m increases to 0.3—0.4. Thus, it is convenient to investigate deformation when the concentration of the background electrolyte is low. This allows one not only to exclude any corrections in Eq. (2), but also to carry out the measurements when $\kappa\delta < 1$ and the adsorption layer is within a diffusion layer of ions. In this case, ζ values can be measured with a higher accuracy.

The first results obtained by the capillary electrokinetic method for adsorbed layers of PEO with molecular mass M = $6 \cdot 10^5$ on the surface of quartz capillaries,[18,19] led us to the conclusion that the saturated adsorption layer becomes noticeably deformed as soon as τ is more than 20 N $\mathrm{m^{-2}}$. At $\tau > 100$ N $\mathrm{m^{-2}}$, δ decreases to half of the starting thickness, but with a further increase in τ, deformation fades.

The study was continued on PEO samples with different molecular masses: M = $2.1 \cdot 10^4$ (PEO-1), M = $4.5 \cdot 10^4$ (PEO-2), M = $2.7 \cdot 10^5$ (PEO-3), and M = $6.0 \cdot 10^5$ (PEO-4). Investigations were carried out by the capillary electrokinetic method using thin (r = 5÷10 μm) quartz capillaries drown from high grade purity of fused quartz tubes. When stretched with a shooting method, thin capillaries up to 5 m long with constant diameter are obtained. Pieces of the capillary with l = 7÷8 cm were used in the electrokinetic experiments. They were sealed when stored and were opened directly before the beginning of the experiments. The juvenile surface of the capillaries does not require additional cleaning. Measurements of the streaming potential in a standard 10^{-4} mol $\mathrm{L^{-1}}$ KCl solution showed that the equilibrium values of the ζ-potential are established within a few minutes of contact with a solution and do not change further for several months.

The experiments first involved measurements of the surface φ_l-potentials of the original quartz capillaries, and then measurements of the ζ-potentials after the formation of a PEO adsorption layer equilibrated with a solution of polymer with fixed concentration C_p (in the same capillary). ζ-Potentials were measured at different rates of solution flow through a capillary, and these rates determine different values of the tangential shear stress τ. All of the experiments were carried out at the same concentrations of the background electrolyte (10^{-4} mol $\mathrm{L^{-1}}$ KCl). Solutions were prepared using trice distilled water with specific electroconductivity 10^{-6} Ω^{-1} $\mathrm{cm^{-1}}$ and pH 6.5.

The φ_l and ζ-potentials were calculated with Eq. (1) using the ε and h values for the bulk solutions. Specific electroconductivity K was determined by the volt-ampere characteristics of the electrokinetic cell[19,26] during the experiment, and the radii of the capillaries were determined by the electric resistance $R_0 = l/\pi r^2 K_0$ of a 0.1 mol $\mathrm{L^{-1}}$ KCl solution, which filled a capillary. In this case, the surface conductivity is completely suppressed, therefore the bulk specific conductivity of the solution K_0 could be used for the determination of r.

Computer processing of the experimental results was used to find the values of the φ_l and ζ-potentials from the electrokinetic data. Error of the potential measurement was less than 1.5—2 %.

Results and Discussion

Figure 1 presents the results of the measurements of the surface potentials of quartz capillaries φ_l and the ζ-potentials of AL of PEO-1 equilibrated with PEO solutions of different concentrations C_p (from 10^{-4} to 10^{-1} g $\mathrm{L^{-1}}$) flowing through the capillaries. The φ_l- and ζ-potentials are given versus the pressure drop Δp,

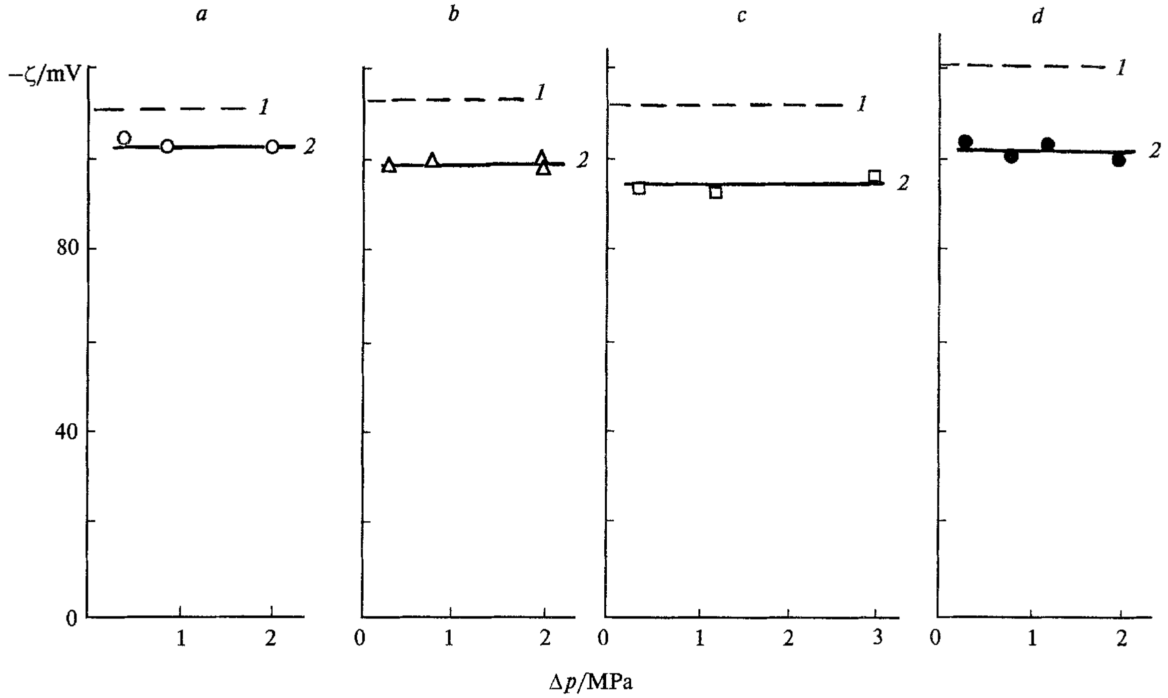

Fig. 1. Surface potentials φ_l (*1*) of quartz capillaries and ζ-potentials (*2*), measured after adsorption of PEO with $M = 2.1 \cdot 10^4$ versus pressure drop Δp at different equilibrium concentrations of PEO solution, $g \cdot L^{-1}$: *a*, $C_p = 10^{-4}$, $\varphi_l = -111$, $\zeta = -103$; *b*, $C_p = 10^{-3}$, $\varphi_l = -113$, $\zeta = -98$; *c*, $C_p = 10^{-2}$, $\varphi_l = -112$, $\zeta = -95$; *d*, $C_p = 10^{-1}$, $\varphi_l = -121$, $\zeta = -101$.

which is characteristic for the shear stress τ affecting a surface of the adsorption layer. In this series of experiments the τ values varied from 7 to 110 N m^{-2}. Before each series of experiments the surface of the capillary was treated with a flowing solution of C_p concentration at the pressure drop value $\Delta p = 0.2$ MPa for 1—1.5 h. It is known[1,19] that within this time interval the equilibrium values of the ζ-potential of the adsorption layer are established. Adsorption kinetics is determined not by diffusion rate, but by adsorption itself and by the conformational reconstruction of the adsorption layer. The time of establishment of adsorption equilibrium in thin capillaries does not exceed 10 s.[18] The ratio of the capillary surface A = 0.02 cm^2 to the solution volume is A/V = 3 m^2 L^{-1}. At this A/V value the surface of the capillary is preferentially enriched with longer molecules, if the polymer is polydispersional.[27,28]

The pressure drop was then gradually increased and at each Δp the corresponding values of the ζ-potential were measured. Constant ζ-potential values were established during the time required for creating a new pressure drop, *i.e.*, within several minutes.

The data presented show the ζ-potentials to be lower in absolute value than the φ_l-potentials and, therefore, formation of the adsorption layer of PEO moves the position of the slip plane deeper into the solution. It can also be concluded that, in the case of PEO with low molecular weight, the increase in the τ value to 110 N m^{-2} hardly changes the ζ-potential, *i.e.*, no notable deformation of the adsorption layer is observed.

If a shift of the slip plane is considered to be the single reason for the difference between ζ and φ_l, then the hydrodynamic thickness of the adsorption layer calculated by Eq. (2) increases from 1.3 to 3 nm as C_p increases (Fig. 2, curve *1*). Saturation of the adsorption layer occurs at $C_p > 10^{-2}$ g L^{-1}, in accordance with the isotherms of adsorption of PEO on silicon oxide.[16,17]

An alternative approach implies the possibility of a correlation between the change in the ζ-potential and changes in the surface potential of the quartz under the PEO layer. At low concentrations of PEO in solution ($C_p = 10^{-4}$ g L^{-1}) the hydrodynamic thickness of the adsorption layer does not exceed 0.3 nm according to measurements by the photon-photon correlation method.[16,17] This corresponds to an almost flat conformation of the molecules of the adsorption layer. The corresponding changes in potential calculated by (2) should not exceed 1 mV, which is less than experimental error. Therefore, it is reasonable to account for the decrease in the potential from 111 to 103 mV mainly by the change in the surface potential of quartz under influence of PEO adsorption. It is known that PEO adsorption occurs through the formation of hydrogen bonds between the oxygen atoms of PEO and the non-dissociated hydroxyl groups on the quartz surface. The latter effect can also be caused by a decrease in the dielectric permeance of the medium within the adsorption layer and by the relative decrease in the rate constant of the dissociation of the surface hydroxyls.

If the value of the ζ-potential measured at C_p =

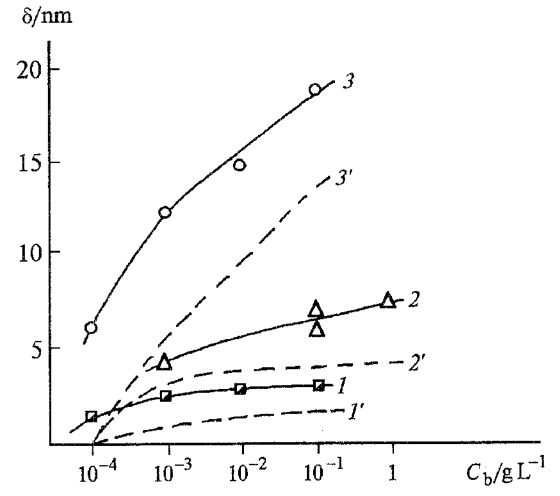

Fig. 2. Dependencies of δ of PEO adsorption layers versus C_p at M: $2.1 \cdot 10^4$ (*1, 1'*); $4.5 \cdot 10^4$ (*2, 2'*); $2,7 \cdot 10^5$ (*3, 3'*).

10^{-4} g L^{-1} is accepted to be the value of the φ_{1o}-potential under the adsorption layer of PEO, then the thicknesses δ should naturally be lower (curve *1'* in Fig. 2). A choice in favor of one or another interpretation of the results can be made only if φ_{1o} are measured by an independent method.

Independently of the chosen procedure for the calculation of δ, the results of the first series of experiments show that AL of PEO with low molecular weight are only very slightly deformed by the tangential shear stresses used by us. The possible deformation does not exceed the experimental errors of the measurement of δ by the methods described above.

The results of experiments with polymer PEO-2, which has a higher molecular weight ($M = 4.5 \cdot 10^4$), in capillaries with $r = 6.5 \div 7$ μm are shown in Fig. 3. As follows from the $\zeta(\Delta p)$ correlations obtained, in this case also, no significant deformation of the adsorption layer is observed, *i.e.*, the ζ-potentials do not change when Δp is increased to 4 MPa and τ increases to 180 N m^{-2} accordingly. In this case, the hydrodynamic thickness is higher and attains 7.8 nm for the saturated adsorption layer at $C_p = 0.1$ g L^{-1} (Fig. 2, curve *2*). Unfortunately, no measurements of the ζ-potentials at $C_p = 10^{-4}$ g L^{-1} were carried out in this case, which made it impossible to determine the corresponding value of φ_{1o} for this polymer. If φ_{1o} is accepted to be −103 mV, then the values of δ correspond to the data of curve *2'* in Fig. 2. According to this calculation method, the limiting values of δ_{max} for PEO with molecular weight $M = 4.5 \cdot 10^4$ are ~4 nm, and this is close to the data obtained in Ref. 29, in which the hydrodynamic thickness δ_{max} of a saturated adsorption layer was determined by an independent method based on a decrease in silica gel pore diameter after pumping of PEO water solutions. For $M = 4 \cdot 10^4$, δ was 4.5 nm. The same value of δ was also obtained by the measurement of the Brownian diffusion coefficient of silica drop hydrosol particles with 19 nm radius before and after adsorption of PEO.[16,17] These data give some evidence for the validity of our calculations of δ, taking into account the change in the surface potential after adsorption of PEO.

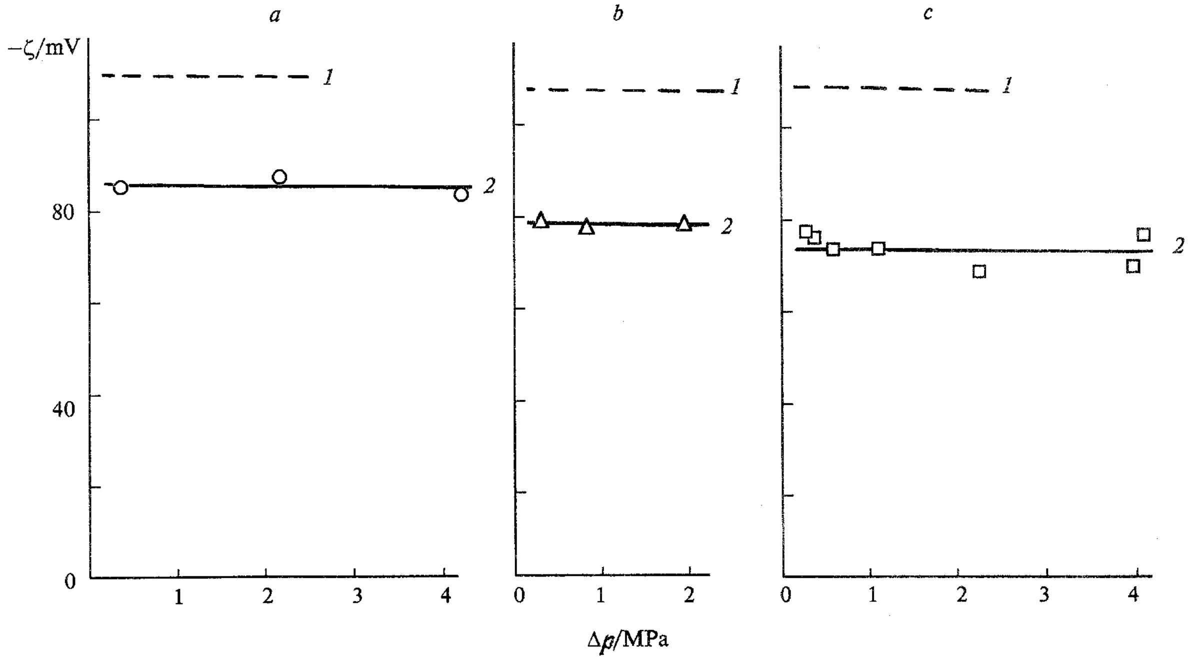

Fig. 3. Surface potentials φ_1 (*1*) of quartz capillaries and ζ-potentials (*2*), measured after adsorption of PEO-4 with $M = 4.5 \cdot 10^4$ versus pressure drop Δp at different equilibrium concentrations of PEO solution, g $\cdot$ L^{-1}:*a*, $C_p = 10^{-3}$, $\varphi_1 = -110$, $\zeta = -87$; *b*, $C_p = 10^{-2}$, $\varphi_1 = -108$, $\zeta = -79$; *c*, $C_p = 1$, $\varphi_1 = -109$, $\zeta = -74$.

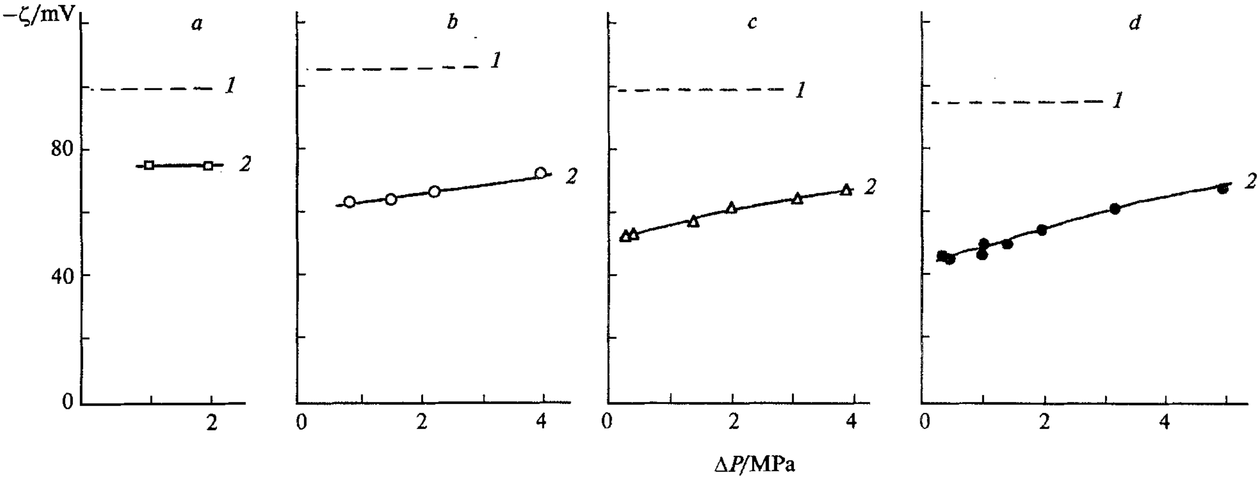

Fig. 4. Surface potentials φ_l (*1*) of quartz capillaries and ζ-potentials equal to −75 (*2*), measured after adsorbtion of PEO with M = $2.7 \cdot 10^5$ versus pressure drop Δp at different equilibrium concentrations of PEO solution, g L^{-1}:*a*, $C_p = 10^{-4}$, $\varphi_l = -100$; *b*, $C_p = 10^{-3}$, $\varphi_l = -106$; *c*, $C_p = 10^{-2}$, $\varphi_l = -99$; *d*, $C_p = 10^{-1}$, $\varphi_l = -95$.

AL of PEO-2 formed at $C_p = 10^{-3}$ g L^{-1} can be partly washed off the capillary surface by constant pumping of the background electrolyte solution at Δp = 2 MPa for 24 hours. After this treatment the surface potential of the capillary changed from −87 mV to −97 mV (see Fig. 3, *a*). However, the potential of the pure quartz surface (φ_l = −110 mV) did not reappear. Calculations show that the hydrodynamic thickness of the adsorption layer decreased from 3 to 1 nm as a result of desorption. It was found that the saturated adsorption layer formed at C_p = 1 g L^{-1} (Fig. 3, *c*) can be more readily removed from the surface of the capillary.

Similar desorption processes at decreased concentrations of the equilibrium PEO solution have been observed earlier,[30] but they were explained by preferential desorption of small molecules less strongly bound with surface molecules.

For PEO with M = $2.7 \cdot 10^5$ the situation is noticeably different (Fig. 4). Measurements were carried out in quartz capillaries with 5.6÷6.9 μm radii. Only at $C_p = 10^{-4}$ g L^{-1}, when the adsorption layer was thin, did increasing τ to 100 N m^{-2} not cause changes in the ζ-potential (Fig. 4, *a*). It can be proposed that, in this case also, the differences between ζ and φ were mostly caused by a change in the surface potential of the quartz under the adsorption layer. Analysis of the stability of wetting films of water solutions of PEO on a flat quartz surface[18,19] gave independent evidence of latter assumption. In these works the φ_{l_0} values were obtained on the basis of the theory of electrostatic forces which define the thickness of water films.[31] Ellipsometric measurements of the film thicknesses *h* made it possible to find φ_{l_0}, using a portion of the isotherm of the disjoining pressure Π(*h*) and the values of the potential of the second surface of the film, which is contiguous with the gas phase.

The results of calculating the values of δ by both methods are given below. Fig. 2 (curve *3*) shows δ calculated by Eq. (2) using the φ and ζ potentials and also using φ_l = −75 mV and the ζ potentials (curve *3'*). The ζ values for the non-deformed equilibrium layers measured at the lowest Δp were used in these calculations.

The value of hydrodynamic thickness obtained for a saturated adsorption layer (δ_{max} = 13.8 nm) is equal to that measured earlier[30] for PEO with a similar molecular weight (M = $4 \cdot 10^5$) at the same equilibrium concentration of solution (0.1 g L^{-1}). In Fig. 2 the horizontal lines represent the values of δ_{max} taken from Ref. 30 published previously. Values close to these (δ_{max} = 13.6 nm) were also obtained by two independent methods, *i.e.*, by the coefficients of Brownian diffusion[16,17] and by filtration of PEO solutions through silica gels.[29] For PEO with M = $2.7 \cdot 10^5$ these values were somewhat lower (δ_{max} = 10 nm, see Ref. 21, 32).

In all cases the values of δ_{max} calculated assuming a change in the surface potential under the adsorption layer coincide better with the experimental results obtained by independent methods. The value δ_{max} = 18.6 nm (Fig. 2, curve *3*) is probably overestimated. All of these facts attest to the validity of the proposal that the adsorption of PEO affects the surface potential of quartz. The ζ values measured at low concentrations of equilibrium PEO solution ($C_p = 10^{-4}$ g L^{-1}), when the PEO molecules are spread out in the plane of the quartz surface, can be used as estimations of φ_{l_0}.

Comparison of the δ_{max} values with the radians of gyration of polymer molecules in bulk solution $<s^2>^{1/2}$ shows that the ratio $\delta_{max}/<s^2>^{1/2}$ increases together with the molecular weight of PEO from 0.3 at M = $2 \cdot 10^4$ to 0.5 at M = $4 \cdot 10^4$ and to 0.7 at M = $2.7 \cdot 10^5$. This fact means that the strongest conformational changes during adsorption occur with molecules of low M, which acquire a stretched shape in the adsorption plane. The shape of molecules with higher M is changed less after adsorption.

Washing out the adsorption layer of PEO-3 (M $= 2.7 \cdot 10^5$) with background electrolyte gives an increase in the absolute values of ζ to -75 mV at $C_p = 10^{-3}$ g L^{-1} and to -86 mV at $C_p = 10^{-4}$ g L^{-1}. A pure capillary surface free of PEO can not be attained. After pumping background electrolyte solution at $\Delta p = 3$ MPa for 72 h, the most strongly bound molecules were still left on the surface.

The results of electrophoresis measurements of ζ for particles of silica hydrosol with a 69 nm radius at various pH values are given in Fig. 5. Tabulated data taking into account the effect of polarization of the double electric layer of the particles[21] were used for converting the electrophortic mobility measured on a Malvern Zetasizer-2C instrument into the ζ values. The measurements were carried out with a $3 \cdot 10^{-4}$ mol L^{-1} NaCl background concentration at 20 °C. Curves *4, 5* characterize the ζ values expected in the case when the hydrodynamic thicknesses of AL measured for the same sols ($\delta = 4.5$ nm for PEO-2 and $\delta = 15$ nm for PEO-4) are taken into account in Eq. (2). The curves calculated with this method lie considerably higher than the experimental ones, which indicates a decrease in the ζ surface potential of the sol particles under the AL of PEO.

The experimental dependencies of δ versus Δp and τ are shown in Fig. 6. In this plot the values of δ are calculated by Eq. (2) using the surface potential of quartz under the adsorption layer of PEO ($\varphi_{1o} = -75$ mV). As follows from Fig. 6, the thicker the adsorption layer, the greater is the relative thinning of the adsorption layer. Thus, a saturated adsorption layer is thinned from $\delta_{max} = 13.6$ nm to 3 nm (curve *3*), and an unsaturated one is thinned from 5 to 1.5 nm (curve *1*).

The results of similar measurements for PEO-4 with the still higher M $= 6 \cdot 10^5$ are given in Fig. 7. Deformation of the unsaturated adsorption layer (curve *2*) proceeds in the same way as of that of the saturated layer (curve *1*).

Changes in δ are not caused by desorption processes. It has been shown previously[18,19] that the establishment of an adsorption equilibrium and desorption require considerable time. Deformation proceeds rapidly and reversibly during the time required for a change in pressure drop. The positions of the points in a $\delta(\tau)$ plot are independent of the consequence of maintaining the pressure drop.

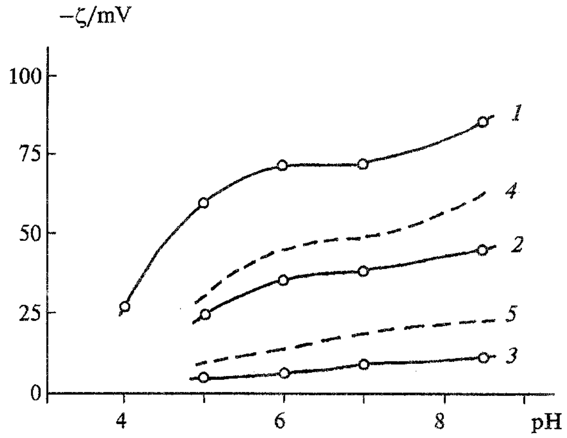

Fig. 5. Influence of pH on ζ-potentials of silica hydrosol particles before (*1*) and after adsorption of PEO-2 with M $= 4.5 \cdot 10^4$ (*2*) and PEO-4 with M $= 6.0 \cdot 10^5$ (*3*), and results of the calculation of φ_{1o} by Eq. (2) using δ values for adsorption layers of PEO-2 (*4*) and PEO-4 (*5*).

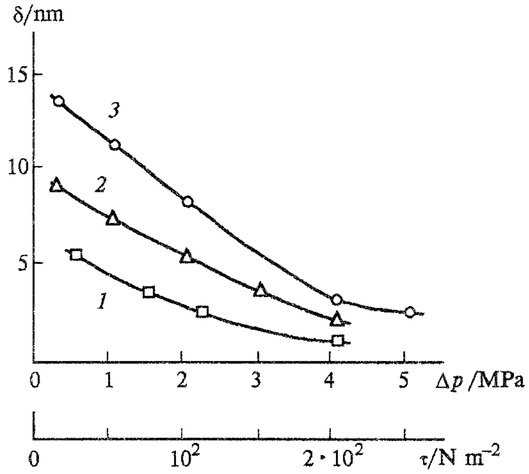

Fig. 6. Changes of δ (M $= 2.7 \cdot 10^5$) under the influence of tangential shear stress created by the flow of equilibrium PEO solution through a capillary at pressure drop Δp C_p (g L^{-1}): 10^{-3} (*1*); 10^{-2} (*2*); 10^{-1} (*3*).

Based on the known exponential profile of PEO segment concentration near a quartz surface,[9,28,33] it can be concluded that at first, when shear stresses are small, deformation of "tails" of the molecules occurs. As τ increases, the "loops" zone disposed deeper is also affected by deformation. The effect of deformation manifests itself in pressing of the adsorption layer and its compression, which leads to gradual deformation decay at $\tau > 150$ N m^{-2}. The compression of the adsorption layer leads to an increase in the volume fraction of the polymer to $m = 0.3$. Therefore, the estimations of δ obtained at $\tau > 100$ N m^{-2} should be regarded with care. In the area of such m values, corrections taking into account the change in dielectric permittivity in the adsorption layer zone and the change in the ion concentration within the adsorption layer caused by the dielectric exclusion effect[34–37] should be introduced into Eq. (2). The increase in the Debay length as the ion concentration in the adsorption layer decreases leads to underestimated δ values, and a decrease in ε reduces $1/\kappa$. The extent to which these effects can compensate

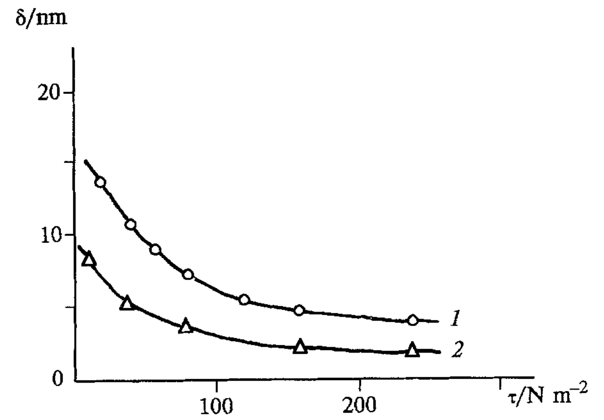

Fig. 7. Hydrodynamic thickness of PEO adsorption layers with M $= 6 \cdot 10^5$ versus τ at C_p (g L^{-1}): 10^{-1} (*1*) and 10^{-2} (*2*).

for one another can be established after the development of an appropriate theory of the diffusion layer of ions near surfaces covered with AL of nonionic polymers.

References

1. V. Nepper, *Stabilizatsiya kolloidnyh dispersii polimerami* [*Stabilization of Colloid Dispersions with Polymers*], Mir, Moscow, 1986 (Russ. Transl.).
2. A. A. Baran, *Polimersoderzhashchie dispersnye sistemy* [*Dispersion Systems Containing Polymers*], Naukova Dumka, Kiev, 1986 (in Russian).
3. J. N. Israelachvili, R. K. Tandon, and L. R. White, *Nature*, 1979, **277**, 120.
4. J. Klein and P. Luckham, *Nature*, 1982, **300**, 429.
5. J. Klein, *J. Chem. Soc. Faraday Trans. 1*, 1983, **79**, 99.
6. P. F. Luckham and J. Klein, *J. Colloid Interface Sci.*, 1987, **117**, 149.
7. E. Kiss and C. G. Golander, *Colloids Surf.*, 1990, **49**, 335.
8. M. Malmsten and P. M. Claesson, *Langmuir*, 1991, **7**, 988.
9. G. J. Fleer and J. M. H. M. Scheutjens, *J. Colloid Interface Sci.*, 1986, **111**, 504.
10. Th. Tadros, *J. Colloid Interface Sci.*, 1978, **64**, 35.
11. B. V. Eryomenko and M. A. Malysheva, *Kolloidn. Zh.*, 1986, **48**, 351 [*Colloid. J. USSR* (Engl. Transl.)].
12. T. Okubo, *J. Chem. Soc. Faraday Trans. 1*, 1987, **83**, 2497.
13. Van den Th. Boomgard, Th. Tadros, and J. Lyklema, *J. Colloid Interface Sci.*, 1987, **116**, 8.
14. B. V. Eryomenko, M. A. Malysheva, and A. A. Baran, *Kolloidn. Zh.*, 1988, **50**, 449 [*Colloid. J. USSR* (Engl. Transl.)].
15. E. C. M. Pelssers, M. A. Cohen Stuart, and G. J. Fleer, *Colloids Surf.*, 1989, **38**, 15.
16. E. A. Nikologorskaja, V. A. Kosaikin, and N. V. Churaev, *Kolloidn. Zh.*, 1990, **52**, 502 [*Colloid. J. USSR* (Engl. Transl.)].
17. N. V. Churaev and E. A. Nikologorskaja, *Colloids Surf.*, 1991, **59**, 71.
18. E. K. Gasanov, I. P. Sergeyeva, V. D. Sobolev, Z. M. Zorin, and N. V. Churaev, *Kolloidn. Zh.*, 1991, **53**, 617 [*Colloid. J. USSR* (Engl. Transl.)].
19. N. V. Churaev, I. P. Sergeeva, V. D. Sobolev, Z. M. Zorin, and E. K. Gasanov, *Colloids Surf.*, 1993, **76**, 23.
20. M. A. Cohen Stuart, F. H. W. H. Waajen, T. Cosgrove, B. Vincent, and T. L. Crowley, *Macromolecules*, 1984, **17**, 1825.
21. E. Killman, H. Maier, P. Kanint, and N. Gutling, *Colloids Surf.*, 1985, **15**, 261.
22. A. E. Yaroshchuк, *Kolloidn. Zh.*, 1985, **47**, 369 [*Colloid. J. USSR* (Engl. Transl.)].
23. J. M. H. M. Scheutjens, G. J. Fleer, and M. A. Cohen Stuart, *Colloids Surf.*, 1986, **21**, 285.
24. B. V. Eryomenko and Z. F. Sergienко, *Kolloidn. Zh.*, 1979, **41**, 422 [*Colloid. J. USSR* (Engl. Transl.)].
25. N. Churaev, A. Kotov, Y. Solomentsev, and V. Starov, *Progr. Coll. Polym. Sci.*, 1991, **84**, 290.
26. V. D. Sobolev, I. P. Sergeeva, and N. N. Churaev, *Poverkhnostnye sily i granichnye sloi zhidkosti* [*Surface Forces and Boundary Layers in Liquids*], Nauka, Moscow, 1983, 102 (in Russian).
27. M. A. Cohen Stuart, J. M. H. M. Scheutjens, and G. J. Fleer, *J. Polym. Sci. Polym. Phys.*, 1980, **12**, 559.
28. G. Flear and I. Liklema, in *Adsorbtsiya iz rastvorov na poverkhnostyakh tvyordykh tel* [*Adsorbtion from Solutions on Surfaces of Solids*], Mir, Moscow, 1986, 182 (Russ. Transl.).
29. M. Kawaguchi, M. Mikura, and A. Takahashi, *Macromolecules*, 1984, **17**, 2063.
30. J. C. Dijt, M. A. Cohen Stuart, and G. J. Fleer, *Macromolecules* (in press).
31. Z. M. Zorin, N. V. Churaev, N. E. Esipova, I. P. Sergeeva, V. D. Sobolev, and E. Gasanov, *J. Colloid. Interface Sci.*, 1992, **152**, 170.
32. G. P. van der Beek and M. A. Cohen Stuart, *J. Phys. Fr.*, 1988, **49**, 1449.
33. T. Cosgrove, T. G. Heath, K. Ryan, and B. van Lent, *Polym. Comm.*, 1987, **28**, 64.
34. A. Parsegian, *Nature*, 1969, **221**, 884.
35. S. S. Dukhin, N. V. Churaev, and A. E. Yaroshchuk, *Khimiya i tekhnologiya vody* [*Chemistry and Technology of Water*], 1984, **6**, 291 (in Russian).
36. N. V. Churaev, *Kolloidn. Zh.*, 1985, **47**, 112 [*Colloid. J. USSR* (Engl. Transl.)].
37. S. S. Dukhin, M. P. Sidorova, and A. E. Yaroshchuk, *Elektrokhimiya membran i obratnyi osmos* [*Electrochemistry of Membranes and Reversed Osmosis*], Khimiya, Leningrad, 1991 (in Russian).

Received June 21, 1993