

# MODIFICATION OF QUARTZ SURFACE WITH AQUEOUS SOLUTIONS OF POLYELECTROLYTES AND SURFACE-ACTIVE SUBSTANCES

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The influence of anionic [polyacrylic (PAA), polymethacrylic (PMAA) acids] and cationic [hydrochlorides of poly-2-methyl-5-vinylpyridine (PMVP) and copolymer of 2-methyl-5-vinylpyridine with butylmethacrylate (MVP-BMA)] polyelectrolytes (PE), and also their mixtures with cationic (cetyltrimethylammonium bromide (CTAB)) and anionic (sodium dodecylsulphate (DDS)) surface-active substances (SAS) on surface properties of quartz was investigated. The greatest modification of PE and their mixtures with SAS is displayed when they are preliminary deposit on quartz surface from aqueous solutions and dried. The modification act of PE and SAS is displayed in exchanges of the contact angle of wetting with water and electrokinetic potential of quartz.

The current stage in the development of colloid chemistry is characterized by the use of high-molecular surface-active substances (HMSAS) in the processes of wetting, stabilization and flocculation of dispersed systems, *i.e.* in processes connected with their surface characteristics [1—5]. The influence of HMSAS on dispersed systems is connected with their adsorption on interphase boundaries [6], which results in changes in the surface state of the system particles, and the structure of the double electric layer (DEL) in particular. A value that is easily measured practically and characterizes the parameters of the DEL, is the electrokinetic  $\zeta$ -potential. The value of the  $\zeta$ -potential is used by some research workers to characterize the binding strength between macromolecules and mineral particles [1] and to find the mechanism of their interaction [7].

On the other hand, the contact angle ( $\theta$ ), which is a measure of the wetting occurring in three-phase systems, is determined by the correlation of the interfacial tension ( $\sigma$ ) of the contacting phases. A change in surface tension in the presence of HMSAS on any phase boundary will influence the value of  $\theta$ . By studying the wetting of solid surfaces with various liquids, we can get information about the state of the solid surface in the presence of polymers.

In our opinion, a complex study of wetting and electrokinetic characteristics of solids will make it possible to find out more peculiarities pertaining to the formation of adsorption layers of diphilic macromolecules, which determine the stabilizing and flocculating actions of the latter. Further, a study of the possibilities of regulating wetting processes with the help of HMSAS, including diphilic polyelectrolytes, is in itself of practical importance.

This paper presents the results of a systematic study of the influence of the nature molecular mass and degree of diphil character of HMSAS on the water wetting and the  $\zeta$ -potential of one of the hidrophilic minerals most widely spread in nature quartz. The simple composition and low solubility make this the most convenient substance to study.

We have used the following cation-active HMSAS: hydrochlorides of poly-2-methyl-5-vinylpyridine (PMVP) with an average molecular mass ( $M_n$ )  $1.9 \times 10^4$  and  $3.4 \times 10^5$ , and of copolymers of 2-methyl-5-vinylpyridine (MVP) with butyl methacrylate (BMA) in initial molar ratios 9:1 (copolymer 1) and 7:3 (copolymer 2). PMVP and its copolymers were obtained by free-radical polymerization in the block at 70 °C in the presence of the dinitrile of azo-bis-isobutyric acid (DAA) in a quantity of 0.2% of the polymer weight [8]. After fractionation in the hexane-petroleum ether system, we determined the average molecular masses viscosimetrically [9]. The constants required for the calculation of  $M_n$  were taken from [8].

Anion-active polymers were polyacrylic acid (PAA) with  $M_n$   $1.7 \times 10^4$ ,  $5.7 \times 10^4$ ,  $9.9 \times 10^4$ ,  $1.8 \times 10^5$  and  $2.7 \times 10^5$ , and polymethacrylic acid (PMAA) with  $M_n$   $1.8 \times 10^5$ ,  $2.7 \times 10^5$  and  $5.6 \times 10^5$ . We prepared PAA by radical polymerization in 30% dioxane solution in the presence of benzoyl peroxide [10]. PMAA was also obtained by radical polymerization in a benzoyl peroxide solution. The initiator was DAA.

The molecular masses of PAA and PMAA fractionated in the dioxane-petroleum ether [11] methanol-ethyl acetate systems: acetic acid (9:1), respectively [11], were determined viscosimetrically with the help of the equation constants of Mark-Houwink-Kuhn given in [12].

The contact angles ( $\theta$ ) of wetting of a polished plate (polishing class 14) of optical quartz glass K-8 made by the Lytkarinsk Optical Glass Works were measured with the help of a horizontal microscope with a goniometric attachment and a special movable stage [13]. The value of  $\theta$  was found by the tangent method, the measurement error being  $\pm 0.5^\circ$ . At the same time the value of  $\theta$  was calculated according to the main parameters of the adherent drop [14]. The measurement error here was not more than  $\pm 0.25^\circ$ . The discrepancies in the values of  $\theta$  determined by the above two methods did not exceed  $\pm 0.5^\circ$ .

The values of  $\theta$  were read five minutes after the drop was applied to the surface of the quartz plate. During this time  $\theta$  diminished by 3–5° and then in the course of five hours it remained constant. Check measurements were taken every 30 minutes during five hours. Before each measurement the plates were treated with a newly-prepared chromic acid mixture, then thoroughly washed with distilled water and dried in a vacuum exsiccator over phosphorus pentoxide.

The  $\zeta$ -potential was determined by the flow potential method, with the surface conductivity taken into account [15]. To make the measurement we used crystal powder ground to a particle size of 17 to 20 mcm. The quartz powder was preliminarily washed free of  $\text{Fe}^{3+}$  ions with sulphuric acid while being heated, and was then washed with distilled water and dried at 105–11 °C. Owing to the high resistance of the quartz powder diaphragm, the HMSAS solutions were prepared using a  $10^{-4}$  M solution of KCl. Before each measurement of the  $\zeta$ -potential, HMSAS solution of appropriate concentration was let through the quartz diaphragm until the electrical conductivity of the outflowing solution was equal to that of the initial solution.

1. Effects of polyelectrolytes on water wetting and electrokinetic potential of quartz

The contact angles of quartz wetted with aqueous solutions of the above-mentioned polyelectrolytes ( $\theta=4-6^\circ$ ), in spite of their marked surface activity on the liquid-gas boundary [16], differ little from those of quartz wetted with pure water

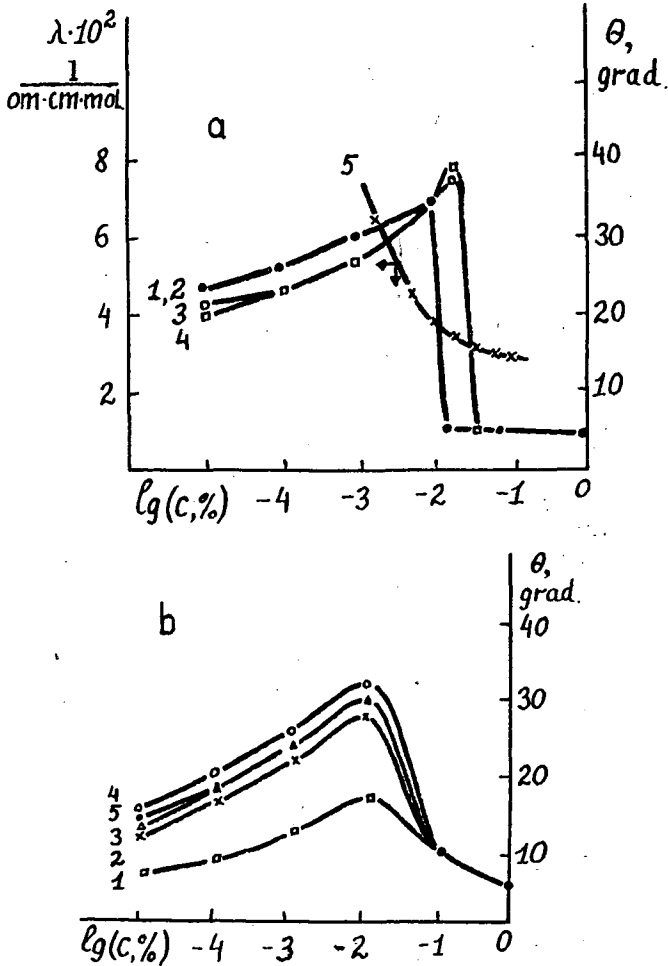


Fig. 1. Contact angles of quartz wetted with water modified by HMSAS solutions:  
 1a) PMVP hydrochlorides with  $M_n(190.000$  (1) and  $340.000$  (2), copolymers MVP:BMA=9:1 (3) and 7:3(4); and PMVP equivalent electric conductivity with  $M_n=190.000$  (5);  
 1b) PAA with  $M_n=17.300$  (1),  $180.000$  (2),  $270.000$  (3),  $513.000$  (4), and PMAA with  $M_n=180.000$  (5).

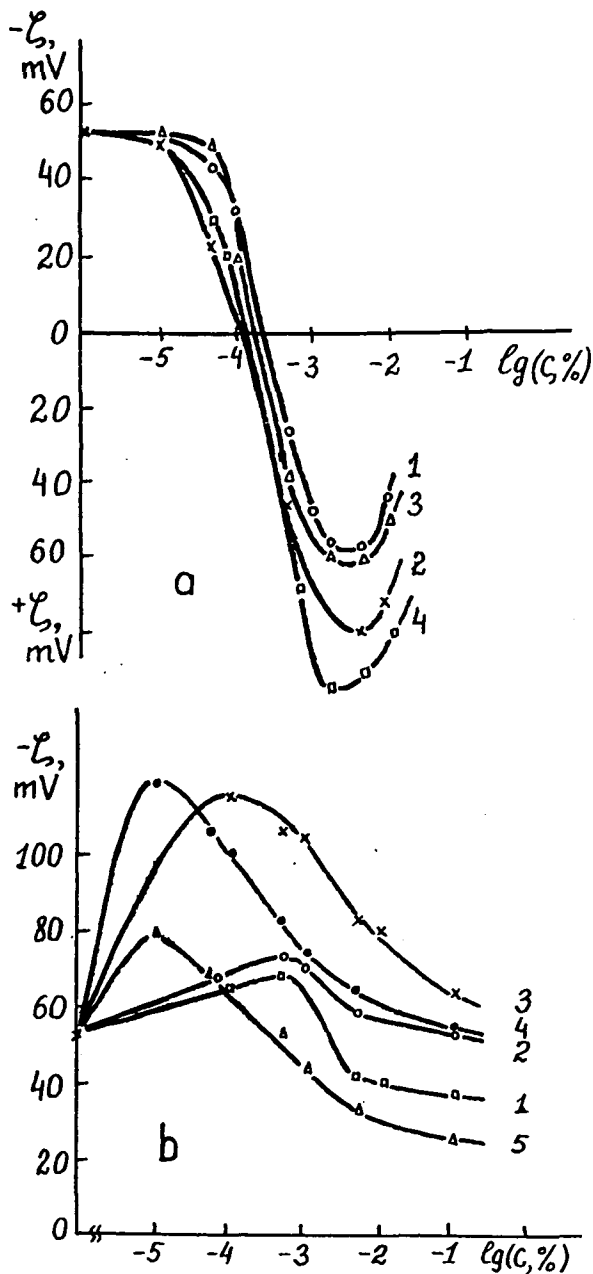


Fig. 2. Electrokinetic potential of quartz in aqueous solutions of HMSAS:  
 2a) PMVP hydrochlorides with  $M_n=190.000$  (1) and  $340.000$  (2),  
 copolymers MVP:BMA=9:1 (3) and 7:3 (4);  
 2b) PAA with  $M_n=17.300$  (1),  $57.000$  (2),  $99.000$  (3),  $180.000$  (4) and  $513.000$  (5);

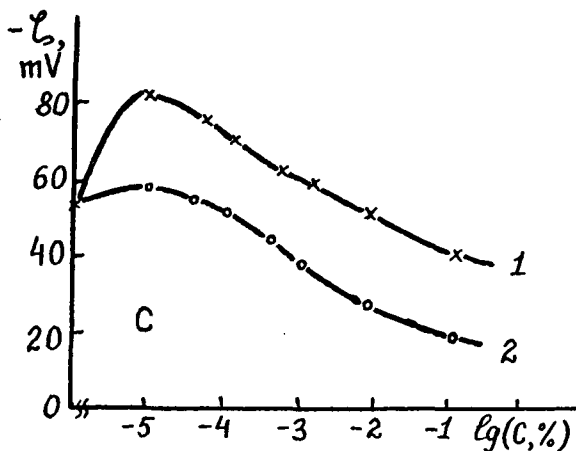


Fig. 2

2c) PMAA with  $M_n = 180,000$  (1) and  $560,000$  (2).

[17], except for copolymers which give a slight ( $8-10^\circ$ ) increase of  $\theta$  at high concentrations. This insignificant change in  $\theta$  may be explained by the fact that the process of drop spreading on the quartz surface occurs faster than the adsorption of HMSAS. Thus, for instance, the adsorption equilibrium on the HMSAS aqueous solution air boundary becomes stable in the course of 12–24 hours owing to the low rate of diffusion of macromolecules to the interface [16]. This small increase in  $\theta$  in the case of copolymers is apparently connected with their greater surface activity.

The preliminary treatment, *i.e.* keeping the quartz plates in aqueous solutions of HMSAS for 6 hours, brings about quite a different regularity. In this instance, even if the concentration of the HMSAS solutions is very low ( $C \approx 10^{-5}\%$ ),  $\theta$  noticeably changes; it rises with concentration increase, reaching its maximum at  $C \approx 10^{-2}\%$  (Fig. 1).

The increase of  $\theta$  along with the rise of the concentration during such a long-term contact of the quartz with HMSAS solutions may be explained by the formation of an adsorption layer of HMSAS on the quartz plate surface. The identical type of the concentration-dependence of  $\theta$  for both cationic (Fig. 1a) and anionic (Fig. 1b) HMSAS suggests that in both instances the macromolecules are oriented in the adsorption layer according to the classical mechanism "similar to similar", which is accompanied by hydrophobization of the quartz surface.

The measurement of the  $\zeta$ -potential of quartz in aqueous solutions of the HMSAS under study confirms the quartz adsorption of HMSAS (Figs 2, 4). Thus, solutions of PMVP and its copolymers give typical S-shaped curves with a change in the surface charge sign at a specific polymer concentration for each molecular mass. The change in the  $\zeta$ -potential sign is due to the superequivalent adsorption of macrocation on the quartz surface. This kind of dependence is observed in the presence of multivalent ions, in solutions of potential-determining ions, surface-active substances when the charges of the dispersed phase particle and of the ion introduced into the solution have opposite signs [18–21].

The probable cause of adsorption of PAA and PMAA macromolecules is the formation of hydrogen bonds between the carboxylic groups of the polyelectrolyte and the silanol groups of quartz [1, 2]. However, it was found that the total surface charge of quartz is composed of the charge of the active centres, which differ in value and sign [22, 23]. Therefore, the possibility of adsorption of the HMSAS polyion on the oppositely charged centres of the quartz surface is not excluded [20]. Quartz adsorption of the PAA and PMAA polyions is accompanied by an increase in the negative charge, and therefore in the negative  $\zeta$ -potential of the latter (Fig. 2) at low concentrations of polyelectrolyte. An increase in the negative values of the  $\zeta$ -potential in PAA and PMAA solutions is observed in suspensions of clay minerals, too [24].

It is noteworthy that the maximum values of  $\theta$  of water-wetted quartz preliminarily treated with HMSAS aqueous solutions are observed in the concentration range in which there is a break in the conductometric titration curve [25] (Fig. 1a, curve 5). It is known that high-molecular compounds, and polyelectrolytes in particular, are capable of considerable conformational transformations on ionization, these being especially noticeable in aqueous solutions [11, 26]. Hence, a concentration which brings about a break in a curve showing the dependence of different physicochemical properties on the polymer concentration is called by us a concentration of the conformational transition (CCT), on the analogy of the critical concentration of micelle formation (CCM) of hemicolloid SAS. Proceeding from this, the extremal dependence  $\theta$  *v.s.*  $\log C$  can be explained, with the different characters of the polymer adsorption layer formation on the quartz surface above and below the CCT taken into account. At concentrations of HMSAS lower than the CCT, when the intermolecular hydrophobic interactions are comparatively weak, the macromolecules are of less compact conformation. It may be admitted that such macromolecules, when moving to the adsorbent surface, are able to develop due to the adsorption forces. (The possibility of macromolecular coil deformation in the adsorption layers is discussed in the literature [27].) As a result of this, a proportion of the hydrophobic groups become "uncovered", which leads to hydrophobization of the quartz surface, manifested in an increase in  $\theta$ .

In the concentration range higher than the CCT the adsorption layer is formed of more compacted macromolecule coils. Apparently, the great compactness of the macromolecule segments in the adsorption layer makes it difficult for the segments to differentiate according to the polarity, as a result of which the HMSAS adsorption layer on the quartz surface remains hydrophilic.

Further, when the concentration of the HMSAS under study increases, the pH of their solutions falls and approaches 2 in the concentration range  $\sim 10^{-1}$ –1%, which corresponds to the isoelectric point (IEP) of quartz [28]. It is known that at the IEP of quartz the wettability of solids becomes worse (for quartz at the IEP  $\theta=40^\circ$ ) [28–30]. However, despite the fact that the pH approaches the IEP of quartz, as Fig. 1 shows, concentrations higher than  $10^{-2}$ % give an abrupt decrease in  $\theta$ , which is confirmation of the possible adsorption of macromolecules in the form of compact coils.

It is interesting to compare the influence of the above-mentioned polyelectrolytes on the quartz surface properties with the action of polyethylenimine (PEI), which is known [31] to be characterized by insignificant intermolecular interactions and weakly expressed conformational transitions. The interest in PEI is due to the wide range of

its practical uses. In the case of PEI\* the concentration-dependence of the contact angle is of an extremal kind (Fig. 3). A change in the value of  $\theta$  as the concentration grows is linked with the quartz surface adsorption of PEI. Quartz adsorption of PEI is insignificant (0.2—3.5 mmole/g), which is apparently connected with the small specific surface of quartz (0.12 m<sup>2</sup>/g). The adsorption was determined by the spectrophotometric method and confirmed by IR-spectrometry. Thus, the IR-spectra of

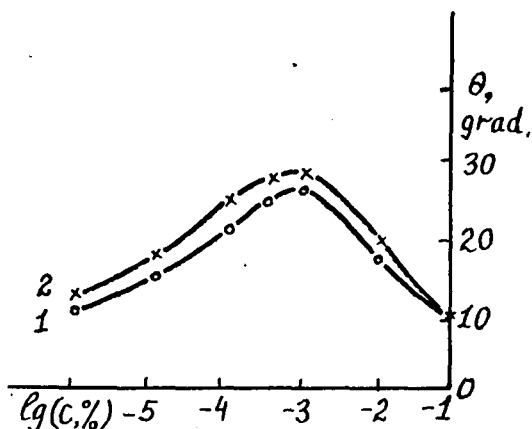


Fig. 3. Contact angles of quartz wetted with water modified by PEI solutions with  $M_n = 30,000$  (1) and 100,000 (2).

quartz surface owing to the dissociation of silanol groups when the pH of the PEI solution increases with the growth of the concentration (to pH=10.2). With the increases of the solid-phase surface charge, the expected rise in polymer adsorption is probably compensated by a fall in the degree of PEI dissociation as the pH of the solution increases.

Thus, the results obtained show that the conformational state of the macromolecules in the solution considerably influences their hydrophobizing action.

The results of measurements of the  $\zeta$ -potential and  $\theta$  of water-wetted quartz confirm the well-known regularity about the increase in the adsorption of the polymer along with the growth of its molecular mass [32]. Thus, with an increase in  $M_n$  the maximum in the  $\zeta$  vs. log C curves for anionic HMSAS (Fig. 2b, c) and a change in the charge sign of the quartz surface in PMVP solutions (Fig. 2a) are observed for lower concentrations. A noticeable influence of the polymer molecular mass reveals itself in the lower-molecular region ( $M_n < 1 \cdot 10^5$ ). For example, the difference in the maximum values of the  $\zeta$ -potential for PAA with  $M_n = 1.7 \times 10^4$  and  $9.9 \times 10^4$  is  $\sim 60$  mV (Fig. 2b), while the difference in the values of  $\theta$  is  $15^\circ$  (Fig. 1b). The values of  $\theta$  for HMSAS with a molecular mass higher than  $1 \times 10^5$  do not differ considerably. The value of the quartz  $\zeta$ -potential decreases as both  $M_n$  and the concentration of the HMSAS solutions increase.

\* Polyethylenimine was synthesized at the A. V. Topchiev Institute of Petrochemical Analysis (Moscow) by Dr. P. A. Gembitsky.

quartz samples kept in PEI solutions of various concentrations, in comparison with the spectra of pure quartz, show bands corresponding to the valency and deformational fluctuations of bonds in the CH- of CH<sub>2</sub>-groups (2930, 2830, 1460, 1290, 1180 cm<sup>-1</sup>).

Unlike PMVP, PAA and PMAA, PEI does not show abrupt decreases in  $\theta$  to those of pure quartz  $\theta$ . When the concentrations of PEI are higher than  $10^{-3}\%$ ,  $\theta$  decreases. In this instance the quantity of adsorbed polymer practically does not depend on the concentration ( $C > 10^{-3}\%$ ). Therefore, the reduction in  $\theta$  is apparently connected with an additional negative charge which appears on the

The fall in the  $\zeta$ -potential as the concentration of HMSAS increases is apparently linked with a reduction of the ionization degree of the polyelectrolytes under study, the sliding surface shift into the liquid phase, an increase in the solution viscosity and, hence, a reduction in the mobility of the double layer anions. (In calculations of the  $\zeta$ -potential, the viscosity of the solution was considered to be equal to that of water.)

The effects of an increase in the solution viscosity and the shift of the sliding surface into the liquid phase are probably the more significant, the greater the HMSAS molecular mass. Therefore, the  $\zeta$ -potential values for the PAA with high  $M_n$  (Fig. 2b, curves 4, 5) are lower than those for polymers of smaller molecular masses. A similar relation was found for PMAA, too (Fig. 2c). It must also be taken into account that not only the solution viscosity but also the dielectric penetrability changes near the solid surface. All the above factors will lead to a decrease in the  $\zeta$ -potential when the polymer concentration in the solution increases [33].

The hydrophilic surface adsorption of polymer macromolecules may lead to their hydrophobization. It is known that hydrophobization intensifies as the diphil character of macromolecules increases. The hydrophobicity ( $m$ ) of macromolecules of the polyelectrolytes studied, which was estimated as the number of hydrophobic ( $-\text{CH}_3$ ,  $=\text{CH}_2$ ,  $=\text{CH}-$ ,  $=\text{C}=\text{}$ ) groups *per* functional (hydrophilic) group, increases from PAA to PMAA and in the sequence PMVP—I  $\rightarrow$  PMVP—II  $\rightarrow$  copolymer I  $\rightarrow$  copolymer II. For PAA and PMAA  $m$  is equal to 2 and 3, respectively, while for PMVP and its copolymers  $\theta$  is within the range 8—11. In the sequence mentioned above, on account of the greater hydrophobization of the quartz particles, a greater fall in the  $\zeta$ -potential value and a rise in  $\theta$  are to be expected, the concentration and molecular mass of the polymer being the same. This is the regularity for anionic HMSAS; the dependent curves  $\zeta$  vs.  $\log C$  ( $\theta$  vs.  $\log C$ ) for PMAA are located lower (higher) than the similar curves for PAA (Fig. 2b, curves 4, 5; Fig. 2c, curves 1, 2). In the case of PMVP and its copolymers the influence of diphil character is of a lesser extent (Fig. 2a). It follows from this that the influence of the diphil character is manifested noticeably at low values of hydrophobicity.

Thus, the investigations carried out show that it is possible to modify the surface of dispersed particles with both cationic and anionic polyelectrolytes.

## *2. Influence of polyelectrolyte mixtures with low-molecular surface-active substances on quartz surface electric properties*

At present great attention is being paid to the interactions of macromolecules of different natures. The majority of the studies of this kind have been carried out on albumens. A study of cooperative reactions involving polyelectrolytes is of theoretical and practical interest, as the products of these reactions (intermolecular complexes) possess a number of specific features not found in the original components. The most convenient subjects providing an understanding of the specificity of inter-macromolecular reactions are polyelectrolytes. Studies of the interactions of polyelectrolytes with surface-active substances (SAS) have begun in the past few years [34, 35]. The polyelectrolyte-SAS interaction is an insufficiently well known type of macromolecular reaction; the products of such reactions can be used to regulate various colloid-chemical phase boundary processes.

We have studied the influence of mixtures of PMVP and sodium dodecyl



sulphate (NaDDS), PAA (PMAA) and cetyltrimethylammonium bromide (CTMAbr) on the wetting ability and the  $\zeta$ -potential of quartz.

Each time  $\theta$  and the  $\zeta$ -potential were measured, the quartz plates and the powder were treated with a mixture of polyelectrolyte and SAS at a different molar ratio  $n = \frac{[\text{SAS}]}{[\text{HMSAS}]}$ . The value  $n$  was regulated by changing the quantity of SAS, the volume of HMSAS being kept constant. The initial concentrations of HMSAS and SAS were equal.

As pointed out in the first part of the paper, the macromolecular conformation depends on the concentration of the polyelectrolyte solution. The measurement of PMVP viscosity shows that the sharpest change in  $\eta_{\text{red.}}$ , and therefore that in the coil conformation, takes place when the concentration of the PMVP solution is of the order of 0.01%. It is to be expected that, depending on the polyelectrolyte solution concentrations, its interaction with the SAS and the influence of their mixtures on the quartz wetting  $\theta$  will be different.

The relation  $\theta$  vs.  $n$  for all the polyelectrolytes studied is maximum at a definite value of  $n$ , which depends on the nature of the polyelectrolyte (Figs. 4, 5). The addition of SAS to the polyelectrolyte intensifies the hydrophobizing action of the latter. However, the results obtained for the mixture of PMVP and NaDDS reflect the dependence of the degree of quartz surface hydrophobization on the initial concentration of the polyelectrolyte. The sharpest increase in  $\theta$  is observed when the concent-

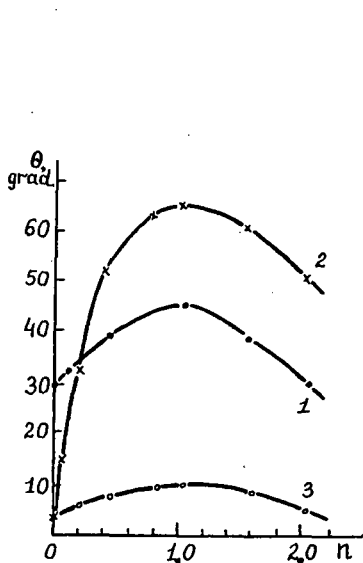


Fig. 4. Dependence of contact angles of quartz wetted with water upon the relative concentration of DDS in a mixture with PMVP with  $M_n = 340,000$ ,  $C_{\text{PMVP}} = 0.01\%$  (1),  $0.155\%$  (2) and  $0.465\%$  (3).

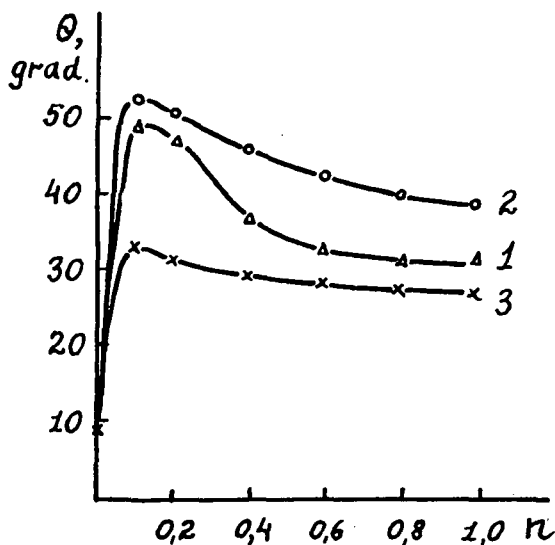


Fig. 5. Dependence of contact angles of quartz wetted with water upon the relative concentration of CTMAbr in a mixture with PAA with  $M_n = 17,300$  (1) and  $1,000,000$  (2), PMAA with  $M_n = 1,000,000$  (3),  $C_{\text{PAA}} = 0.072\%$ ,  $C_{\text{PMAA}} = 0.086\%$ .

ration of PMVP is 0.155% (curve 2, Fig. 4) and is noticeably weaker when the concentration is 0.465% (curve 3, Fig. 4,  $\theta_{\max} \approx 8-10^\circ$ ).

The intensification of the hydrophobizing action of the polyelectrolyte in the presence of NaDDS is connected with the formation of a polyelectrolyte complex and its adsorption on the quartz surface. As a result of the interaction of PMVP and NaDDS according to the ion-exchange mechanism [35, 36], some of the ionized polyelectrolyte groups appear to be blocked by  $\text{DDS}^-$  ions, and this results in the hydrophobization of the polymer chains. In this case the macromolecules roll into coils compacted by hydrophobic interactions of non-polar radicals of NaDDS. This effect reveals itself most vividly in the  $n=1$  region. With other values of  $n$  the compactization of coils of PMVP macromolecules is less clearly expressed. Proceeding from this, the change in the hydrophobizing action of PMVP with the change in its concentration in the solution (when the values of  $n$  are the same) may be explained by a change in the degree of NaDDS binding by the polyelectrolyte.

The greatest hydrophobization of the quartz surface is observed when the concentration of PMVP solutions is 0.01%. At such a concentration the PMVP macromolecules are in a more developed conformation and can therefore bind a greater amount of NaDDS, which leads to a greater hydrophobization of the polyelectrolyte chains. The quartz surface adsorption of such hydrophobized coils results in higher  $\theta$  values. From this point of view the extremal dependence  $\theta(n)$  is explained by the greatest compactization of coils of PMVP macromolecules, as they interact with NaDDS in the  $n \approx 1$  region [35].

The possibility of adsorption of  $\text{DDS}^-$  ions on the macromolecule coil surface is confirmed by the results of measurement of the quartz  $\zeta$ -potential in aqueous solutions of NaDDS and PMVP mixtures (Fig. 6, curves 1, 2). It is seen from the Figure that in a 0.155% solution of PMVP the quartz surface has a positive charge, probably conditioned by the superequivalent adsorption of the polyelectrolyte macrocation. However, when NaDDS is added, first we see a further increase in the positive values of the quartz  $\zeta$ -potential, which is probably connected with the quartz surface adsorption of compacted PMVP and NaDDS complexes and a rise in the density of the positive charge. When the value of  $n$  is approximately 0.3–0.4, the  $\zeta$ -potential falls and reaches the zero value when  $n$  equals 1. The fall in the  $\zeta$ -potential is accompanied by a rise in the value of the quartz  $\theta$ . Such a change in  $\theta$  may result from the effects of two factors: a decrease in the quartz surface charge [37], and the hydrophobization of PE micelles by SAS anions. A comparison of the figures shows that the greatest value of  $\theta$  corresponds to the zero value of the  $\zeta$ -potential. The result obtained conforms to literature information about the maximum values of  $\theta$  at the quartz IEP [28–30]. A further increase in  $n$  ( $n > 1$ ) shows a change in the quartz surface charge, the negative values of the  $\zeta$ -potential ( $\sim 70$  mV) exceeding those of quartz in a  $1 \times 10^{-4}$  M solution of KCl ( $\sim 56-60$  mV) without PE and SAS. This may be explained proceeding from the assumption that if the mixture contains a greater amount of NaDDS, the ions of the latter are adsorbed by the PMVP coils, orienting their polar groups into the aqueous phase [34]. The compound complex formed will have an overall negative charge because of the superequivalently adsorbed  $\text{DDS}^-$  ions, and its quartz surface adsorption causes a decrease in  $\theta$ .

Inversion of the  $\zeta$ -potential sign and a decrease in  $\theta$  are also observed in mixtures PAA and PMAA with CTMABr (Fig. 6, curves 3–5). In this instance the inter-

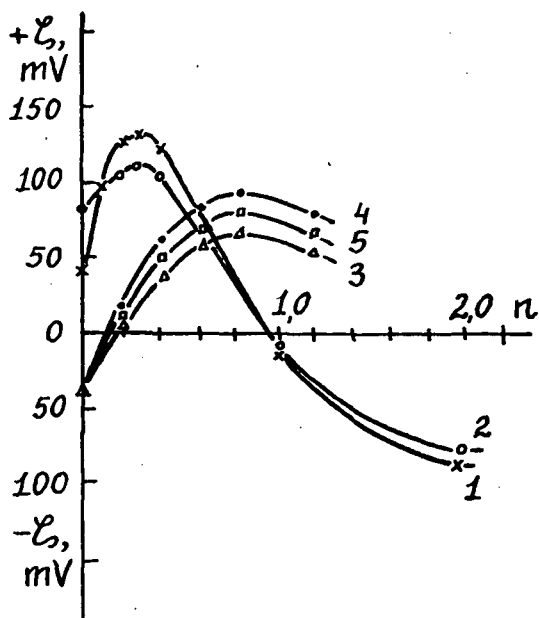


Fig. 6. Dependence of quartz electrokinetic potential upon the relative concentration of SAS in a mixture with polyelectrolytes:

1. PMVP with  $M_n = 190.000 + \text{NaDDS}$   $C_{\text{PMVP}} = 0.155\%$ .
2. PMVP with  $M_n = 340.000 + \text{NaDDS}$   $C_{\text{PMVP}} = 0.155\%$ .
3. PAA with  $M_n = 17.300 + \text{CTMABr}$   $C_{\text{PAA}} = 0.072\%$ .
4. PAA with  $M_n = 1,000.000 + \text{CTMABr}$   $C_{\text{PAA}} = 0.072\%$ .
5. PMAA with  $M_n = 1,000.000 + \text{CTMABr}$   $C_{\text{PMAA}} = 0.086\%$ .

action also occurs according to the ion-exchange mechanism and the maximum degree of SAS binding by the polyelectrolyte takes place when the concentration of the latter is  $\sim 0.01$  M and  $n = 0.1 - 0.2$  [36].

When the concentrations of PMVP and NaDDS are high (0.465%), the polyelectrolyte macromolecules are extremely compact, and the SAS is in the form of micelles. The interaction of compact coils of the polyelectrolyte and SAS micelles apparently leads to the formation of hydrophilic complexes, whose quartz surface adsorption does not result in the hydrophobization of the latter (Fig. 4, curve 3).

Thus, the obtained information shows the possibility of widening the ways of regulating physicochemical properties of solid surfaces with the help of polyelectrolyte complexes of SAS.

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## МОДИФИЦИРОВАНИЕ ПОВЕРХНОСТИ КВАРЦА ВОДНЫМИ РАСТВОРАМИ ПОЛИЭЛЕКТРОЛИТОВ И ПОВЕРХНОСТНО-АКТИВНЫХ ВЕЩЕСТВ

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Изучено влияние анионных [полиакриловая (ПАК), полиметакриловая (ПМАК) кислоты] и катионных [гидрохлориды поли-2-метил-5-винилпиридина и сополимера — 2-метил-5-винилпиридина с бутилметакрилатом (МВП-БМА)] полиэлектролитов (ПЭ), а также их смесей с катионным [цетилтриметиламмоний бромистый (ЦТАБ)] и анионным (додецилсульфат натрия (ДДС) поверхностно-активными веществами (ПАВ)] на поверхностные свойства кварца. Наибольшее модифицирующее действие ПЭ и их смесей с ПАВ проявляется тогда, когда они предварительно наносятся на поверхность кварца из водного раствора и сушатся. Модифицирующее действие ПЭ и ПАВ проявляется в изменениях краевого угла смачивания водой и электрокинетического потенциала кварца.