ADSORPTION OF POLY(VINYL ALCOHOL) AND ITS EFFECT ON THE ELECTROSURFACE CHARACTERISTICS OF SOME OXIDES

By

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The adsorption of poly(vinyl alcohol) (PVA) from dilute (up to 3 g/l) aqueous and electrolyte solutions onto some oxides, and its effects on the surface charge density σ and the ζ-potential, have been studied. With rise of the acetate group content (from 2% to 18%) in the PVA molecule the adsorption increases on Fe_2O_3 and gives a maximum at 12% on ZnO. The adsorption values on ZnO, NiO, Fe_2O_3, ZrO_2 and MnO_2 increase with the pH, whereas on SiO_2 the opposite picture is observed. The assumption is made that on the surface of oxides with high points of zero charge (ZnO) the PVA adsorbs on the water layer tightly bound with the surface, without squeezing out the water molecules. The adsorption data are explained from the standpoint of the formation and adsorption of aggregates of macromolecules. The effect of PVA adsorption on the ζ-potential of quartz is due to the shift of the slipping plane toward the solution as a result of the formation of thick polymer sheaths around the particles, whereas for ZnO this effect operates together with the changing of the surface charge density.

Introduction

The increasing interest in polymer-containing disperse systems is due to the important role of these systems in different branches of modern technology. Water-soluble polymers are widely used as effective flocculants and stabilizers, soil-improvers and structure-regulating agents, *etc.* In particular, poly(vinyl alcohol) (PVA) is used in the ceramic, metallic and oxide power industries, and in the building materials industry as plastifiers and adhesives. The development of a scientific basis for the regulation and prognosis of the properties of such dispersions presupposes the investigation of PVA adsorption on the surface of oxides. Valuable information on the structure of adsorption layers may be obtained from electrosurface measurements.

Technical oxides represent complex multicomponent systems with different contaminations and with low specific surfaces; therefore, as the first stage, we have studied the adsorption of PVA from dilute (up to 3 g/l) solutions onto the surfaces of the individual oxides which are the main components of such materials. In some cases the adsorption measurements were completed by electrokinetic and potentiometric experiments.

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Experimental

Materials. Industrial samples of PVA were used. The parameters of the macro-molecules in aqueous solutions, determined from viscosimetric data, are listed in Table I. The polymer was dissolved at 80° during 3—4 hours. PVA working solutions were prepared from stock solutions of 10 g/l concentration. Since the structure and the properties of PVA solutions change with time, the applied solutions were stored for 7 days before use. The polymer and salt solutions were mixed one day before the experiments.

Table I

The Characteristics of the Samples of Polyvinyl Alcohol

Sample of PVA	The content of the acetate groups, %	$[\eta]$, dl/g	$\overline{M}$
PVA-1	2	0.70	56,000
PVA-2	12	0.59	50,000
PVA-3	18	0.57	59,000
PVA-4	18	0.76	98,000

Industrial oxides of zinc, zirconium, iron and silicon were investigated. According to spectral analysis, the admixture content was not more than 0.3% in Fe_2O_3, and less than 0.1% for other oxides. The BET surface areas for ZnO, Fe_2O_3, ZrO_2 and SiO_2 were 4.4, 9.0, 2.2 and 175 m²/g, respectively. For electrokinetic measurements quartz powder with a particle diameter of 45—80 nm was used. The quartz was preliminarily ground, washed with concentrated HCl and distilled water, ignited and fractionated.

All the reactants were of chemical grade and were used without further purification.

Methods. The adsorption values were calculated from the material balance of PVA in the solution before and after its contact with the adsorbent. The polymer concentration was determined by a colorimetric method according to [1]. The solid phase was separated from the solution by centrifugation at 2000 g during 3—4 min. The contact time in all adsorption, electrokinetic and potentiometric experiments was 24 hours.

The electrokinetic potential was determined by the potential streaming method described in detail in [2]. Under the experimental conditions the value of the Rel criterion [3] (Rel$=e^{\psi\sigma/2}-1/\varkappa a$, where a is the mean radius of the capillary, $\varkappa$ is the reciprocal Debye thickness, and $\overline{\psi}_\delta$ is the dimensionless Stern potential $=\psi ez/kT$; for ψ_δ the measured ζ-potential without polymer addition was taken) was considerably smaller than unity; therefore, the correction on polarization of the electric double layer (DL) could be neglected [3], and the ζ-potential values could be estimated according to the Smolouchowsky formula. The conductivity of ZnO particles themselves is insignificant ($\approx 10\%$) in comparison to the general conductivity of a moisture-saturated diaphragm. Nevertheless, taking into consideration such a complication, the obtained values of ζ were used only for qualitative assessment of the effect of PVA adsorption on the DL structure of a ZnO surface.

Potentiometric titration was conducted by the rapid titration method in KCl solutions, as described in [4, 5]. In the case of ZnO the titration was restricted to pH = 8—10, and the correction for dissolution was introduced according to [6]. The following points of zero charge (p.z.c.) (in pH units) were obtained: SiO_2 3.1; ZrO_2 4.0; ZnO 8.9; Fe_2O_3 6.0; these values are in good accordance with data reported in the literature.

pH measurements were carried out with glass electrodes and a "pH—340" pH-meter.

The viscosity of polymer solutions was measured with an Ubbelohde viscosimeter at 25°.

Results

Adsorption isotherms. Figures 1 and 2 show the adsorption isotherms of PVA samples with different acetate group contents on zinc oxide and iron oxide surfaces. For PVA-1 and PVA-2 on ZnO they are characterized by a rapid rise in the low concentration region, reaching a plateau at high concentration. The shapes of the isotherms for PVA-3 and PVA-4 are more complex, with a maximum and a minimum (Fig. 1). Depending on the adsorption values on ZnO, the samples investigated
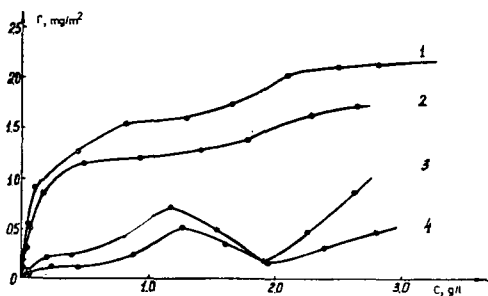

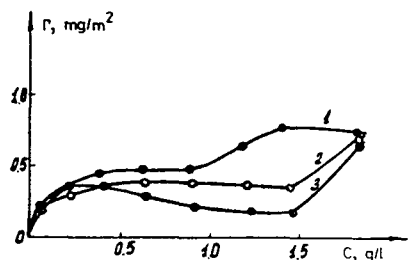Fig. 1. Adsorption isotherms of PVA on ZnO surface: PVA-2 (1), PVA-1 2), PVA-3 (3), PVA-4 (4)

Fig. 2. Adsorption isotherms of PVA on Fe_2O_3 surface: PVA-4 (1), PVA-2 (2), PVA-1 (3)

can be arranged in the order PVA-2 > PVA-1 > PVA-3 ≈ PVA-4. The adsorption value increases with the molecular weight more weakly than with the change of the acetate group content of the molecule (Fig. 1). For iron oxide the adsorption values Γ follow the sequence PVA-4 > PVA-2 > PVA-1. The analogous range for PVA adsorption on aerosil particles was obtained in [7]. The Γ values on Fe_2O_3 are less than on ZnO. This may be due to the considerable aggregation of particles in iron oxide suspensions with polymer additions.

The different adsorption behaviours of the oxides are revealed in the dependence of Γ on the pH (Figs. 3 and 4). In the case of zirconium oxide the adsorption increases with the pH. Such a dependence was obtained for PVA adsorption on zinc, aluminium, nickel and manganese oxides as well, whereas for iron and titanium oxides Γ depends only slightly on the pH. Silica is the only oxide for which the decrease of PVA adsorption with rising pH was observed (Fig. 4).
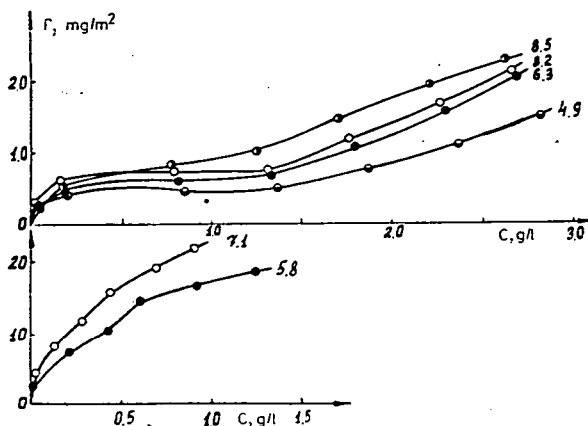
Fig. 3. Adsorption isotherms of PVA-1 on ZnO surface.
pH values are indicated

The adsorptions of PVA-2 and PVA-4 from salt solutions onto the ZnO surface are shown in Fig. 5. The increase of the KCl concentration has practically no influence on the shapes of the isotherms at low PVA content (under 0.1 g/l), but at high polymer concentrations it leads first to the decrease and then to the gradual increase of the adsorption values. At the same time, with the increase of the KCl concentration the bends in the adsorption isotherms disappear or become smooth, then they appear again and shift to lower PVA contents (Fig. 5).
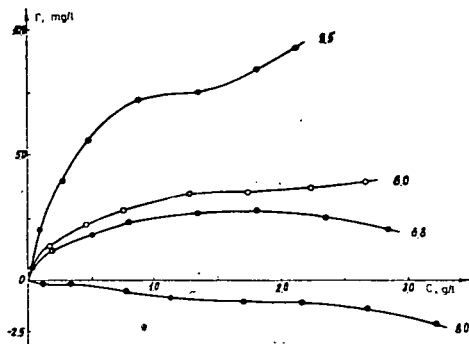

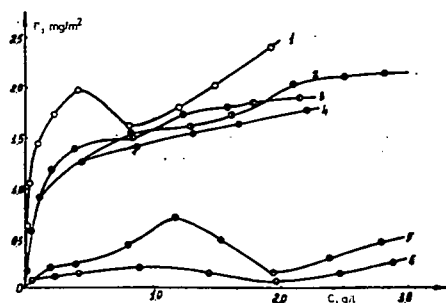*Fig. 4.* Adsorption isotherms of PVA-1 on aerosil surface. pH values are indicated

Fig. 5. Adsorption isotherms of PVA on ZnO surface from aqueous salt solution. Curves 1, 2, 3, 4 — PVA-2; 5, 6—PVA-4. Concentration of KCl in the solutions: $1 — 10^{-2}$ M; $2, 5 — 0$; $3 — 10^{-3}$ M; and $4, 6 — 5 \cdot 10^{-4}$ M

Surface charge density. The potentiometric titration of SiO_2 in KCl solutions shows that PVA adsorption does not change the surface charge density, σ of silica. The adsorption of PVA-1 from 10^{-2} M KCl shifts the p.z.c. of zinc oxide to higher pH and, consequently, σ to more positive values.

Electrokinetic potential. PVA adsorption affects the ζ-potential of oxide surfaces considerably, but in a rather complicated way (Figs. 6 and 7). In the case of SiO_2, for all the KCl concentrations investigated the marked decrease of ζ at low PVA content (under 0.2 g/l) region is observed. Then, with the increase of the PVA content, the dependence of the ζ-potential on the polymer concentration shows a maximum and a minimum. These extrema regions become less pronounced with the increase of the electrolyte concentration in the system. The complex character of the $\zeta(C_{PVA})$ plot for zinc oxide is observed too (Fig. 7). For example, small additions of PVA-4 cause the increase of ζ to values higher than the initial ones. In general, the elevation of the ionic strength leads to the decrease of the ζ-potential, which at high polymer concentrations reaches a value of zero.
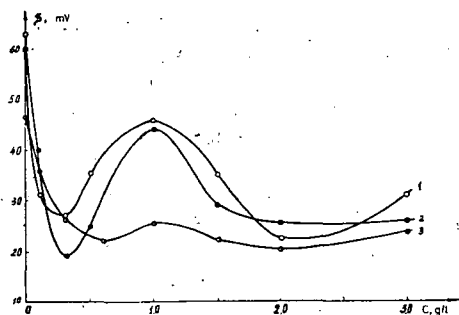

Fig. 6. Dependence of the ζ potential of quartz on the PVA-2 concentration in KCl solution: $1 - 0$; $2 - 5 \cdot 10^{-4}$; $3 - 10^{-3}$ M KCl
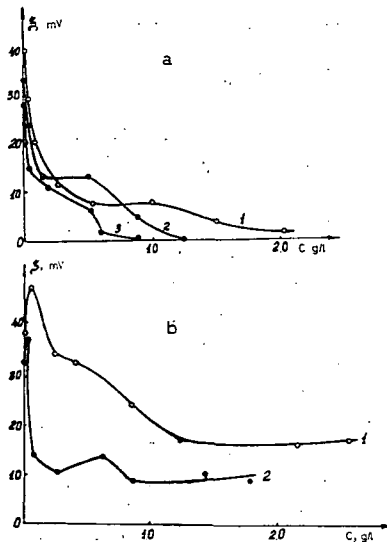
Fig. 7. Dependence of the ζ potential of ZnO on the equilibrium concentration of PVA in KCl solutions: a) PVA-2; b) PVA-4. Concentration of KCl: 0 (1), $5 \cdot 10^{-4}$ (2), 10^{-3} M (3)

Despite the rather complex character of the $\zeta(C_{PVA})$ dependences, in general a correlation exists between the adsorption and electrokinetic data: the addition of better adsorbable samples of PVA causes a more marked decrease of the ζ-potential; the shift of the bend in the $\zeta(C_{PVA})$ curves in KCl solutions corresponds to the shift of the bend in the adsorption isotherms (*cf.* Figs. 5 and 7).

Discussion

According to [9], the second virial coefficients of PVA in aqueous solutions, depending on the acetate group content in a molecule, may be put in the following order $A_2 (12\%) > A_2 (2\%) > A_2 (18\%)$. In other words, the quality of water as a solvent for the polymers studied decreases in this sequence. Thus, it might be ex-

pected that the adsorption values would increase in this order. However, the expected data point to the opposite picture (Fig. 1). This is, perhaps, explained by two factors.

A number of papers [9, 10] indicate that in aqueous solutions a tightly-bound adsorbed water layer (so-called W-layer) is present on oxide surfaces; this is not destroyed even by the addition of 90—95% of such organic solvents as alcohol, acetone, or dioxane [10], *i.e.* solvents which can firmly bind the water molecules with H-bonds. Thus, it is quite reasonable to suppose that in the cases under consideration the polymer adsorbs on the water layer bound with the surface due to the formation of hydrogen-bonds. A polymer possessing a greater affinity for water will adsorb better. The additional polarization of the water molecules in the W-layer affords the hydrogen-bond with it energetically more advantageously than with the water molecules in the liquid phase. Such a mechanism is the more probable because, as follows from [11], the energy of hydration of oxide surfaces increases with the increase of the p.z.c. This is especially valid for zinc oxide, which has a high value of the p.z.c. (8.9 pH units in our case).

On the other hand, it is known [12, 13] that aqueous PVA solutions have a complicated supermolecular structure which depends, among other factors, on the polymer concentration. At low PVA concentration the adsorption of individual macromolecules predominates and the formation of the supermolecular structure is the competitive process. In this region, polymer samples having a greater affinity for the solvent and giving less aggregates in solution, *i.e.* PVA-1 and PVA-2, will adsorb better. With the increase of the PVA concentration, the formation and adsorption of polymer aggregates will play a greater and greater role, which leads to the bends and extrema in the adsorption isotherms. In PVA-3 and PVA-4 solutions the formation of supermolecular structures begins at lower polymer contents than in the cases of PVA-1 and PVA-2. This results in smaller adsorption values for PVA-3 and PVA-4, narrowing the plateau at low polymer concentration, and in the complicated forms of the adsorption isotherms for these samples.

The assumption concerning the adsorption of polymer on the bound water layer is not strictly valid for iron oxide, on which the adsorption of PVA increases with the acetate group content per molecule. As in the case of the adsorption of PVA on silica [7], such regularities may be explained by the fact that even at low PVA-4 concentrations the degree of aggregation of macromolecules is high, and their adsorption leads to the large values of Γ for this sample. At the same time, the competition between adsorption and aggregation of macromolecules leads to a considerable decrease of Γ at PVA-1 concentrations higher than 0.4 g/l (Fig. 2).

The point of view exists that the adsorption of PVA on the surface of silica [14, 15] or metal oxides [16] is due to the formation of hydrogen-bonds between the OH groups of the polymer chain and non-dissociated acidic (basic) centers of the surface. If this is valid, the increase of Γ with approach to the pH of the p.z.c. should be expected (taking into account the shift of the p.z.c. by polymer adsorption). This model is in accordance with our results obtained for zinc, nickel, aluminium and silicon oxides (Fig. 4). At the same time, it does not explain the dependence of Γ on the pH for iron and titanium oxides and, especially, for oxides with low p.z.c. (MnO_2, ZrO_2); for these two oxides the adsorption of PVA continues to increase while the pH value rises by four units in comparison with the

p.z.c. (Fig. 3). The mechanism of adsorption of PVA on the surface of mineral oxides will be considered in detail in the following publications.

The standpoint on the adsorption of aggregates of macromolecules gives a reasonable explanation of the effect of electrolytes on the adsorption of PVA. With rising electrolyte concentration the quality of the solvent becomes worse; this effect promotes the formation of aggregates. The competition between the processes of aggregation and adsorption in $5 \cdot 10^{-4}$ M KCl is intensive, and this causes the decrease of Γ (Fig. 5). The disappearing of bends in the isotherms is evidence of the decrease in the adsorption of the aggregate. With further increase of the KCl content, the quality of the solvent gets poorer, which intensifies the adsorption of aggregates. This process is revealed in the PVA concentrations, which are the lower, the higher the concentration of salt. Accordingly, the bend in the isotherm shifts to smaller PVA concentrations and the Γ value begins to increase sharply (Fig. 5). Thus, the concept on the formation and adsorption of polymer aggregates developed by Lypatov and co-workers [17] enables us to explain the peculiarities of PVA adsorption from aqueous and electrolyte solutions onto the surfaces of oxides.

In [18—20] it was shown that the effect of adsorption of non-ionic polymers on the ζ-potential of disperse particles is due to the changes of the surface charge density and the shift of the slipping plane into solution as the result of formation of thick polymer sheaths around particles. The fact that PVA does not change the σ of SiO_2 shows that the decrease of the ζ-potential with polymer adsorption in this case is due to the second factor mentioned. The appearance of extrema in the $\zeta(C_{PVA})$ curves is connected with the changing of the polymer layer thickness, which reflects the changing of the dimensions of adsorbable kinetic units. In contrast, the appearance of extrema regions in the $\zeta(C_{PVA})$ curves is due to the simultaneous operation of both factors considered. The shift of σ to more positive values when PVA adsorption occurs leads to the increase of positive ζ-potentials; this is observed in experiments at really low electrolyte concentrations (Fig. 7). With increase of the PVA content in the system, the effect of the shift of the slipping plane predominates and the ζ potential decreases.

The increase of the ionic strength of the solution affects the structure of the double layer and the structure of the polymer sheath as well. With the assumption that the slipping plane coincides with the polymer sheath boundary, the calculated values of the thickness of the PVA-2 layer on the surface of quartz are 15—100 Å, depending on the KCl and PVA concentrations in solution. Despite some increase of polymer adsorption with electrolyte addition, the thickness of the adsorption layer decreases, which probably reflects the accumulation of less compact aggregates on the surface. Hence, the decrease of the ζ-potential of SiO_2 in an aqueous salt solution of PVA-1 is due not only to the thickening of the polymer adsorption layer, but to the compression of the DL as well. The latter factor promotes the falling of the ζ-potential in the case of zinc oxide too (Fig. 7).

The data presented in this work demonstrate the correlation between non-ionic polymer adsorption and the electrosurface characteristics of oxides. The mechanism of adsorption and its effect on the parameters of the double layer are probably not the same for different oxides. The further investigation of this problem is of great theoretical and practical interest.