Effect of the Molecular Weight of Polyvinyl Alcohol on Some Adsorption Parameters in the Titania-Polymer Solution System

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Fractions of polyvinyl alcohol (PVA) obtained by separation of the PVA samples of the mean molecular weight of 72000 and 125000 have been studied.

The effect of the molecular weight of PVA, pH value and concentration of the solution on the adsorbed amount and the thickness of the adsorption layer of PVA (δ) were measured. The value of δ was determined from the viscosity change of titania suspensions with adsorbed PVA in relation to the same suspensions without PVA. The volume occupied by a polyvinyl alcohol molecule at the interface region was evaluated from the adsorbed amount and the value of δ. Thus calculated volume was then compared with the volume occupied by a PVA molecule in the bulk solution.

INTRODUCTION

Different experimental methods are applied in the studies of the dispersed solid-polymer solution system according to the aim of these studies. The obtained information may have a qualitative character and may be used *e. g.*, for practical purposes in different industrial processes. More quantitative characteristics of the studied processes occurring at the solid-polymer solution interface, which take into account the chain conformations changes, enables a comparison of the measured parameters with the theoretical ones. The above comparison requires a well defined polymer of monodisperse molecular weight. Therefore, before adsorption experiments, the commercial polymer should be separated, purified and number of the functional groups determined. The physical and chemical properties of the studied adsorbent should be also well defined. The above requirements make the studies very time consuming but many authors have recently studied such well defined systems.[1-5]

The results presented in this paper were obtained for the system with polyvinyl alcohol which was separated into fractions before the adsorption studies. Fractions of a possibly narrow range of molecular weight and as low as possible content of the acetate groups were chosen. During the adsorption experiments with the PVA prepared in this way at the surface of purified titania, the dependence of adsorption and the thickness of adsorption layer on the molecular weight of polymer, pH and concentration

of the solution was studied. Some results have been compared with the previous ones which were obtained using not separated PVA.[6,7]

Crystalline titanium dioxide from Ventron, GMBH Karlsruhe was applied as adsorbent. Before the adsorption studies it was washed with ammonia water obtained by means of isothermal distillation of concentrated ammonia water. The titania was then washed with doubly distilled water until the conductivity of the supernatant differed from the conductivity of the applied water, i. e. about 1.5 μS.

Diffraction analysis shows that the titania consists of rutile (95%) and anatase (5%). The BET specific surface area equal 1.5 m²/g.

The polyvinyl alcohol (PVA) was from Merck, Darmstadt Germany and Koch-Light Lab., Colnbrook England. Samples of the mean molecular weight of 72000 and 125000 underwent separation in order to obtain the fractions of a possibly narrow interval of molecular weight. The separation was carried out using a column of 25 × 900 mm at 20 °C. The column was packed with the chromatographic gel Sephadex G-150 and calibrated with monodisperse dextrane of molecular weight 40000 and 110000. The details of separation are described elsewhere.[8]

The molecular weight of particular fractions was determined by means of viscosimeter, using the Mark-Houwink equation

$$[\eta] = k \cdot M^{\alpha}$$

where k and α are constants, M-molecular weight, $[\eta]$ — intrinsic viscosity. The values of k and α were assumed, after Garvey at al.[9], to be equal to $2.7 \cdot 10^{-4}$ and 0.71, respectively.

Viscosity was measured by means of the rotation viscosimeter Rheotest-2 and Hoppler viscosimeter BH 2, Medingen DDR.

For further studies the samples of molecular weight 36000, 88000, 120000 and 130000 were chosen. The content of acetate groups in the above samples did not exceed 0.5%. This content was determined by means of hydrolysis in 0.1 M NaOH solution, the excess of which was titrated with 0.1 M HCl using bromothymol blue as indicator. Conductivity of the chosen polymer fractions ranged between 2 and 5 μS. The method of adsorption measurements in the titania polyvinyl alcohol system for different concentrations, molecular weight and pH-values was similar as described in the previous papers.[6,7]

In order to study the effect of the molecular weight of the polymer on its adsorbed amount and the thickness of the adsorbed layer at the titanium dioxide surface, four fractions of molecular weight between 36000 and 130000 have been examined. These fractions were obtained through separation of two PVA samples of molecular weight of 72000 and 125000, respectively. Figure 1 presents the adsorption isotherms of the chosen PVA fractions at pH = 7.The same Figure presents also the results for the samples not separated into fractions. The range of plateau is achieved at the PVA concentration of about 400—500 ppm for the PVA fractions of a relatively narrow range of molecular weight, i. e., obtained by separation in a column. In the case of not separated PVA of the mean molecular weight of 125000, the plateau has not been observed in the studied concentration range. It suggests a relatively high degree of polydispersity of this sample.[1]

For such a polymer the gradual increase in the adsorbed amount of PVA does not result from an increase in the overall concentration of the polymer in the solution, but it is rather an effect of competitive adsorption between long and short polymer chains. Therefore, the magnitude of adsorption is determined by the absolute amount of the large — molecule
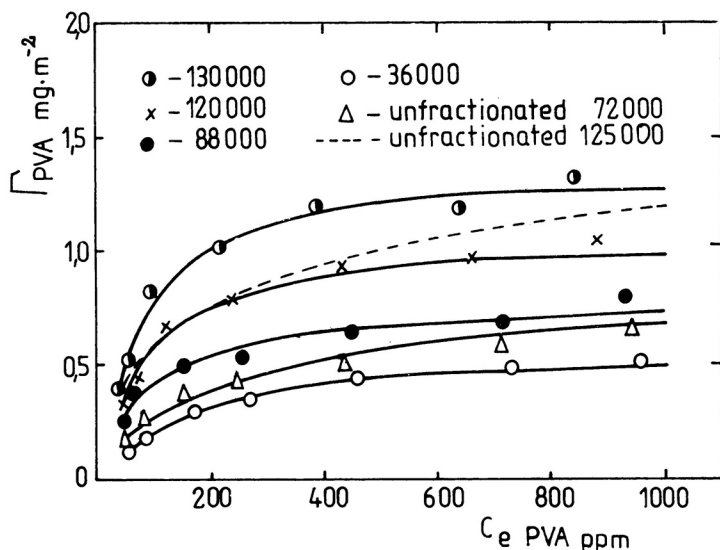
Figure 1. Adsorption isotherms of PVA on titania at pH = 7.

polymer, since the molecules are preferentially adsorbed, thus removing the smaller ones from the surface. Therefore, some suggestions concerning the polydispersity of the polymer may be drawn from the shape of the adsorption isotherms.

For the PVA of the molecular weight of 130000 the effect of pH on the polymer adsorption was studied (Figure 2). The polymer adsorption is
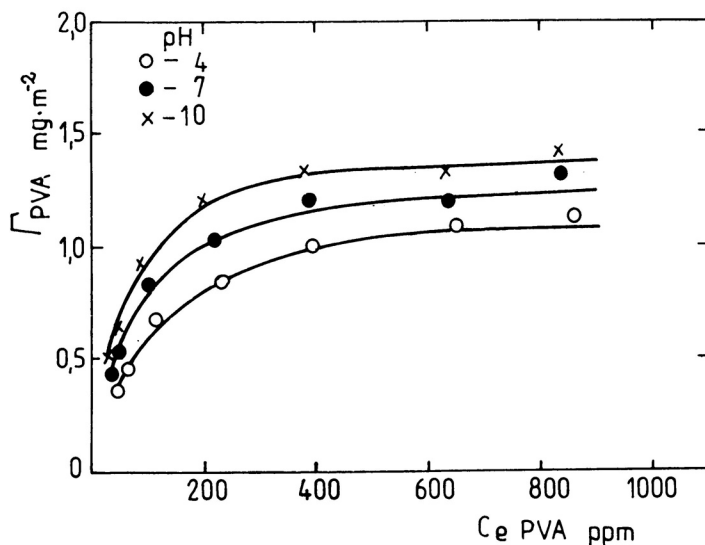

Figure 2. Adsorption isotherms of PVA of molecular weight 130000 on titania at different pH values.

slightly increased when the pH value of the solution increases. This dependence follows from the change of surface properties of the surface groups and the change of their hydration.[10,11] In the case of titania, the increase of the number of the TiO^- groups at higher pH values may favourably affect the character and magnitute of the polymer-solid interactions.

Figure 3 shows the influence of PVA molecular weight on its adsorption at a constant equilibrium concentration equal to 500 ppm. The adsorbed amount is expressed as the number of equivalent monolayers (Θ). In order to calculate the Θ values, 26 $Å^2$ [12] for one PVA segment was assumed in a closely packed monolayer. It gives 0.28 mg m^{-2} for monolayer capacity. Comparing thus determined Θ values with those calculated theoretically from, the Scheutjens-Fleer theory[13,14] it was found that for PVA having molecular weight of above 100000 the experimental values exceed the theoretical ones. The latter are 2.47 and 2.54 for the molecular weight of 120000 and 130000, respectively. In theoretical calculations, it has been assumed that the value of Flory-Huggins polymer-solvent interaction parameter (χ) equals 0.465,[9] differential adsorption energy parameter (χ_s) equals 3 and the lattice parameter λ_o equals to 0.5.
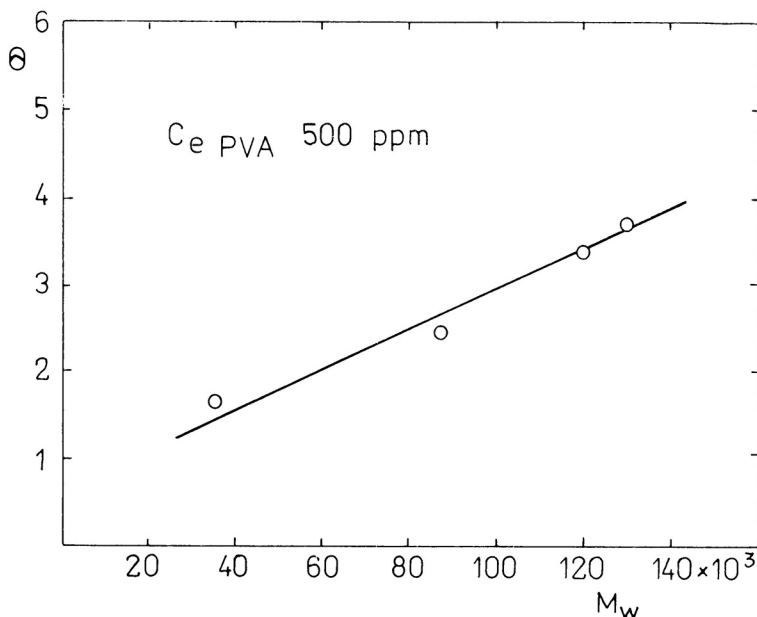

Figure 3. Adsorption magnitude of PVA on titania expressed by means of the number of equivalent monolayers as a function of molecular weight.

Under the same circumstances, the experimental values obtained in the system PVA-polystyrene latex[8] were even higher than in the case of the titania-PVA system. It seems that the value of Θ depends considerably on the nature of the adsorbent and the nature of interactions between the adsorbent and polymer molecules. Taking the above suggestion into account, the theoretical calculations of Θ[13,14] have been repeated assuming the value

of χ_s characterizing the adsorption energy to be equal to 6 and 9 but also in that case the theoretical values of Θ were still lower in relation to the experimental ones. This is probably due to the configuration of polymer chains at the solid-solution interface, which is particullarly important in the case of long chains and, therefore, high molecular weight.

The differences in Θ may also be due to the fact that PVA is a copolymer that can appear in a different adsorption relative to homopolymer. Another factor which can influence the measured adsorption may be connected with a tendency of highly-hydrolized polyvinyl alcohol to precipitate under some conditions. In order to characterize the macromolecules adsorbed at the titania-solution interface more exactly, the thickness of the adsorption layer (δ) of PVA at the solid surface was measured. The measurement of δ was carried out by means of a viscosimeter.

The changes of viscosity of titania suspension with adsorbed PVA in relation to the suspension of pure titania provide the required data because the increase of the radius of titania particle corresponding to the thickness of adsorption layer causes a higher volume fraction (Φ) of dispersed solid which is connected with the viscosity of suspension according to the Einstein equation.

$$\eta/\eta_0 = 1 + k\Phi$$

where η — suspension viscosity, η_0 — viscosity of liquid phase, k — Einstein coefficient.

The more accurate equation describing the dependence of relative viscosity on the volume fraction of solid is,[15]

$$\eta/\eta_0 = 1 + k\Phi + k'\Phi^2 + \ldots$$

Magnitude of Einstein coefficient (k) depends upon the suspension concentration, shape and radius of the dispersed particles. This coefficient is equal to 2.5 only in very diluted suspensions. In more concentrated suspensions its value may change markedly. Also, a decrease of the particle radius leads to an increase in k value.[11] Taking this into account it was neccesary to determine the k value for the TiO_2 used.

For the studied system the value of coefficient k was determined by the measurement of viscosity (η) of a series of suspensions of different volume fractions of titania and of the pure liquid (η_0) — see Figure 4. For the titanium dioxide particles of radius of 0.5 μm coefficient k equals 16.2. The measurements of the thickness of adsorption layers of PVA were carried out at the titania volume fraction (Φ) equal to 0.012 and at pH = 7 examining different molecular weights and initial concentrations of polyvinyl alcohol. The calculated values of the thickness of adsorption layers are presented in Table I.

The values listed in Table I are the average of five successive experiments. The experimental error amounted 0.5—1%. Comparison of the values of δ leads to the conclusion that an increase of molecular weight or concentration of PVA within the same fraction causes an increase of the thickness of adsorption layer. From the adsorbed amount of PVA (Γ) and thickness of the adsorbed layer it was possible to calculate the volume occupied by the adsorbed PVA molecules, and hence the average volume
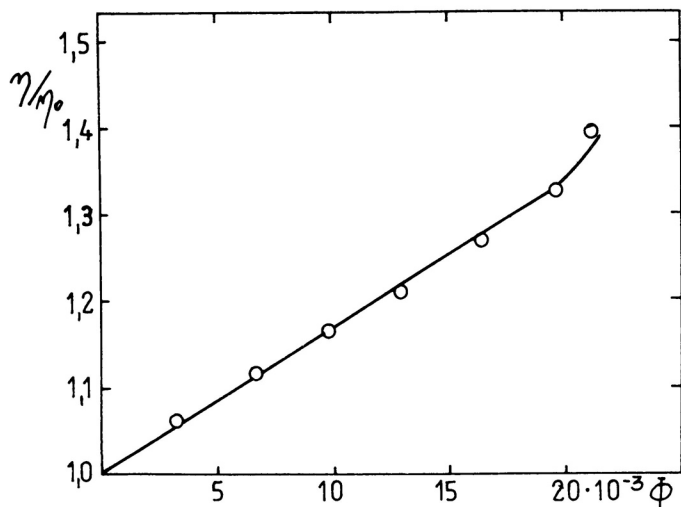
Figure 4. Relative viscosity of suspensions as a function of the volume fraction of titania.

TABLE I

Properties of adsorbed PVA

molecular weight of PVA	initial concentration of PVA (ppm)	Γ_{PVA} (mg/m^2)	δ (nm)	R_s (nm)
130000	100	0.49	11.9	10.7
	300	1.04	20	9.9
	1000	1.33	27.9	10.2
88000	100	0.37	7.4	8.8
	300	0.53	11	8.9
	1000	0.86	17.5	8.9
36000	300	0.35	8	6.8
	1000	0.5	13	6.7

for one molecule. This volume may be expressed as R_s, the radius of equivalent sphere. Values of R_s within the same fraction remain constant, *i. e.* it is independent of the number of adsorbed molecules. In the case of higher adsorption, the polymer chain is probably changed, *i. e.* directed towards the liquid phase. The values of R_s may also be compared with the corresponding hydrodynamic radii (R_h) describing the dimensions of macro-molecules in the bulk liquid. The value of R_h equals to

$$R_h = f\,(s^2)^{1/2}$$

where f is a constant value, independent of the molecular weight of polymer. In the present calculation this parameter has been assumed to be equal to 0.59.[9] The value of $(s^2)^{1/2}$ represents the root mean square radius of gyration and may be evaluated from the molecular weight and viscosity $[\eta]$.

The evaluated radii R_h for the molecular weights 36000, 88000 and 130000 are 4.8, 7.7 and 10 nm, respectively, so they are very close to the corresponding values of R_s. Since R_h and R_s are almost equal, it seems that in the examined system in the studied range of concentrations, there is no interpenetration or compression of the adsorbed molecules.

CONCLUSIONS

It follows from the present study of the titania-PVA solution system that the adsorbed amount depends strongly on the molecular weight of the polymer. Primary conclusions concerning the degree of polydispersity of the molecular weight of polymer may be drawn from the run of adsorption isotherms. An increase of the molecular weight and concentration of the polymer leads to an increase of the thickness of adsorption layer.

It follows from the comparison of the hydrodynamic radius of the polymer molecule in the bulk solution and the radius evaluated from the volume occupied by an adsorbed molecule that interpenetration of the adsorbed chain does not occur in the studied system.

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SAŽETAK

Utjecaj molekulske mase polivinilalkohola na neke adsorpcijske parametre u sustavu TiO₂-polimerna otopina

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Ispitivani su efekti molekulske mase polivinilalkohola (PVA) ($M_r = 72\,000$ i $125\,000$), pH i koncentracije otopine na maksimalnu adsorpciju i debljinu adsorpcijskog sloja PVA (δ). Vrijednost δ određena je iz promjene viskoznosti suspenzija TiO₂ u ovisnosti o adsorbiranom PVA, u usporedbi s jednakim suspenzijama bez PVA. Volumen koji zauzima jedna molekula PVA na međupovršini određen je iz maksimalne adsorpcije i vrijednost δ, i uspoređen s volumenom koji zauzima jedna molekula PVA u glavnini otopine.