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## The Structure of Polyvinyl Alcohol Adsorption Layers at Interfaces with Benzene in Connection with Stability of Concentrated Emulsions\*

V. N. Izmailova, G. M. Pismennaya, T. F. Busol, and B. N. Tarasevich

Department of Colloidal Chemistry, Moscow State University, Leninsky Gory,  
Moscow, USSR

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Determination of PVA adsorption on interfaces between PVA and benzene was performed. Adsorbed layers are formed under dynamic conditions emulsions were prepared by vibrocomminution and ultrasonic dispersion). Adsorption data are used in calculation of the area per adsorbed molecule and the thickness of interfacial adsorption layers. Adsorption isotherms are compared with rheological parameters of adsorbed layers. On the basis of reported data on the distribution of adsorbed segments of PVA molecules, the interfacial thickness of the adsorbed layer is estimated to be several hundreds of Å in a form of gel. The formation of the gel is a result of condensation and phase deemulgation which is in agreement with a similar mechanism of gel formation in solution with diffuse distribution of polymer segments in the adsorbed layer. It is shown that at least one monolayer must cover drops of benzene in order to obtain stable emulsions. Kinetic parameters and the energy of activation of coalescence are dependent on PVA adsorption.

The structure of adsorption layers of surface active polymers at liquid interfaces is very important from the standpoint of the development of theories of foams and emulsions stability, as well as in connection with industrial application of polymers as stabilizers and emulgators in processes of emulsion polymerization and microcapsulation.

Since polyvinyl alcohol (PVA) is a very well-known polymer, adsorption from its solutions appears to be studied most of all<sup>1,2</sup>. The PVA molecule has no charge, so it is unnecessary to consider electrostatic effects<sup>3</sup>. The investigations were not confined to PVA adsorption at interfaces of its solutions with solids and with air. Lankveld and Lyklema<sup>3-5</sup> report certain features of PVA adsorption from emulsions by drops of paraffine hydrocarbons.

The present investigation is an attempt to estimate the structure and properties of polyvinyl alcohol (PVA) adsorption layers formed at liquid interfaces between PVA solutions and benzene. We used adsorption measurements, estimation of rheological parameters<sup>6</sup> and thickness of interfacial adsorption layers, and we also considered the influence of these parameters on stability

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of concentrated emulsions. Data on the structure of PVA adsorption layers, on their composition, on the type of molecular packing in them and thus on molecular mobility of chains on the surface of disperse phase particles may be obtained from adsorption studies. Systems where adsorption can be conveniently measured are those with a developed interfacial surface. In our research we studied adsorption on drops of emulsions obtained by different methods (vibrocomminution and ultrasonic dispergation).

Molecular weight of PVA used was 70 000; the substance was additionally purified by precipitation from aqueous solutions with acetone. The solutions were prepared by staying at 90 °C for 1.5 hours and filtration through glass filters G-4. The non-polar dispersion medium used was benzene («pure for analysis» brand for crioscopy,  $d = 0.879 \text{ g/cm}^3$  at 20 °C).

The size distribution of drops was determined by the «Millipore» particle counter. The results were used, first, to calculate adsorption (from specific surface of the drops,  $S_{sp}$ ) and, second, to study the coalescence process (by the number of drops in the emulsion,  $N$ ).

PVA adsorption ( $\Gamma$ , mol/cm<sup>2</sup>) on the emulsion drops of benzene in PVA aqueous solutions was determined from the material balance according to the formula:

$$\Gamma = \frac{(c_0 - c_i) V_i}{S \times M} \quad (1)$$

where  $c_0$  and  $c_i$  are the initial and the equilibrium concentrations of PVA before and after emulsification respectively, g/100 ml. The concentration was determined by the dry residue.  $S$  is the total interfacial surface per 100 cm<sup>3</sup> emulsion, cm<sup>2</sup>;  $V_i$  is the volume of the aqueous phase,  $M$  is the molecular weight of PVA.

The squares ( $a$ ) per one PVA molecule in the adsorption layer were calculated from the values of adsorption according to the formula

$$a = \frac{1}{\Gamma \times N} \quad (2)$$

where  $N$  is the Avogadro number, and the efficient thicknesses of adsorption layers,  $h$ :

$$h = \Gamma \times V \times M \quad (3)$$

where  $V$  is the PVA specific partial volume,  $\sim 0.77 \text{ g/cm}^3$ .

The interfacial surface formed in the emulsions was calculated according to a formula

$$S = S_{sp} \times v_2 \times d_b \quad (4)$$

where  $S_{sp} = \frac{6}{d_b} \frac{\sum_i n_i D_i^2}{\sum_i n_i D_i^3} (\text{cm}^2/\text{g})$  is the specific interfacial surface in the emulsions;  $v_2$  is the volume of emulsified benzene,  $D_i$  is the diameter of drops whose fraction in the emulsion, %, is  $n_i$ ;  $\sum_i n_i = 100\%$ .

Figure 1 (curve 1) presents the isotherm of PVA adsorption on drops of emulsions obtained by vibrocomminution and ultrasonic dispergating. The isotherm evidently does not reach the plateau, a feature inherent to adsorption

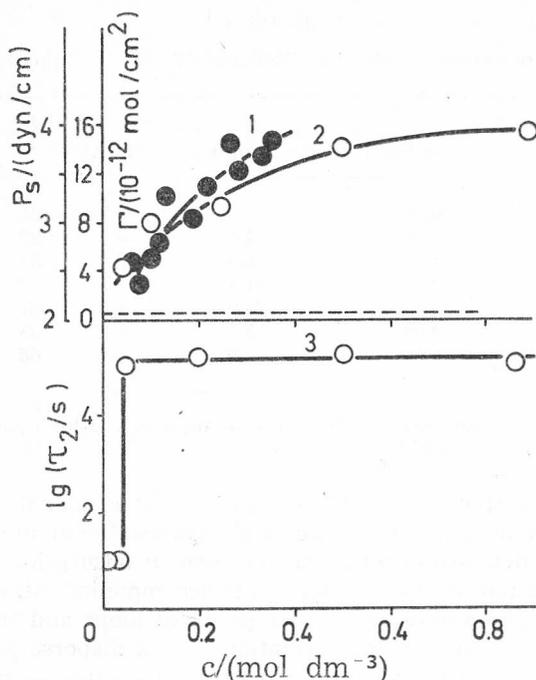


Figure 1. Adsorption on emulsion drops (curve 1), limit shear stress of PVA adsorption layers at flat interfaces with benzene (curve 2), and half-life of drops in PVA-stabilized emulsions (curve 3) vs. equilibrium concentration of the polymer in the bulk of the aqueous phase.

isotherms of synthetic polymers. We did not manage to study the PVA adsorption isotherm at higher concentrations because the emulsions did not display sedimentation of drops. The values for PVA adsorption on benzene drops correspond by the order of magnitude to those obtained by Lankveld and Lyklema with co-workers<sup>3-5</sup> for adsorption on drops of paraffine hydrocarbons emulsions.

Table I presents data on PVA adsorption on emulsified benzene drops calculated by the formulas 1—3. When adsorption is low, the square per one PVA molecule in the adsorption layer is  $3800 \text{ \AA}^2$ , the layer being  $21 \text{ \AA}$  thick. As the PVA adsorption grows ( $c_i = 4$  to  $5 \text{ mol/dm}^3$ ) the square per one PVA molecule decreases to  $1100 \text{ \AA}^2$ , the layer becoming  $68 \text{ \AA}$  thick. We should note that the values of  $h$  in the table ( $20$  to  $70 \text{ \AA}$ ) are the lower limits of thickness at corresponding adsorptions. One more technique of determining the thickness of adsorption layers was that of multiple internal reflection (MIR) of IR rays. At  $1\%$  and  $6\%$  of PVA equilibrium concentrations the thicknesses proved to be of the order of several hundred  $\text{\AA}$ .

As far as the structure of PVA adsorption layers can be determined from the data on adsorption, we have compared the calculated area per one adsorbed molecule ( $a$ ) to the area a macromolecule would have occupied if it were adsorbed in the same state it had in the solution,  $a_0$ <sup>12</sup>

$$a_0 = \pi \bar{r}_{\text{rot}}^2 \quad (5)$$

where  $\bar{r}_{\text{rot}}$  is the rotation radius of the molecule.

TABLE I

*Adsorption Parametres of PVA at Benzene/Water Interface in Emulsions.\**

$c_1$ 10 <sup>5</sup> mol/dm <sup>3</sup>	$\Gamma$ 10 <sup>12</sup> mol/dm <sup>2</sup>	$a$ 10 <sup>3</sup> Å <sup>2</sup>	$h$ Å
0.86	4.4	3.8	21
0.95	4.8	3.5	22
1.50	6.6	2.5	31
2.86	11.4	1.5	53
3.75	13.0	1.3	61
4.00	13.5	1.2	63
5.00	14.6	1.1	68

\*  $c_1$  is the equilibrium concentration of PVA,  $\Gamma$  is adsorption,  $a$  is the square per one molecule,  $h$  is the thickness of the interfacial layer,  $t = 20^\circ\text{C}$ .

The results presented in Table II reveal that  $a$ , i. e. the square occupied by one PVA molecule at the interface, is always smaller than  $\pi \bar{r}_{\text{rot}}^2 = 17\,700 \text{ \AA}^2$ , the ratio  $a/\pi \bar{r}_{\text{rot}}^2$  decreasing with the increase in adsorption. This comparison shows that adsorption of macromolecules is accompanied either by their lateral compression with the simultaneous elongation of loops and tails stretching out into the dispersion medium or by formation of new disperse phase particles.

Baran et al<sup>13</sup> report the isotherms of PVA adsorption on  $\text{Sb}_2\text{S}_3$  sol particles. The shape of their isotherms is very similar to the ones we obtained. By using high resolution NMR spectroscopy<sup>14</sup> we found that the elementary PVA link in the aqueous solution coordinates around it two molecules of strongly bound water. From the density of dry PVA (1.3 g/cm<sup>3</sup>) and the molecular weight of an elementary link we calculated the volume of the hydrated link  $(\text{CH}_2-\text{CH}-\text{OH}) \cdot 2\text{H}_2\text{O}$  and the area occupied by it at the surface (30 Å<sup>2</sup>). The result was that the limit adsorption of PVA cannot exceed  $0.34 \times 10^{-12} \text{ mol/cm}^2$  (at  $M = 70\,000$ ) even when the packing of links at the surface is at its densest. Therefore, the values of PVA adsorption we have measured, as well as those reported in ref 3 to 5 refer to thick adsorption layers.

The thickness of PVA adsorption layer estimated from viscosity measurements<sup>15</sup> and from calculations assuming that the polymer density in the block equals that in the adsorption layer is 12 000 Å. Data obtained by Fleer, Koopal and Lyklema<sup>12</sup>, who determined the thickness of adsorption layers on AgI sol particles viscosimetrically and from electrophoretic mobility of the particles seem to be more reliable. The thickness, which varied from 0 Å to 100 Å as the adsorption grew from 0 mol/cm<sup>2</sup> to  $2.2 \times 10^{-12} \text{ mol/cm}^2$  ( $1.5 \times 10^{-7} \text{ g/cm}^2$ ), coincided

TABLE II

*Comparison Between the Area ( $a_0$ ) Occupied by one PVA Molecule at the Interface and the Area of Projection ( $\pi \bar{r}_{\text{rot}}^2$ ) of the PVA Molecule Having the Same Conformation as in the Solution*

$c/(\text{g}/100 \text{ ml})$	0.060	0.067	0.105	0.200	0.260	0.280	0.350
$a/\pi \bar{r}_{\text{rot}}^2$	0.21	0.20	0.14	0.08	0.07	0.07	0.06

with the theoretical one calculated by Hoeve for the PVA adsorption layers<sup>11</sup>. Sonntag and Strenge found<sup>16</sup> that the thickness of the layer between drops necessary for their stabilization must be at least 800 Å.

We could not measure the isotherm of PVA adsorption in benzene emulsions at  $\Gamma < 3 \times 10^{-7}$  g/cm<sup>2</sup> ( $4.4 \times 10^{-12}$  mol/cm<sup>2</sup>) because at  $c < 0.091$  g/100 ml the 40–60% benzene emulsions instantaneously disintegrate. Assuming that at  $\Gamma > 2.2 \times 10^{-12}$  mol/cm<sup>2</sup> ( $1.5 \times 10^{-7}$  g/cm<sup>2</sup>) the PVA adsorption layers are thicker than 100 Å (Figure 5 in ref 12) the formula  $c_v = \Gamma/h$  enables us to calculate the PVA concentration in the shells stabilizing the drops, which equals several dozen per cent (45%). In ref 6, where the strength of three-dimensional PVA gels was estimated from the strength and thickness of PVA adsorption layers, the PVA concentration at the flat benzene/water interface was found to be 20–35%. At these concentrations a thin layer of the polymer new phase which displays elasticity, viscosity and shear strength emerges at the interface<sup>6</sup>. This assumption is confirmed by the rheological parameters of PVA adsorption layers at flat interfaces with benzene.

Comparison of the adsorption isotherm with strength properties of the same adsorption layers at different equilibrium concentrations demonstrates (Figure 1, curve 2) that as adsorption grows from 0 mol/cm<sup>2</sup> to  $\sim 15 \times 10^{-12}$  mol/cm<sup>2</sup>,  $P_s$  increases to 5.2 dyn/cm. Thus the dependence of  $P_s$  on  $c_i$  is evidently controlled by the growth of thickness of the PVA adsorption layer (Table I).

We should note that the surface active polymer condensates in the adsorption layer in a non-uniform manner, i. e. the density of segments is maximum near the interface, decreasing with distance from the interface. Fler, Koopal and Lyklema<sup>12</sup> have shown with PVA adsorption on AgI particles that the first layer of molecules occupies 60 to 70% of the interface. The layer at this filling is 10 Å thick. The density of segments at  $h > 10$  Å decreases considerably as the distance from the particle surface grows, this indicating that the loops and tails of macromolecules are diffusely distributed in the adsorption layer.

Thus our studies and data found in the literature enable us to reach the conclusion that the PVA adsorption layer at liquid interfaces is a gel several hundred Å thick whose formation results from mass condensation and phase disintegration according to a mechanism analogous to that of gel formation in solutions with diffuse distribution of polymer segments in the adsorption layer.

The resistance of emulsion drops to destruction (coalescence) was studied by the time dependence of the number of drops formed from 1 g benzene:

$$N = S_{sp}/S_s \quad (5)$$

where  $S_s = \frac{\pi D_{av}^2}{4}$  is the average surface of one drop.

One of the  $N(\tau)$  dependences (for the emulsions stabilized by 1% PVA) from which the times necessary for half of the drops to coalesce were determined, is given in Figure 2. It turned out that the presence of just one monolayer of the adsorbed polymer on the drops ( $\Gamma$  shown by dotted line in Figure 1) increases  $\tau_{1/2}$ , i. e. the emulsions resistance to coalescence, by 4 orders of magnitude (Figure 1, curve 3).

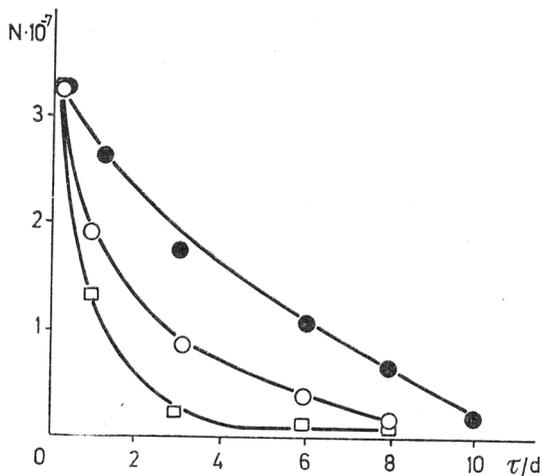


Figure 2. Time dependence of the number of drops formed by 1 g benzene in emulsions stabilized by 1% PVA. ● — 20 °C, ○ — 37 °C, □ — 45 °C; vibrocommutation.

Figure 2 shows that the coalescence rates decrease with time. We have shown earlier that during the coalescence process the limit shear stress of the three-dimensional structures forming in the emulsions increases due to the loss of aggregative stability by the drops. Mobile drops evidently can »find« the stacking faults in adsorption layers, thus providing for coalescence. Formation of the network of contacts, however, confines coalescence to the areas where »coagulation« has taken place.

In such areas stable equilibrium thin or thick films might appear. At late stages of coalescence the probability of the process becomes still lower because the number of contacts in the emulsion structure decreases and the drops can not be rearranged. The assumption that collective interactions decrease the probability of coalescence is confirmed, if we compare the times necessary for half of the drops in the emulsion to coalesce,  $\tau_{1/2}$ , with the coalescence time of isolated benzene drops stabilized by PVA solutions of corresponding equilibrium concentrations,  $\tau_{1/2}^0$ . It turned out that  $\tau_{1/2}$  exceeds  $\tau_{1/2}^0$  by two orders of magnitude (Table III). Short lifetimes of isolated drops at flat interfaces with benzene

TABLE III

*Dependence of Half-Life Time of Emulsion Drops ( $\tau_{1/2}$ ) and Half-Life of PVA Stabilized Benzene Drops at Flat Interfaces with Benzene ( $\tau_{1/2}^0$ ) on PVA Concentration in the Bulk of the Aqueous Phase*

$c_0$ /(g/100 ml)	$\frac{\tau_{1/2}}{10^5 \text{ s}}$	$\frac{\tau_{1/2}^0}{10^3 \text{ s}}$
1	1.1	1.1
1	1.3	1.1
6	4.1	

appear to be associated with the mobility of the drops and their capacity of finding the stacking faults in the stabilizing shell.

The comparison of times necessary for half of the drops in emulsions to coalesce has shown that this value ( $\tau_{1/2}$ ) is affected by the degree of PVA adsorption.

The kinetic parameters of coalescence were determined from the formulae

$$v = -\frac{dN}{d\tau} = k \cdot N^n; \lg v = \lg k + n \lg N \quad (6)$$

where  $v$  is the reaction rate, particles/s,  $N$  is the concentration of drops, particles/cm<sup>3</sup>;  $n$  is the order of the reaction,  $k$  is the reaction rate constant.

The reaction orders estimated from the slope of  $\lg v - \lg N$  curves were close to 2, thus proving that the »drop-drop« mechanism of coalescence is the most likely one. Fractional values of  $n$  indicate that the coalescence reactions are complex, involving possibly a simultaneous process of the »drop-interface« destruction, benzene emerging as a bulk phase. This process is, however, less likely than the drop-drop destruction.

The disintegration rate constants given in Table IV increase from units to several hundred  $10^{-4}$  g<sup>2</sup>/particles s, with increasing PVA concentration and temperature. Let us compare the coalescence rate constants for PVA-stabilized emulsions to those for emulsions stabilized by low molecular surfactants (LMS). The coalescence rate constant for drops of toluene or heptane emulsions in sodium lauryl sulphonate aqueous solution were estimated as  $\sim 10^{-13}$  g<sup>2</sup>/particles s, for the initial number of drops  $N_0 = 10^{10}$  particles/g, assuming the reaction obeys the second order. The rate constant of the second order reaction is connected with  $N_0$  by the equation

$$k = \frac{1}{N_0 \times \tau_{1/2}} \quad (7)$$

Substituting into eq 7 the  $\tau_{1/2}$  estimated from  $k$  corresponding to the emulsions studied in the present paper, we found that the coalescence rate constants for drops of emulsions stabilized by PVA at  $N_0 \sim 10^{10}$  particles/g would equal  $10^{-17}$  to  $10^{-15}$  g<sup>2</sup>/part s. These values are by 2 to 4 orders of magnitude lower than those for the LMS-stabilized emulsions.

TABLE IV

*The Dependence of Kinetic Parametres of Coalescence of Drops in Emulsions on PVA Concentration and on Temperature*

$t/^\circ\text{C}$	K $10^{-14}$ g <sup>2</sup> /s			E kcal/mol <sup>-1</sup>		
	0.1%	1%	6%	0.1%	1%	6%
8	179.5	15.3	1.75			
20	156.4	31.5	2.4	3	8	7
37	286.8	58.9	4.8			

Table IV also presents the activation energies  $E$  for the coalescence of benzene drops stabilized by different concentrations of PVA, as calculated from the Arrhenius' equation. The increase in PVA concentration results in the  $E$  increase from 3 to 7 to 8 kcal/mol particle.

The physical sense of  $E$  depends on the mechanism of destruction of the film separating the two drops. The break-through of the film stabilized by soap-like surfactants is regarded as the result of desorption or displacement of the stabilizing molecules from the destruction zone<sup>17</sup> or as a result of rupture of hydrogen bonds between molecules in the emulgator adsorption layer<sup>19</sup>. In case of emulsions studied in the present paper, it was shown that adsorption of macromolecules is irreversible and that the adsorption layers of stabilizers are solid-like gels with certain rheological characteristics. Thus the activation energy of coalescence must be treated here in terms of energies necessary for destruction of quasi-solid bodies. It would be interesting therefore to compare the activation energies of coalescence in emulsions to the activation energy of destruction of stabilizing adsorption layers. However, the deformation moduli of interfacial layers cannot be regarded as their absolute parameters unless the thickness of the shells at different temperatures is taken into account.

The activation energies are comparable by the order of magnitude to the energies of interaction between drops at distances of several angstroms. Coalescence of drops results possibly from the approach of drops at such distances on account of collision of mobile drops, or under the action of Van-der-Vaals attraction forces, or due to fluctuations of the layer thickness under quasi-equilibrium conditions. The mechanism of destruction of stabilizing films is not clear yet. We may assume, however, that destruction of emulsion drops is a thermofluctuation process which depends on rheological properties of adsorption layers and on the balance of forces acting between the drops.

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### SAŽETAK

#### **Struktura adsorpcijskih slojeva polivinil-alkohola na graničnim površinama s benzenom i stabilnost koncentriranih emulzija**

V. N. Izmailova, G. M. Pismennaya, T. F. Busol i B. N. Tarasevich

Određivana je adsorpcija PVA na graničnoj površini s benzenom. Adsorbirani slojevi nastali su pod dinamičkim uvjetima (emulzije su pripremane vibrokominucijom i ultrazvučnom tehnikom). Adsorpcijski podaci su bili upotrijebljeni za izračunavanje površine po 1 molekuli i debljine adsorpcijskih slojeva. Uspoređivane su adsorpcijske izoterme s reološkim karakteristikama adsorbiranih slojeva. Na temelju iznesenih podataka o raspodjeli segmenata adsorbiranih molekula PVA, zaključeno je da je sloj adsorbiranog PVA na granici tekućina nekoliko stotina Å debeo gel. Nastajanje gela rezultat je kondenzacije mase i faznog deemulgiranja u skladu sa sličnim mehanizmom nastajanja gela u otopinama s difuznom raspodjelom polimernih segmenata u adsorbiranom sloju. Pokazano je da najmanje jedan monosloj mora pokriti kapljice da bi se dobile stabilne emulzije. Kinetički parametri i aktivacijska energija koalescencije ovise o adsorpciji PVA.

DEPARTMENT OF COLLOIDAL CHEMISTRY  
MOSCOW STATE UNIVERSITY  
LENINSKY GORY, MOSCOW, USSR

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