Structure of the adsorption layers of linear polymers

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Abstract – Using the adsorption from dilute solutions, infrared spectroscopy and gas chromatography the thicknesses of the adsorption layers of flexible-chain macromolecules and the fractions of macromolecular chain units bonded with the surface functional groups have been determined. The assumptions taken in calculating the adsorption layer thicknesses from the experimental adsorption isotherms, the retention vs. the amount of adsorbed polymer dependences and the shift of absorption bands in adsorption systems IR spectra are considered. It is shown possible for the conformation of macromolecules to change ("coil" – "straightened chain" transition) under the influence of the adsorption field of adsorbent during weak interactions of the solvent molecules with the surface of a solid. Causes of the formation of poly- and monolayers of slightly deformed macromolecular polymer coils are discussed.

INTRODUCTION

Beginning in 1960 A.V. Kiselev was preoccupied with the idea of developing fundamental research into the adsorption and chromatography of not only molecules and atoms but also of large natural and synthetic polymer macromolecules, including their complex constructions: viruses, phages, cells and colloids. In this research A.V. Kiselev directed his main attention at the role played by the chemistry of the surface and the chemical and other ways of modifying the adsorbents in the intermolecular interactions taking place in adsorption systems. The first work on the adsorption of polymers was devoted to the questions regarding the influence of the chemistry of the surface and the porous structure on the adsorptive interactions (Kiselev et al. 1963, 1965; Bogacheva et al. 1964, 1965). In subsequent work was discussed the result of studying such factors as the chemical nature of the solvent, the degree of polymerizaton and the temperature (see e.g. Kiselev et al. 1968, 1975; Bogacheva et al. 1969; Eltekov & Kiselev 1972). In the last chapter of his monograph (Kiselev 1986) the author, summing up all the previous research, concludes that the nature of intermolecular interactions of macromolecules with the adsorbent surface is determined by the conformational mobility of the adsorbed chain of macromolecules and by the possibility of the macromolecular coil straightening out in the field of adsorption forces.

The problem of the adsorption phase structure and properties has quite a long history. It can be definitely said that a substance in the adsorbed state has specific properties, differing from its properties in the bulk phase. This is not difficult to understand when we examine adsorption at a molecular level.

Behaviour of the macromolecules of synthetic and natural polymers on the surface of solids has been dealt with in numerous studies (see e.g. Lipatov & Sergeeva 1972; Ash 1973; Hesselink 1977). A lot, however, still remains unclear: in particular as regards the question of the thicknesses of polymer adsorption layers. Different techniques of investigating and treating the results of these experimental studies of thicknesses produce values differing by more than an order of magnitude.

In the present work, based on examining the results of the experimental studies of polymer-containing systems and on certain substantiated assumptions, the thicknesses of the adsorption layers of flexible-chain macromolecules have been calculated and the adsorbed macromolecules arrangement and orientation on the surface of nonporous and macroporous adsorbents estimated.

THEORY

The experimentally determined value of adsorption $\Gamma_1^{(v)}$ of the component 1

$$\Gamma_1^{(v)} = (C_{o,1} - C_1) \, v \, / \, A \,, \tag{1}$$

where $C_{o,1}$ and C_1 are the initial and the equilibrium concentration (mol/1) of the component 1; v is the volume of solution poured on the adsorbent with the surface A,

constituting the excess of a substance (in moles per m^2) in the adsorption phase, as compared with its content in an equal volume remote from the action of the adsorptive forces; A is the adsorbent surface (m^2/g). The $\Gamma_1^{(v)}$ value is related to α_1 – the total content by

$$\alpha_1 = \Gamma_1^{(v)} + \frac{v_a}{A} C_1 , \tag{2}$$

where v_a is the adsorption volume (cm^3) i.e. the volume occupied by the adsorption space. In the case of microporous adsorbents (zeolites, active carbons) the v_a value is practically equal to the volume of micropores. Determining v_a for nonporous and wide-porous adsorbents is not a simple problem in the general case. During the adsorption of vapours by nonporous adsorbents a poly-layer is known to be observed. The action of adsorptive forces can be supposed to extend over comparatively large distances. However, the values of the heat of formation for the second and third layers are close to the heats of condensation, which is indicative of a sharp drop in the adsorption potential at distances equal to a double (or triple) equilibrium distance between the centre of adsorption and the centre of force in the adsorbate molecule. A.V. Kiselev and K.D. Scherbakova (1948) proposed a method of calculating v_a, based on the assumption that v does not change with a change in C_1 and that after C_1 corresponding to the completion of the formation of a compact adsorption layer a linear drop is observed on the adsorption isotherm

$$\frac{d\alpha_1}{dC_1} = \frac{\delta\Gamma_1^v}{\delta C_1} + \frac{\delta(v_a/A)C_1}{\delta C_1} \tag{3}$$

$$-\frac{\delta\Gamma_1^{(v)}}{\delta C_1} = \frac{v_a}{A} = \tau \tag{4}$$

The slope of the linearly descending branch of the adsorption isotherm, $\Gamma_1 = f(C_1)$, thus makes it possible to estimate directly the value of τ – the adsorption layer thickness.

In the case of polymer adsorption, usually restricted to the region of dilute solutions, one observes a characteristic plateau on the adsorption isotherm – a region of the constancy of Γ_1 (i.e. of only a slight dependence of the Γ_1 value on the bulk phase composition). For this region one can estimate the adsorption layer thickness from the approximate formula

$$\tau \approx \frac{\Gamma_m}{\rho} \approx \Gamma_m \bar{v} , \tag{5}$$

where Γ_m is the value of adsorption in mg/m^2, corresponding to the plateau on the isotherm; ρ is the polymer density, g/cm^3; $\bar{v}$ is the specific volume, cm^3/g. The formula (5) presupposes the formation on the adsorbent surface of a compact layer of macromolecules that have displaced practically all the solvent molecules. The validity of this assumption is confirmed by the fact that the adsorption growth stops with an increase in polymer concentration in the bulk solution and by the non-competitiveness of the solvent molecules in the interaction with the adsorbent surface.

However, in the adsorption of polymers, apart from the isotherms with a "limit" (plateau) obeying the Langmuir equation, one also observes Freundlich's isotherms

$$\Gamma_1^{(v)} = A_1 c^n , \tag{6}$$

where A_1 and n are the coefficients of Freundlich's equation. The shape of this adsorption isotherm is indicative of a continuous growth of the adsorption layer thickness. Such adsorption isotherms are characteristic for the adsorption of polystyrene from solutions in cyclohexane (Kiselev et al. 1975), polyneopentylphthalate from n-hexane (Bogacheva et al. 1975) on silica and titanium oxides.

EXPERIMENTAL

The following polymers have been studied: polyoxyethylene (POE) with molecular weights (MW) equal to 300, 3000, 20 000; polybutadiene (PB) with MW = 3000 and 170 000; polyvinylacetate (PVA) with MW = 180 000; polystyrene (PS) with MW = 40 000 and 300 000; polydimethylsiloxane (PDMS) with MW = 350 000; and polymethylmethacrylate with MW = 330 000.

Used as the solvents were: twice distilled water, tetrachloromethane and n-heptane. n-Heptane and tetrachloromethane were dried with NaA zeolite pellets.

Used as the adsorbents were: nonporous channel carbon black (specific surface s = 85 m^2/g) treated at 3200 K in helium stream, highly dispersed nonporous silica – aerosil (s = 170 m^2/g), macroporous silica – Silochrome C-80 (s = 100 m^2/g) obtained under hydrothermal conditions, dried at 180°C for 4 hours.

Procedure of the adsorption experiments is described in (Kiselev et al. 1963; Bogacheva et al. 1964). Equilibrium concentrations were analysed with the help of an ITR-2 interferometer, IR spectra of the polymers adsorbed on aerosil were measured on a UR-10 spectrometer (GDR) (Kiselev et al. 1968), gas-chromatographic studies were performed on a Tsvet-102 chromatograph (USSR) (Eltekov et al. 1968).

RESULTS AND DISCUSSION

Presented in Tables 1 and 2 are the Γ_m values of adsorption corresponding to a clearly defined maximum or a blurred maximum (plateau) on the adsorption isotherm, the latter being usually observed in the region of polymer equilibrium concentrations equal to 0.1 - 1.0 mg/g. The Γ_m values were calculated on the assumption that the construction of a layer of adsorbed macromolecules is completed, i.e. with a further growth of the bulk solution concentration no changes are taking place in the adsorbed layer organization.

Table 1. Γ_m and τ values of polymers on graphitized carbon black

Polymer	MW, kd	Solvent	Γ_m, mg/m^2	τ, nm
Polyethyleneglycol	15	Water	0.7	0.7
Polyacrylic acid	20	Water	0.6	0.6
Polyvinylacetate	180	Methanol	0.9	0.8
Polybutadiene	3	n-Heptane	0.6	0.6
Polymethylmethacrylate	330	MEK	0.6	0.6
Polyisobutylene	280	Cyclohexane	0.8	0.8
Polystyrene	300	Tetrachloromethane	0.8	0.9

Table 2. Γ_m and τ values of polymers on silica

Polymer	MW, kd	Solvent	Adsorbent	Γ_m, mg/m^2	τ, nm
Polybutadiene	170	n-Heptane	Silica	1.2	1.2
Polydimethyl-siloxane	350	n-Hexane	Aerosil	0.7	0.8
		do.	Silica gel-750	0.8	0.8
Polyvinyl-acetate	180	Tetrachloro-methane	Aerosil	0.8	0.8
Polymethyl-methacrylate	260	Chloroform	do.	0.4	0.5
Polystyrene	300	Tetrachloro-methane	do.	0.9	0.9
			Silica gel-750	0.9	0.9
Polyoxy-ethylene	20	Benzene	Silochrome	0.6	0.6

As early as in 1961 Fontana and Thomas, proceeding from the studies of the IR spectra of polymethacrylates (PMMA) and polylaurylacrylates (PLA) adsorbed on the aerosil surface, used the absorption bands intensity and shift to estimate the P-fraction of the bound carbonyl groups. This fraction is taken equal to the fraction of the macromolecular chain segments (or units) bound with the surface. Table 3 shows the P values for some adsorbed polymers. If a PVA or a PMMA molecule were adsorbed as a coil, then, naturally, the number of CO groups in contact with the adsorbent surface would be small and P→0. In the case of the straightening (spreading out) of macromolecular coils on a flat adsorbent surface P = 0.33 - 0.67, because the ester groups seem to be situated at an angle of 120° with respect of each other, and with sufficiently strong (localized) adsorption one of the three ester groups is in contact with a surface functional group. In some cases two of the three ester groups can interact with the surface functional groups.

Thus, the P values equal to 0.3 - 0.5, shown in Table 3, indicate a sufficiently strong adsorption of the macromolecules of PVA, PMMA, PLA and other polymers from solutions in CHCl$_3$ and CCl$_4$, accompanied by the straightening of molecular coils. Therefore, both the maximum adsorption values of linear polymers and the IR spectra of these polymers in the adsorbed state indicate the spreading out of macromolecular chains near the surface and the formation of the monolayers of macromolecules extended along the surface. In this case all the macromolecular chain units are in contact with the adsorption centres. It should be natural to assume that the surface relief (roughness, dislocations, cracks, gaps between the adjacent adsorbent particles) influences both the limiting adsorption value and the value of P.

The fact that macromolecules in dilute bulk solution are coiled is also clearly confirmed by the results of studying the adsorption of flexible-chain polymers with the help of macromolecular sieves - porous silicas with a narrow distribution of pore volume sizes (Kiselev & Eltekov 1964) (See Table 4). From the data in Table 4 it is not difficult to see that the coils of the macromolecules of polystyrene with MW = 40 kd practically freely penetrate into pores of 14 nm and larger size, whereas the macromolecular coils of polystyrene with MW = 300 kd are adsorbed with difficulty and not completely on the walls of pores with a size less than 28 nm. The use of a set of standard porous silicas (porous glasses, silica gels or silochromes) thus makes possible estimating the size of flexible-chain polymer coils in dilute solutions.

Table 3. Values of the P-fractions of bonded segments on aerosil
(IR spectroscopy data for adsorbed polymers)

Polymer	Solvent	P	References
Polyvinylacetate	HCCl$_3$	0.4	(Kiselev et al. 1968)
do.	CCl$_4$	0.5	(Kiselev et al. 1968)
Polymethylmethacrylate	HCCl$_3$	0.35	(Kiselev et al. 1968)
do.	CCl$_4$	0.4-0.5	(Killmann et al. 1983)
Polylaurylmethacrylate	n-C$_{12}$H$_{26}$	0.36	(Fontana & Thomas 1961)
Polyvinylpyrolidone	HCCl$_3$	0.5	(Kalninjsh et al. 1976)
Polybutylmethacrylate	CCl$_4$	0.5	(Kalninjsh et al. 1976)
Polystyrene	C$_6$H$_{12}$	0.4	(Linden & Liamput 1978)

Table 4. Γ_m values of the adsorption of polystyrenes P 1 (MW = = 40 000) and P 2 ($\overline{MW}$ = 300 000) by porous silicas, D - pore diameter in nm, Γ_m in mg/m^2

Polystyrene	$\underline{D}$, nm						
	10	14	22	28	41	55	80
P 1	0.02	0.60	0.65	0.72	0.95	0.85	0.75
P 2	0.01	0.20	0.25	0.32	0.65	0.75	0.85

Table 5. Values of $\underline{a}$ in the log Γ_m = $\overline{A}$ + $\underline{a}$ log $\overline{M}$ equation
($\overline{M}$ - polymer molecular weight)

Polymer	MW range, kd	$\underline{a}$	References
Polyoxyethylene	1 - 20	0.06	(Eltekov et al. 1968)
Polymethylmethacrylate	30 - 300	0.01	(Herd et al. 1971)
Polystyrene	40 - 300	0.05	(Kiselev et al. 1975)

Table 6. Values of $\underline{v}_e$, ml/g, on graphitized carbon black, $100°C$, $\ominus$- fraction of surface occupied by adsorbed PEG

Adsorbates	$\ominus$				
	0	0.70	0.87	4.00	4.70
n-Hexane	250	18	15	13	13
Benzene	170	20	18	16	16
n-Butanol	80	30	25	25	30

Table 7. Thickness of the adsorbed layers of proteins on silochrome (Eltekov et al. 1973)

Protein	Solvent	Γ_m, mg/m^2	τ, nm
BS Albumin	0.1 M phosphate buffer, pH=6.4	3.0	3
do.	water	2.0	2
Lysozyme	0.1 M CH$_3$COOH	0.2	-

Dependence of adsorption on the degree of polymerization

To estimate polymer adsorption layer thicknesses some investigators use the dependence between the limiting adsorption value of a polymer on the surface of nonporous or macroporous adsorbents and the average molecular weight $\overline{M}$. If, in the course of adsorption, macromolecular coils are straightened out in the field of adsorptive forces and practically all the macromolecular chain units are in contact with the adsorption centres on the surface, then it should be expected that the Γ_m vs. $\overline{M}$ dependence is very slight. Usually the dependence of Γ_m on $\overline{M}$ is expressed in a linear logarithmic form as

$$\log \Gamma_m = \overline{A} + a \log \overline{M} \tag{7}$$

Therefore, if a is less than 0.1 it indicates a planar (horizontal) orientation of the adsorbed macromolecules on the adsorbent surface. In the case of perpendicular (vertical) orientation of the adsorbed straightened macromolecules it is expected that a = 1. When macromolecules are adsorbed as undeformed coils the coefficient a = 0.5 - 0.7. Table 5 shows the values of the coefficient a for different ranges of the molecular weights of some polymers. The cited a values are also indicative of considerable conformational changes in polymers, taking place in going from the bulk dilute solution phase to the adsorption phase. It seems that for other adsorption systems the values of the coefficient a higher than 0.1 can be found. A possibility of comparatively thick adsorption layers being formed on the surface of adsorbents of a different chemical nature will be shown and discussed below.

Dependence of retention on the amount of adsorbed polymer

It is known that gas-adsorption chromatography not only makes it possible to solve analytical problems but is also used in physico-chemical studies of adsorption, as well as of the structure and properties of adsorbents. To reduce the adsorptive activity of the adsorbents conventionally used in chromatography the surface of such adsorbents is covered with layers of a polymer (Eltekov et al. 1968).

Table 6 shows the values of v_e - retention volumes of n-hexane, benzene and n-butanol on graphitized carbon black samples the surface of which was covered with different quantities of adsorbed polyethylene glycol (MW = 3 kd). The data in Table 6 show that with $\ominus$ growing up to $\ominus = 1$ the v_e value drops, and then remains practically unchanged. Thus, determining the point on the v_e vs. Γ_1 (mg/m^2) curve, which corresponds to the beginning of v_e constancy with a further growth of $\Gamma\{v\}$, makes it possible to estimate Γ_m answering to the formation of a completed compact adsorption layer.

It should be noted that ellipsometric measurements of the thickness of polystyrene (MW = 300 kd) adsorption layers from dilute solutions in CCl$_4$ on the surface of polished quartz (the measurements were made by V.I. Pshenitsyn in Leningrad State University and by Yu. A. Sorokin in I Moscow Medical Institute) allowed estimating the thicknesses at the limiting sensitivity of the method as no less than 1.5 nm. A justified question arises: is it possible for polylayers or monolayers of undeformed macromolecular coils to be formed in the course of adsorption from dilute solutions ?

Thick polymer layers

The possibility of a macromolecular coil straightening is also connected with the competition of intermolecular interaction forces in the adsorption system. Polystyrene solution in cyclohexane constitutes a unique case of a weak interaction of the solvent (θ - solvent) with the polymer and a rather strong intramolecular interaction between the units of one macromolecular chain, which facilitates the formation of a low-permeability coil. During the adsorption the intramolecular interaction forces do not allow the macromolecular coil to straighten out, and thicker layers of 2 - 3 nm thickness are formed on the adsorbent surface. This follows from the value of adsorption Γ_m = 2.5 mg/m^2 of Silochrome C-80 for PS with MW = 160 kd (Kiselev et al. 1975) and 2.6 mg/m^2 of aerosil for PS with MW = 40 kd. Comparatively thick adsorption layers, of the order of 2 nm, are formed in the adsorption of proteins and nucleic acids from aqueous buffer solutions (Table 7). In this case the intramolecular interaction in protein molecules opposes the complete straightening of protein macromolecules. It should be noted that even in the case of flexible macromolecules, when adsorption is sufficiently strong, the intramolecular forces can hinder the straightening of coils and the formation of compact thin mono-molecular layers of macromolecular chains extended along the surface.

Of interest for chromatography is the case of weak adsorption of macromolecules on a modified surface of the particles of macroporous silica (porous glass, silica gel or silochrome). Here the adsorptive interaction is greatly weakened, and macromolecular coils undergo only a slight deformations in the pores. That is why in the general case there is hardly any sense in speaking of adsorptive interaction. Nevertheless, very weak adsorptive interactions of biopolymer macromolecules, their associates and organizations are undoubtedly of great practical importance in the chromatography and biotechnology of purified and concentrated medicinal preparations and biochemical media.

CONCLUSIONS

A.V. Kiselev's ideas regarding the importance of taking into account the inter- and intramolecular interactions in adsorption polymer-containing systems have found their further development in preparative chromatography and in creating polymeric compositions.

With comparatively small energies of the adsorption of a polymer from dilute solutions a macromolecular coil can be straightened out, and a surface monolayer of straightened adsorbed macromolecules extending along the surface can be formed. Various adsorption systems can be encountered in practice, and a qualitative estimation of the thickness and structure of adsorption layers is only possible if one takes into account the adsorbent surface chemistry and the chemical structure of the molecules of the bulk solution components.

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