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Modern Theories of the Adsorption of Polymers on Solid Surfaces

Yu.S.Lipatov

Studies concerned with the theoretical description and experimental assessment of the state of adsorbed macromolecules as well as the experimental estimation of the thickness of the adsorption layer are examined. The methodological approaches based on modern physical and physicochemical procedures for the investigation of the structure of the adsorption layers are discussed and the accumulated experimental data are analysed in detail. The role of the configurational state of macromolecules in the adsorption layer and of its structure in the establishment of the properties of polymeric compound materials is emphasised.
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I. INTRODUCTION

Despite the large number of studies carried out on the adsorption of polymers from solutions on solid surfaces, questions associated with the theoretical description of the process and the experimental determination of its fundamental features still remain at the centre of attention. This is because it has not been so far possible to bridge the gap between theoretical predictions and experimental results. This review deals with the present state of the problem of adsorption on the basis of the results of studies carried out predominantly during the last five years. Hitherto the only surveys of this field have been a monograph[1] and reviews specially devoted to adsorption from concentrated solutions[2,3].

II. THEORETICAL DESCRIPTION OF THE CONFIGURATIONAL STATE OF ADSORBED CHAIN MOLECULES

One of the central problems of the theory of adsorption is that of the conformations of the adsorbed chains. In a number of studies, examined in detail previously[1], ideas were developed according to which adsorption takes place in the form of sequences of segments ["trains"], linked to the surface, and loops extending into the solution. The lengths of the trains and loops have been calculated by methods of statistical thermodynamics on the basis of the existing theories of polymer solutions as a function of the principal parameters of the polymer chain. In most cases simplified models, which do not take into account the real behaviour of macromolecules in solutions, were used for the calculations. Therefore, despite the fairly complex mathematical procedures, the theoretical density distributions of the segments of the polymer chain obtained near the surface permitted only a qualitative description of this distribution.

1. The Lal-Stepto Theory

A significant improvement of the model of adsorbed sequences of segments and loops was achieved by the studies of Lal and Stepto[4-6]. In contrast to the previous theories, in order to attain a better agreement between the results of the calculation and the real behaviour of the adsorbed chain, they took into account the excluded volume for the chain interacting with the surface and also considered the influence of the nature of the solvent, manifested by its interaction with the segments of the polymer chain and sites on the adsorbent surface.

However, the study was confined to the case of an isolated chain. It was based on the model of a chain on a tetrahedral lattice, the lattice sites being occupied either by chain segments or solvent molecules. The chain conformations in the lattice were calculated by the Monte Carlo method, with successive generation of different conformations. Homogeneous Markov sequences were generated with probabilities of a single-step transition P_{ij} specified in a way such that the resulting set of conformations was characterised by a Boltzmann distribution within the limits of a fairly long sequence. The conformations generated differed in their energies and, when the condition $U \leq 0$ was valid for the energy change in the generation of a new conformation, this conformation was adopted with a probability of unity, while in the case $U > 0$ the new conformation was adopted with a probability $\exp(-U/kT)$ and was rejected with a probability $1-\exp(U/kT)$. If the new conformation was rejected, the previous ("current") conformation was recalculated. In this case one can write

$$P_{ij}=1 \text{ for } U_j \leqslant U_i;$$

$$P_{ij}=\exp(-U_j/kT)/\exp(-U_i/kT) \text{ for } U_j > U_i;$$

$$P_{ii}=1-P_{ij}.$$

The initial conformation was selected arbitrarily as any allowed conformation. As stated above, the conformation whose energy U' was smaller or equal to the energy of the preceding conformation U was included in the sequence of chain conformations on the lattice, i.e. a random number x between 0 and 1 was selected and compared with the quantity

$$r=\exp(-U'/kT)/\exp(-U/kT).$$

If $r \geq x$, then each new conformation was added to the sequence of conformations and a sequence of any length could thus be constructed.

In previous studies no account had been taken of internal rotation. In the model developed here it was assumed that the transition from one conformation to another takes place as a result of changes in the rotational positions, following one after another, of only a small number of consecutive linkages (in the given case four), subject to the condition that the remainder of the chain does not undergo any changes. The position of this transitional region in the molecule is assumed to be stochastic in nature. Four is the minimum number of linkages which can be used to generate all possible chain configurations on a tetrahedral lattice.

In a calculation made by the Monte Carlo method account was taken of only those conformations in which the macromolecule interacted with the surface. The chain is then described by three energy parameters characterising the transition from the *trans*- to the *gauche*-conformations with an energy difference $\Delta\varepsilon_g$ (the *gauche*-conformation is known to have a higher energy). In the lattice account is taken of the energies corresponding to the following angles between groups of three or four bonds: 0°, +120°, and −120°.

We believe that the main disadvantage of the model[4] is the initial postulate in the calculations of the conformations of the adsorbed chain consisting in the assumption that one end of the chain is permanently fixed in the plane of the absorbent ("anchor" units). This postulate appears relatively unjustified and is not introduced by the same workers in other instances[6]. The normal excluded volume conditions for the lattice chain, namely the exclusion of multiple occupations of a single site in the lattice, were automatically included in the program for calculations of the conformations[6]. In addition account was taken of the interaction between segments at the nearest neighbouring sites with the aid of the parameter of the Flory theory:

$$\Delta\varepsilon_{12} = \varepsilon_{12} - \frac{1}{2}(\varepsilon_{11} + \varepsilon_{22}).$$

In the model proposed the solvent molecule and the segment occupying adjacent sites have an energy ε_{12}, the solvent molecules in the lattice have an energy ε_{11}, and the adjacent segments have an energy ε_{22}. Thus, when the configuration changes, the segment passes to a site adjoining another segment, two segment–solvent contacts are broken, and solvent–solvent and segment–segment contacts are formed, the overall energy change being $-2\Delta\varepsilon_{12}$. For a chain on a tetrahedral lattice, the number of possible non-bonded nearest neighbours in relation to a given chain segment is two. Hence, for an infinite chain and a random distribution on the lattice of both segments and solvent molecules, the quantity $2\Delta\varepsilon_{12}/kT$ can be set equal to χ (the usual Flory–Huggins interaction parameter). It is assumed that adsorption also takes place for negative adsorption energies:

$$\Delta\varepsilon_s = \varepsilon_{2s} - \varepsilon_{1s}.$$

The calculations were performed for $\Delta\varepsilon_g = 0$, and $\Delta\varepsilon_{12} = 0$, i.e. for a chain with free rotation and adsorption from an athermal solution. For numerical calculations, use was made of segment–surface energies of $-0.5kT$ and $-0.9kT$ and of numbers of chain segments $n+1 = 31$, 51, 76, and 101 (which correspond to 30, 50, 75, and 100 bonds). The calculations made it possible to determine the average fraction of the adsorbed segments $\langle\nu\rangle$ as a function of the adsorption energy $\Delta\varepsilon_s/kT$ for a chain of 100 segments[4] and also the average maximum thickness of the layer $\langle\tau_m\rangle$. The quantity $\langle\tau_m\rangle$ is expressed in units of the distance between two planes in the lattice, which is $\sqrt{2}l/\sqrt{3}$, where l is the "skeletal" bond length.

A general tendency in the variation of conformations in the adsorption layer is that the fraction of bound segments increases and the thickness of the layer diminishes with increase in the energy of the bond between the segment and the surface[6]. The changes in $\langle\nu\rangle$ and $\langle\tau_m\rangle$ following a change in chain length are more pronounced for weak adsorption; $\langle\nu\rangle$ and $\langle\tau_m\rangle$ are less sensitive to chain length than the adsorption energy. It follows from calculations that, when $\Delta\varepsilon_s/kT = -0.9$, the adsorbed molecule is tightly fitted on the surface and the slight increase of $\langle\nu\rangle$ and decrease of $\langle\tau_m\rangle$ with chain length indicate an increased compatibility between the chain and the surface with increase in chain length.

The use of the familiar scheme of adsorbed trains and loops, differing in the allowance for the presence of unbound tails, in order to describe the conformations of adsorbed macromolecules, makes it possible to estimate the changes (in units of the number of segments) in the average lengths of the trains $\langle L_{tr}\rangle$, loops $\langle L_l\rangle$, and tails $\langle L_e\rangle$ as functions of the energy of adsorption and to show that $\langle L_{tr}\rangle$ and $\langle L_l\rangle$ do not vary significantly with adsorption energy (the length of the trains increases, while the size of the loops diminishes as the adsorption energy increases).

The changes in $\langle L_e\rangle$ are more significant consequently, at least in the case of weak adsorption, the thickness of the adsorbed layer is determined by the length of the tails. For $\Delta\varepsilon_s/kT = -0.8$, $\langle L_e\rangle$ is twice as large as $\langle L_l\rangle$ for all chain lengths. For weak adsorption, the chain length is proportional to the length of the tail. Analysis of the size distribution of the trains and loops shows that it is very narrow, while that for tails it is very broad. The quantities $\langle L_{tr}\rangle$, $\langle L_l\rangle$, and $\langle L_e\rangle$ can be used to characterise the so-called average adsorbed chain. If these quantities are known, the number of trains and loops can be determined[6].

Suppose that m is the number of trains which can be found from the equation

$$m\langle L_{tr}\rangle + (m-1)\langle L_l\rangle + 2\langle L_e\rangle = n+1,$$

and the fraction of bound segments is

$$\nu' = m\langle L_{tr}\rangle/(n+1).$$

Thus the quantities m and ν determine, together with $\langle L_{tr}\rangle$, $\langle L_l\rangle$, and $\langle L_e\rangle$, the configurational characteristics of the average adsorbed chain. Such quantities have been calculated for different n and $\Delta\varepsilon_s/kT$.

The size and shape of the adsorbed chain can be treated also in terms of mean square dimensions of the molecule $\langle r^2\rangle$ and the radius of rotation $\langle s^2\rangle$. The ratio $\langle r^2\rangle/\langle s^2\rangle$ for the adsorbed chain and the chain with free rotation in solution depends on n. The quantities $\alpha_r^2 = \langle r^2\rangle/\langle r_0^2\rangle$, where $\langle r_0^2\rangle$ are the unperturbed dimensions in solution, have also been calculated. They indicate an appreciable extension of the chains on the surface.

The results of the calculations make it possible to describe also the density distribution of the segments with respect to the thickness of the layer for different adsorption energies. For $\Delta\varepsilon_s = 0.5kT$, the density of the segments changes little in the first layers near the surface and then slowly decreases. For strong interactions, the initial sharp fall of the density is followed by a very much slower decrease. For adsorption from a non-athermal solvent, the model of an anchored chain has been adopted and $\Delta\varepsilon_g = 1.0kT$ and $\Delta\varepsilon_s = -0.5kT$.[4] The calculations were performed for a chain consisting of 100 segments.

The quantities $\langle r^2 \rangle$, $\langle s^2 \rangle$, $\langle \nu \rangle$, and $\langle \tau \rangle$ were calculated (see Table). The calculation showed that, for good solvents ($\Delta\varepsilon_{12}/kT = 0.50$ and 0.00), the molecules exist on the surface in the extended state. In a bad solvent the chain conformation is close to that of a coil[5]. Calculation[4] showed that the average fraction of adsorbed segments increases as the solvent becomes less effective and the thickness of the layer diminishes.

Calculated values of $\langle r^2 \rangle$, $\langle s^2 \rangle$, $\langle \nu \rangle$, and $\langle \tau \rangle$.

Curve	$\langle r^2 \rangle$	$\langle s^2 \rangle$	$\langle \nu \rangle$	$\langle \tau \rangle$
		a		
1	7327	709	33	19
2	5771	606	35	20
3	4307	493	39	18
4	2755	295	19	21
5	5355	682	34	27
		b		
1	1859	170	28	14
2	2267	172	44	9
3	2147	155	42	10
4	3011	247	34	14
5	1867	222	42	8
		c		
1	299	106	31	8
2	563	98	41	6
3	203	89	45	7
4	83	86	30	6
5	123	73	36	6

On the assumption of the "anchored" model, the conformations of the adsorbed chains are illustrated schematically in Fig. 1,[4] and the density distribution of the segments is shown in Fig. 2.[4] The conformation is shown as the height of each segment above the surface in a non-dimensional representation. Fig. 1 shows that, in a good solvent ($\Delta\varepsilon_{12} = 0.5kT$), there is a distinct tendency towards the formation of long trains in the initial part of the chain and there is an appreciable fraction of non-adsorbed segments in the tails.

The formation of loops is less favoured and only a few configurations contain more than two loops. The configuration consists very often of a bound train and a tail.

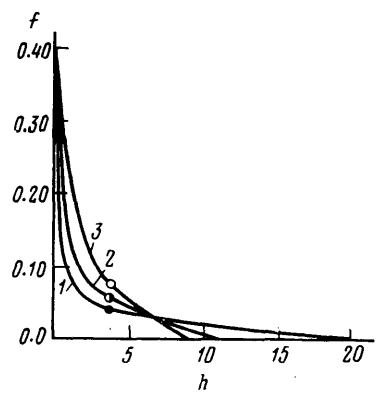


Figure 1. The calculated average fractions of bound segments in each successive layer over the plane of the adsorbent for different values of $\Delta\varepsilon_1$ (Clark et al.[4]); *1*) $0.5kT$; *2*) $0.0kT$; *3*) $-0.5kT$.

In a good solvent the repulsion of the segments leads to an extended rigid state of the chain together with a positive value of the parameter $\Delta\varepsilon_g$. This state induces a cooperative effect among the segments, leading to the formation of trains adjoining the anchored sections. This effect also leads to the appearance of groups of non-adsorbed segments behind the adsorbed train. Long trains and tails in a system with $\Delta\varepsilon_{12}/kT = 0.5$ can be regarded as the manifestation of the cooperative effect. The absence of loops can be attributed to the high energy required to bend the molecules.

In a bad solvent the probability of a strong interaction of the segments with one another and with the surface is a maximum. Therefore in the given case the molecules are in a tightly coiled state with a large number of segments bound to the surface. The presence of a relatively large number of loops is inevitable under these conditions.

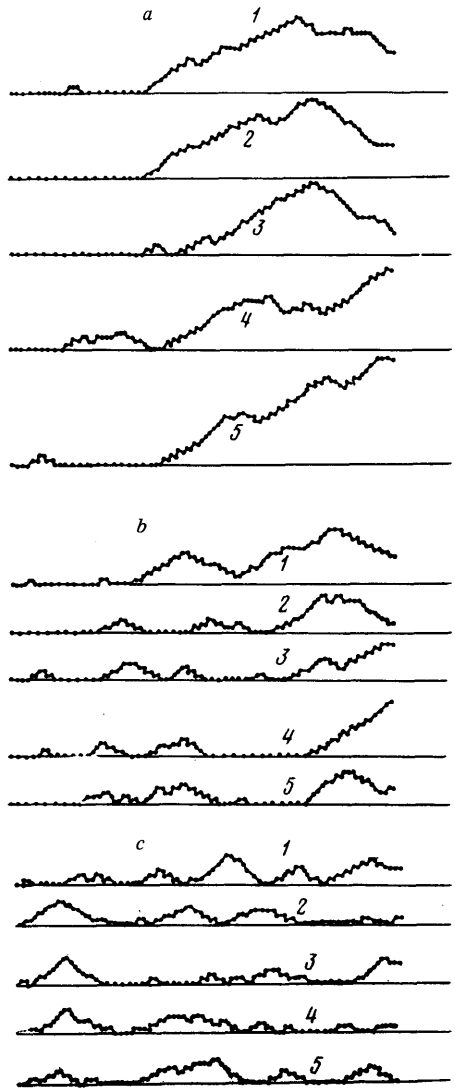


Figure 2. Certain typical configurations appearing with high frequencies in calculations by the Monte Carlo method[4]; $\Delta\varepsilon_1$: *a*) $0.5kT$; *b*) 0.0; *c*) $-0.5kT$; for the parameters of the curves, see Table.

The ideas of Lal and Stepto were described here in fair detail, since they must be regarded as a significant step forward in the theoretical description of adsorption, despite the fact that the model was developed for an isolated chain. On the basis of calculations of the conformations on a computer, the authors produced a cine-film demonstrating the behaviour of macromolecules near the interface and on the surface. This film was shown by Stepto at the IUPAC Microsymposium on Interfacial Phenomena in Prague in 1976. The film characterises the conformations of molecules in dynamic adsorption and desorption equilibrium and shows that in weak adsorption the molecules frequently leave the surface and assume the conformation typical for the molecules in solution. For strong adsorption, the molecule is retained closer to the surface and assumes an extended conformation. The author of this review was present at the showing of this film and can testify that the clarity of the representation makes it possible to illustrate the real picture of adsorption. A cartoon film characterising the behaviour of macromolecules in adsorption has also been made by Lumb[7].

2. The Hoeve Theory

Another fundamental approach to the theoretical estimation of the density distribution of segments in the adsorption layer as a function of the distance from the adsorbent surface is that developed by Hoeve[8-11]. The calculations were made for a single adsorbed chain consisting of n segments on the assumption that the loops are fairly large, but Hoeve did not take into account the effect of the excluded volume.

The number of segments at a distance from the surface in the range between z and $z+dz$ is defined as $n\rho(z)dz$, where $\rho(z)dz$ is the normalised function of the density distribution of the segments. The calculation performed for a one-dimensional lattice model yields[8]

$$\rho(z) = 4\pi^{1/4}\beta_1 C \exp[-4\beta_1 z(-\lambda)^{1/4}](1 + S_{-1/4} + S_{-3/4})^{-1}, \qquad (1)$$

where β_1 is determined by the condition

$$\beta_1^2 = 2\langle r_n^2\rangle_0/3n,$$

where $\langle r_n^2\rangle$ is the mean square distance between the ends of the free chain in the absence of volume effects, C a constant characterising the rigidity of the chain, λ the Lagrange multiplier, and $S_{1/2}$ and $S_{3/2}$ are functions of λ and of the size of the loops i.

Eqn.(1) is valid for $r > \delta$, where δ is the effective thickness of the segments adsorbed on the surface. It is seen that $\rho(z)$ is an exponential function of z for large loops and weak adsorption. For strong adsorption, the average size of the loops is small and the latter are not Gaussian chains. In this case the distribution depends on specific interactions, which are different for different chains. It is significant that in the chosen model there is a sharp decrease in the density distribution at distances from the surface exceeding the effective thickness of the segment $z = \delta$. In the adsorption layer near the surface ($0 < z < \delta$) Eqn.(1) is inapplicable; the fraction of bound segments is given by another relation and the density $\rho_a = P\delta^{-1}$, where

$$P = (1 + S_{-3/4})(1 + S_{-1/4} + S_{-3/4})^{-1}.$$

The density of the segments in solution at a distance $z = \delta$ is given by the equation

$$\rho(\delta) = K(1 + S_{-1/4} + S_{-3/4})^{-1},$$

where K is a numerical coefficient. Comparison of this equation with Eqn.(1) shows that the density falls for $z = \delta$.

For a real chain, more rigid than that assumed in the calculations, the decrease of density will be greater the more rigid the chain. This decrease is consistent with expectation, since there must be a compromise between the random distribution of the segments in all the layers and the greatest possible saturation of the first layer, where attraction takes place.

Hoeve[8] also calculated conformations taking into account the rigidity of the polymer chain. The rigidity parameter was introduced into the calculation of the number of random movements of the chain in a three-dimensional lattice in the form of a factor w when the step taken in the lattice was in the same direction as the previous one; if the step was taken in any of the four directions perpendicular to the previous one, the factor was unity.

The factor $w = \exp(-\varepsilon/kT)$, where ε is the difference between the energies of conformations in one of which two consecutive bonds lie in the same direction while in the other they are perpendicular to one another. If ε/kT diminishes, then w and hence the rigidity of the chain increase. In the limit, where ε/kT tends to an infinitely large negative value, the chain becomes rigid and rodlike. In the case where the first step in the lattice begins at the interface the partition function for a single chain is defined. The grand partition function for a chain fixed at one end at the interface is

$$\theta(s) = |E|^{-1}\{\{(\lambda - sw)^{-1} + s(1 - sw\lambda)^{-1}\}4s^2t + \{s + s^2(\lambda - sw)^{-1} + s(1 - sw\lambda)^{-1}\}\{1 + (2 - w)st\}(1 - \lambda)^{-1}\};$$

where $s = \exp\mu/kT$, $|E|$ is a function of w, s, t and λ, and μ is the chemical potential of a monomer unit under the conditions of the equilibrium distribution of the N-mers bound to the surface by one end only; $t = \exp(-\varepsilon_a/kT)$, where ε_a is the adsorption energy (the necessary condition for adsorption is $\varepsilon_a < 0$ and $t > 1$) and λ is the Lagrange multiplier. The average number of bonds in the chain can be found from the equation:

$$\langle N\rangle = \partial \ln\theta/\partial \ln s$$

while the average number of bonds adsorbed at the interface is $\langle N_0\rangle = \partial \ln\theta/\partial \ln t$. Then at a distance from the surface the average number of segments in the layer is $\langle N_0^k\rangle = [\partial \ln\theta/\partial \ln u]$, where u is the exponent of the polynomial in the function describing θ. Calculations showed that, for low values of λ, the density of the segments decreases sharply on moving away from the surface and that the majority of the segments are adsorbed in the first layer. Only when λ approaches 1 does the density of the segments near the surface become appreciable. In the limit at $\lambda = 1$ the density of the segments near the interface is a maximum and constant for all the layers. The critical values of t for adsorption are in this case defined by the relation

$$t = (w+4)^2(w^2+6w+12)^{-1}.$$

Thus, whereas previously Hoeve[8] introduced the flexibility parameter C for the Gaussian chain, which is difficult to determine quantitatively, in the present model the flexibility of the chain is taken into account by the parameter w, which constitutes an advantage of the approach under consideration. For an adsorbed chain consisting of a sequence of adsorbed segments and loops, the following relation holds:

$$\theta=\theta_{tr}+\theta_{loop}=1,$$

where θ is the grand partition function, which is a function of the ratio of the activities of the adsorbed and free chains and θ_{tr} and θ_{loop} are the grand partition functions for trains and loops. It can be shown that

$$\theta_{tr}=(w+2)st[1-(w+2)st]^{-1},$$
$$\theta_{loop}=4s(\lambda-sw)\ (1-sw\lambda)^{-1}(w+2)^{-1}.$$

At the same time Hoeve[9] emphasises the unrealistic nature of the model which he chose, as well as all other models examined previously. However, he reaches the important conclusion that the sharp subdivision into surface and diffuse layers is artificial. In practice density as a function of distance depends on specific chain conformations. Unfortunately, the thickness of the layer cannot be determined exactly experimentally regardless of theoretical postulates. A specific density profile is usually postulated beforehand after which the average thickness of the layer is calculated.

Hoeve notes that in such calculations one cannot ignore the effect of the excluded volume, which is bound to occur in real systems as a result of the interchain interaction. However, one can assume that, in the diffuse layer beyond the interface[10,11], the effects of the excluded volume are insignificant if the volume fraction of the segments is much lower than at the interface.

3. Other Theories

The distribution functions examined above contain parameters which are virtually impossible to estimate for real systems. Despite this, the segment distribution functions have been modelled in a number of studies. Hoffman and Forsman[12] attempted to estimate the parameters of the distribution function on the basis of the Flory–Huggins theory of polymer solutions, but they began with the inadequately justified hypothesis that the adsorbed segments have the normal density. They analysed the Gaussian distribution and the distribution proposed by Hoeve[8] and proposed a double Gaussian model of the type

$$\rho=\rho_0[\exp\{-B^2(x^2+y^2)/\alpha_{xy}\}]\times[A\exp\{-z^2/B\}+(1-A)\exp\{-z^2/C^2\}],$$

where ρ is the density of the segments, α_{xy} the broadening factor for chains in the x and y directions, z the distance from the surface, x and y the distances along the surface, and A, B, and C are independent model parameters. In the z direction, perpendicular to the surface, the model can be reduced to the Gaussian distribution for $A=0$ and is close to the Hoeve distribution for $B>C$.

A probability density distribution function has also been proposed[12] for the radius of inertia and has been used to represent the configurational entropy as a component of the free energy of the adsorbed molecules. A numerical algorithm has been proposed for the determination of the parameters of the distribution function by minimising the free energy at the interface. However, the calculations are very difficult and require a very large amount of computation.

A statistical method for finding the density distribution of the segments for an anchored chain has been proposed[13]. For a layer of constant density, the parameters of the distribution function have been determined from the equilibrium degrees of adsorption and the area of the monomer unit[14]. A distribution function taking into account the formation of surface layers of different thickness and the deformation of macromolecules in adsorption has been proposed[14] and used to estimate the average thicknesses of the layer. The results indicate a satisfactory description of the conformations of the macromolecules in the surface layer by the proposed distribution function and the possibility of its employment for the determination of the thickness of the adsorption layer.

Lax[15] examined the configurational behaviour of an isolated polymer molecule and the influence on the latter of the interaction with the solvent. The necessity for taking this into account was pointed out in an earlier study by Silberberg[16], who demonstrated theoretically that the influence of the solvent and concentration can induce appreciable conformational changes. Lax calculated the conformations by generating random self-avoiding movements in the lattice in the presence of an interacting rigid barrier. Relations were obtained for the mean square distance between the ends of the chain $\langle R_N^2\rangle$ corresponding to different numbers of segments N and different adsorption energies and for the average and mean square distances from the end of the chain to the surface $\langle z_N\rangle$. Calculations showed that the latter quantities, determined taking into account the influence of the interaction with the solvent, are large. The average maximum quantity $\langle z_N^{max}\rangle$ increases with decrease in adsorption energy. The average numbers of segments on the surface have also been calculated as functions of the adsorption energy and the attainment of saturation for high energies ($\varepsilon > 2.2\ kT$) has been demonstrated.

The influence of the excluded volume of the conformations of the adsorbed polymers has also been examined in a study[17] where it was assumed that the density of the adsorbed molecules is high and homogeneous and that partial overlap of the molecules and their interaction take place on the surface. An expression was found for the critical value of the free energy of the adsorbed segments:

$$\varphi_c=\varphi_c^0(1+6n\nu z_0/l^2+\ldots),$$

where ϕ_c^0 is the critical free energy of the adsorption of the segment at the θ-point, n the total number of adsorbed segments, l the bond length, z_0 the range of action of the adsorption potential, and ν the excluded volume defined by

$$\upsilon=(1/2-\chi/V_2^2)V_1$$

(χ is the interaction parameter and V_2 and V_1 are the volumes of the segment and the solvent molecule).

The average thickness of the adsorption layer is

$$t(\gg z_0)=t_0(1+6n\nu t_0)/l^2,$$

where t_0 is the average thickness of the layer at the θ-point.

In recent years Hesselink developed a model of the structure of the adsorption layer[18,19], according to which the adsorption layer consists of a dense first layer, at whose boundary there is an abrupt change in the density of the segments, and of a loose layer of tails and loops directed towards the bulk of the solution. Hesselink[19] determined for a cubic lattice the distribution of the units in a macromolecule adsorbed by its end in a tail of i segments and in a loop (adsorption via two terminal groups) using a method similar to that developed by Hoeve[14].

The following function has been obtained for the distribution of segments in a molecule attached via the tail[19]:

$$\rho_1(x) = 6\,(il_c^2)^{-1} \int_x^{2x} \exp\{-3t^2/2il_c^2\}\,\mathrm{d}t,$$

where x is the distance from the surface, i the number of segments in the macromolecule, and l_c the length of the segment. The distribution of the segments in the loop is

$$\rho_2(x) = 12\,(il_c^2)^{-1} \exp\{6x^2/il_c^2\}\,.$$

From these equations, it is possible to find the mean square distance between the segments and the surface. For a chain attached at one end, $\langle x^2\rangle = \frac{7}{18} il_c^2$, and for a chain attached at two ends, $\langle x^2\rangle = \frac{1}{6} il_c^2$. This calculation shows that the loop is more tightly compressed on the surface than the tail comprising the same number of segments only by a factor of $\sqrt{7/3}$. This distribution can be applied also to a chain adsorbed by several loops, provided that the number of segments in each loop is the same. This problem was examined in detail by Hesselink[19], who analysed statistically the changes in the configurational properties of adsorbed macromolecules as an impermeable surface is approached.

The distribution functions have also been calculated for the adsorption of the molecules of copolymers in which the size distribution of the loops is determined by the distribution of the lengths of sequences of different units. The distribution curve for the case of a large number of loops is less steep than for the distribution in the case of only one loop. It is significant that in the adsorption of a copolymer via one loop the density in the immediate vicinity of the surface is lower than at some distance from the latter. This is because in a homopolymer any segment can be sorbed, while in a copolymer only a segment capable of interaction can be sorbed[19].

Next Hesselink examined the configurational free energy of the tails, loops, and bridges formed by macromolecules between particles (in connection with the consideration of the problem of the stabilisation of colloid particles and the behaviour of macromolecules between two adsorbing planes). The case of the mutual approach of particles coated by adsorbed molecules, where the adsorption layers should be capable of interpenetration, was examined; the density distribution of the segments in the tails and loops then changes as the two surfaces approach one another[20].

It has been suggested[21,22] that the density of the segments decreases with the distance from the surface and that the effective density of the adsorption layer is related to the average size of the loops in the same way as the change in the density of the segments $\rho(\tau)$ of a free coil with the distance from its centre of gravity is related to the number of segments in the macromolecule, i.e. it is assumed that $\rho(\tau) = \rho_{\text{eff}}$ for $\tau = \Delta$ (Δ is the thickness of the layer). This is a fairly rough approximation, since the density distribution of the segments in solution is Gaussian and that in the adsorption layer is in most cases exponential.

Theoretical calculations of the density distribution of the segments and of the thickness of the layers are important for the description of processes involving the stabilisation of dispersed particles by polymers or their flocculation. These problems, associated with the structure of the adsorption layer, have been discussed in detail in a number of studies[20,23,25]. They are based on the postulate of the adsorption interaction of the macromolecules with two flat plates.

Using a simple model of the macromolecules adsorbed on two parallel plates with a specific surface area A and separated by a distance L, it is possible to calculate the resultant pressure on the plates under conditions of repulsion associated with configurational entropy[24]. Neglecting the adsorption of the polymer on the surface, the conformations of a chain with a specified length N, beginning at a point r on the surface and terminating at a point r' in the gap between the plates, are then calculated by statistical methods. The free energies can then be found from the expression for the partition function for such a chain and can be used to obtain the effective pressures. For plates remote from one another ("short" polymer chains) and for plates close to one another (long chains), the following equations have been found (l is the chain length):

$$p = -\frac{1}{A}\frac{\partial F}{\partial L} = \frac{kT}{AL}\left[1 + \frac{2}{\pi^{1/4}}\left(2\,\frac{Nl}{3L^2}\right)^{1/4}\right],$$

for the case where $2Nl/3L^2 \ll 1$ and

$$p = \frac{kT}{AL}\left[\frac{4\pi l^2 N}{3L^2} + 1 \ldots\right].$$

for $2Nl/3L^2 \gg 1$.

These theoretical results show that the polymer adsorbed on the surface can stabilise colloid particles by virtue of the repulsion due to the entropy factor. On the other hand, flocculation can occur in the case of strong adsorption of polymer segments on the surface of the colloid particles.

4. The Adsorption Isotherm of Compact Macromolecules

In the studies discussed above the problem of adsorption isotherms, which had been the subject of thorough investigations in previous years[1], was not considered. A new feature in this field is Silberberg's attempt[26] to derive an equation for the adsorption of compact macromolecules, which include those of biopolymers present in solution in the form of dense self-aggregated globules. It is assumed that the electrostatic effects specific to given systems are of secondary importance compared with the large size of the macromolecules (for a high ionic strength of the solution and a sufficient charge separation in the molecules) and one considers a compact ("cubic") macromolecule whose volume is greater by a factor P than that of the solvent molecule. In a three-dimensional lattice such a macromolecule occupies P sites. If each site in the lattice has c_B neighbours in the

bulk phase and c_S neighbours on the surface, then the macromolecule itself in its natural coiled conformation is characterised by the following number of interactions:

$$\frac{1}{2}Pc_B-(P-1)-\frac{1}{4}P_S(c_B-c_S),$$

where P_S is the number of segments on the surface of the compact molecule. In adsorption z out of the P_S outer segments are bound to the surface. Then, for a cubic molecule, the adsorption would extend from the surface into the bulk phase over $1/p=P/z$ layers, forming the surface phase, among which only the first layer is in direct contact with the surface, but all the $1/p$ layers have the *same* concentration of polymer segments (in contrast to the adsorption of the usual flexible chains)[26] (here p is the fraction of segments bound to the surface).

If there are M^S sites and N_p^S polymer molecules on the surface and N_0^S solvent molecules form the surface phase, then

$$(1/p)M^S=N_0^S+PN_p^S.$$

If the system contains N_p^T polymer molecules and N_0^T solvent molecules, then the bulk phase contains $N_p=N_p^T-N_p^S$ polymer molecules and

$$N_0=N_0^T-N_0^S=N_0^T-(1/p)M^S+PN_p^S$$

solvent molecules.

We shall define $\theta=xN_p^S/M^S$ and $\Phi^*=PN_p/(N_0+PN_p)$ as the degree of surface coverage and volume saturation. For specified M^S, N_p^T, and N_0^T, these quantities are a function of N_p^S alone. If the unmixed pure polymer phase comprising N_p^T molecules and the solvent phase comprising N_0^T molecules in contact with M^S sites are regarded as the initial state, it is possible to determine the number of different configurations on mixing in contact with the surface subject to the condition that all the configurations have the same energy. When there is a difference between the energies of the configurations, i.e. when the energies of the polymer–polymer, solvent–solvent, and polymer–solvent junctions are different, it is possible to determine the energy of mixing of the macromolecules with the solvent in the presence of a surface:

$$\Delta U/kT=\chi(c_pz/c_BP)(PN_p)N_0/(N_0+PN_p)+$$
$$+\chi\{(c_p-1)z/c_BP\}(PN_p)N_0^S/(N_0^S+PN_p^S)-\chi_S(z/c_{SB}P)(PN_p^S),$$

where χ is the usual Flory–Huggins parameter, χ_S a parameter characterising the sorption of a flexible molecule, and c_p the coordination number.

Starting with these postulates, one can find the partition function determined by the maximum in the derivative of $\Omega\exp(-\Delta U/kT)$ with respect to the single independent variable N_p^S:

$$\partial\ln[\Omega\exp(-\Delta U/kT)]/\partial\ln N_p^S=0.$$

Hence we obtain finally an expression for the adsorption isotherm:

$$\ln(\theta/\Phi^*)=P\{\ln(1-\theta)/(1-\Phi^*)+p\ln p+(1-p)\ln(1-p)+$$
$$+(p\chi/c_B)[c_p(1-2\Phi^*)-(c_p-1)(1-2\theta)]+p\chi_S/c_{SB}\}.$$

Comparison of the theoretical isotherms obtained by plotting the number of equivalent monolayers $\theta/p=P^{1/3}\theta$ against the volume fraction of the polymer in the solvent with the degree of adsorption of flexible chains shows that the degree of adsorption of compact chains is greater and the fraction of the polymer on the surface $p=P^{-1/3}$ and the degree of surface coverage θ are smaller than for flexible chains. Consequently the surface layer is less compact. Calculation also shows[26] that in this case the possibility of a change in conformation in the surface layer (the uncoiling of the chain) plays an insignificant role.

However, in real systems, in the case of the adsorption of charged and compact macromolecules, there is a possibility of other relations. It has been shown[27] that there is virtually no adsorption of poly(methacrylic acid) (PMAA) in the globular unionised form from aqueous solutions. However, the nature of the adsorption of ionised PMAA [28] is determined by the charge on the adsorbent surface (the ζ-potential of its particles). The surfaces of alumina and quartz are negatively charged and the degree of adsorption of negatively charged macromolecules diminishes. Thus electrostatic effects, which cannot be described by statistical theories of adsorption, can play a decisive role in the given case.

The complexity of the theoretical description of the adsorption interaction of polymers with the surface of a solid absorbent consists in the fact that in such systems a number of inter-related phenomena occur during the adsorption process. It has now been established that the degree and nature of adsorption depend significantly on the formation of aggregates of macromolecules and the development of coagulation in the disperse phase[2,3,20]. On the other hand, the adsorption of the polymer is responsible for the establishment of a new aggregate–macromolecule equilibrium and also alters the rate of coagulation of dispersions. As a consequence of such correlation, an unambiguous interpretation of the experimental data obtained is in many instances impossible.

For a theoretical determination of the mechanism of the adsorption interaction at the interface, it is necessary to consider also the kinetics of all the processes occurring in the adsorption of macromolecules in the dispersions, namely the adsorption and aggregation of macromolecules and the coagulation of the disperse phase. Such a treatment, carried out by Lipatov et al.[29], has been based on Smoluchowski's kinetic equations for the coagulation of dispersions[30]. If macromolecules and their aggregates are considered as separate kinetic units, analogous to colloidal particles, then the kinetics of the aggregation of macromolecules and the kinetics of adsorption can be described by analogous equations.

The system of differential equations thus obtained cannot be solved analytically but, with the aid of numerical methods, it is possible to obtain on a computer the overall time pattern of the changes in the number of macromolecules, the particles of the solid phase, and their aggregates, as well as adsorbed macromolecules as functions of the size distribution of the micro-objects. The size distribution functions of macromolecules, the particles of the disperse phase, and the adsorbed macromolecules, characterising

the establishment of an equilibrium between the macromolecules, the particles of the solid phase, and their aggregates as a function of time and making it possible to follow the transition from the initial to the final equilibrium, were thus obtained.

5. The Application of Computer Modelling Methods in the Calculation of the Conformations of Adsorbed Chains

Computer modelling methods have been widely used recently to estimate the conformations of adsorbed polymer chains[31-35]. The configurational properties of oligomers have been calculated by the total sorting method, based on the generation of all possible N-unit chains, with subsequent extrapolation to high polymers[33]. Computer modelling has been carried out for chains with $N \leq 14$ on a cubic lattice with four selections, the energy of the junction between a section of the chain and the surface being varied from 0 to $1.5kT$. The number of segments on the surface, the number of returns to the surface (the number of loops), the length of the normal from the end of the molecule to the surface and its square, the distance from the surface to the most remote segment, and the distance between the ends of the chain were determined. These computer simulations showed that, with increase of adsorption energy, the mean square distance between the ends initially diminishes to a minimum at $-\varepsilon/kT = 0.375$ and then increases. The curves relating the number of loops to $-\varepsilon/kT$ pass through a maximum at $-\varepsilon/kT = 0.75$.

Thus the extremum values of different properties of the polymer chain are observed for different energies of their interaction with the surface. The calculations demonstrated the validity of the empirical relations $\langle R_N^2 \rangle = \alpha N^{\gamma}$, where α and γ are constants. For $-\varepsilon/kT \cong 0.5$, the quantity γ is close to 1.30, while for high interaction energies γ increases until it reaches, at $-\varepsilon/kT = 0.875$, the value 1.47 characteristic of two-dimensional lattices (1.50). This finding demonstrates the virtually complete adsorption of the polymer on the surface for $-\varepsilon/kT \geq 0.875$. It has been shown that, for energies $-\varepsilon/kT \geq 0.75$, the average distance between the most remote atom of the chain and the surface is less than two lengths of the chain.

The mean squares of the distance between the ends of the chains $\langle R_N^2 \rangle$ and of the radius of inertia $\langle s_N^2 \rangle$ as well as the average number of closed chains (not only beginning but also terminating on the surface) have also been estimated[32]. The conformational characteristics have been calculated for $N \leq 14$ and for different values of $-\varepsilon/kT$. It has been shown that, for open chains at $-\varepsilon/kT \to 0$, surface effects do not play any role, the ratio $\langle s_N^2 \rangle / \langle R_N^2 \rangle = 0.1314$, and the power exponent $\gamma = 1.20$. With increase of $-\varepsilon/kT$, these quantities change somewhat and the ratio $\langle s_N^2 \rangle / \langle R_N^2 \rangle$ diminishes sharply only for $-\varepsilon/kT \geq 1.6$ (critical value). The oligomer chain is then virtually completely sorbed on the surface. The behaviour of closed chains obeys another statistic. For such chains, $\langle s_N^2 \rangle / \langle R_N^2 \rangle \to 0.200$ and $N \to \infty$. It has been noted that the models considered in computer simulations are also useful for the derivation of information about the entropy effect associated with the folding of the chains in crystals, about the role of configurational effects in the stabilisation of colloidal solutions, etc.

The dependence on the molecular weight of the first and second moments of the extent of the chains attached to the surface at one end (by extent, we understand the maximum distance between the planes bounding the chain segments[34]) has also been calculated by the method of the total sorting of configurations. The calculations were performed for a tetrahedral lattice with prohibition of self-intersections of the chain and $N = 5-14$. It was shown that, if the average extent is represented by the expansion $\langle x_N \rangle = AN^{\gamma} + BN^{\gamma-1} + \ldots -1$, then the asymptotic value of γ for the adsorbed chains at $1/N \to 0$ is 0.53, which is somewhat smaller than the corresponding value for chains which do not interact with the surface (0.61). The mean square of the radius of inertia $\langle s_N^2 \rangle$ is proportional to a $N^{1.27}$ according to calculated data, i.e. the power exponent for adsorbed chains differs from the exponent characteristic of all non-intersecting three-dimensional chains (6/5). Apart from the average characteristics, different distribution functions have also been obtained[34]. It has been shown that they change sharply if, instead of the prohibition of self-intersections, one introduces the parameter of the interaction between chain segments. If this parameter is sufficiently large, certain distribution functions become bimodal or multimodal.

One should note that the average changes in the internal and free energies, the entropy, the heat capacity, and the effective coordination number have been calculated as a function of $-\varepsilon/kT$ by the total sorting method for non-intersecting chains at the boundary with the surface[35]. For certain values of $-\varepsilon/kT$ (1.8), the plots of C_V/k against $-\varepsilon/kT$ (C_V is the heat capacity at constant volume) pass through a maximum, which indicates a second-order phase transition. At the transition point the mean squares of the distance between the chain ends and of the radius of inertia reach a minimum. When the specific energy of the interaction of the chains with the surface is attained, the system becomes two-dimensional, which corresponds to the adsorption of the polymer on the surface.

The machine experimental methods in relation to problems of the adsorption of polymers were developed further by Birshtein and coworkers[36-39]. It was shown that increased rigidity of the chain facilitates the adsorption process and increases the fraction of adsorbed units. It follows from the results of [38,39] that, in the region of strong interactions with the sorbent, the chain "spreads out" on the surface via its extended sections. Calculation of the free energy of adsorption showed that, for the critical energy of adsorption, the polymer chain undergoes a second-order phase transition, which is consistent with Lax's results[35]. The computer simulation also made it possible to estimate the fraction of chain segments linked directly to the surface as a function of chain length and the adsorption energy[38]. The calculation of the structure of the chains in the surface layer[39] is also of interest.

III. EXPERIMENTAL ESTIMATION OF THE STRUCTURE OF THE ADSORPTION LAYER

Despite the different attempts to calculate the conformation of adsorbed chains near the interface, a direct comparison of the results of such calculations with experiment still does not yield satisfactory agreement. This is because in the majority of calculations simplifying assumptions, which do not hold in real systems, are made. For example, one always calculates the conformation of isolated chains, whereas all the experimental results reflect the existence of a large number of chains competing for surface sites. As a result, the conformations of real chains are very different from those calculated theoretically for isolated chains. From this standpoint, the experimental estimation of the conformations of adsorbed chains and of the thickness of the adsorption layer is still of significant interest.

1. The Hydrodynamic Thickness of the Adsorption Layer

Theoretical ideas concerning the hydrodynamic thickness of the adsorption layer, based on fundamental hydrodynamic equations, have been developed[40]. The calculations are based on the following experimental fact: the rate of flow of the polymer solution through a capillary diminishes as a result of the adsorption of the polymer on the walls. The measurement of this change makes it possible to calculate the hydrodynamic thickness of the adsorption layer, which is defined as follows:

$$L_H = R[1-(I_v/I_v^0)^{1/4}],$$

where I_v and I_v^0 are the volumes of the liquid which pass through the capillary in the presence and in the absence of the polymer for the same shear stresses and R is the radius of the capillary.

The ratio I_v/I_v^0 is a complex function of R, b (where b is the average distance between the given monomer unit and the wall of the capillary), and the shielding factor b/d, where $d=(\eta/fn_0)^{1/2}$, η is the viscosity of the liquid, n_0 the density of the segments in the first layer at the surface, and d the frictional force between the polymer molecules and the liquid. An exponential distribution of the density of the segments near the interface and the parameters introduced in Hoeve's theory were used for the theoretical calculations. Theoretical relations between L_H and R/b were plotted for a number of values of b/l, for different volume fractions of the polymer in the first layer, and for three different chain lengths.

Comparison of the theoretical calculations with experiment showed that L_H varies linearly with the intrinsic viscosity $[\eta]$ and that the experimental thickness of the layer is of the order of magnitude of the size of the coil in the polymeric solvent. This yields the conclusion that the dimensions of the polymer coils are not distorted in the adsorption process[40].

The behaviour of the adsorbed molecule in the layer in contact with the flowing solvent is significant for the determination of the hydrodynamic thickness relative to the thickness of the adsorption layer of the polymer. This problem has been considered theoretically[41] on the basis of the Rouse-Zimm model for a polymer chain attached to the surface by one end. The main result of the calculations of the dynamic behaviour of the chain was to show that, in the Brownian movement of the anchored chain, the energy scattering exceeds by a factor of two the corresponding value for a free molecule in solution. These effects are attributed to the influence of the surface on the number of accessible conformations of the macromolecule.

Methods are available for the determination of the thickness of the layer from the apparent increase in the effective volume of the dispersed particles carrying the adsorption layer, which is determined viscometrically using an equation of the Einstein type and from sedimentation data[42,43].

The thickness of the layer is calculated with the aid of the sedimentation coefficient, which can be expressed in terms of the thickness of the layer δ and its density ρ_z for a particle with a radius a and a density ρ_1 in a liquid having a density ρ_0 by the following equation:

$$s^0=[2a^2(\rho_1-\rho_0)+2(3\delta a^2+3a\delta^2+\delta^3)\times(\rho_2-\rho_0)]/9\eta_0(a+\delta),$$

where s^0 has been adjusted to the zero concentration of particles. It is then assumed that the adsorption layer is a rigid impermeable cell. The density of the layer is determined as follows:

$$\rho_z=0.997+2.39\cdot10^{-7}\cdot4\pi a^2\Gamma/[{}^4/_3\pi(a+\delta)^3-{}^4/_3\pi a^3],$$

where Γ is the degree of adsorption on the plateau of the isotherm. When account is taken of this, one obtains

$$s^0=[2a^2(\rho_1-\rho_2)+1.434a^2\Gamma\cdot10^{-6}]/9\eta_0(a+\delta),$$

which is in fact used for the calculations[42,43].

As a result of the sedimentation and flocculation of particles coated by the adsorption layer, the rate of sedimentation decreases and the sedimentation half-period and the sedimentation volume increase, which can, in principle, yield information about the thickness of the adsorption layer. Thus the adsorption of poly(vinyl alcohol) has been studied[43] in the form of fractions with different molecular weights on polystyrene. It was found that the degree of adsorption and the thickness of the adsorption layer δ, calculated from the sedimentation data, increase with increase of $\bar{M}_w^{1/2}$. The volume occupied by the macromolecule in the adsorbed state is approximately equal to the volume of the effective hydrodynamic sphere of the poly(vinyl alcohol) molecules in the solution. However, δ is smaller than the effective hydrodynamic diameter of the polymer coils in solution. The results were interpreted in terms of the possible deformation of the coils without the mutual interpenetration or compression of neighbouring adsorbed macromolecules.

2. Calorimetric Methods

The use of direct calorimetric measurements of the heats of adsorption of polymers and the establishment of relations between them and adsorption isotherms, which makes it possible to estimate the enthalpy of adsorption and the number of bound segments, constituted definite progress in the study of adsorption[42,44-46].

The integral heat of adsorption is determined by the relation

$$-\Delta H(\theta)=-n\Delta H_{P,A}+n\Delta H_{L,A}+n\Delta H_{P,L}+\Delta H_{P,P},$$

where n is the number of points on the surface coated by the polymer segments, $\Delta H_{P,A}$ the enthalpy of binding per mole of monomer units, $\Delta H_{L,A}$ the heat of wetting per mole of active points on the surface, $\Delta H_{P,L}$ the enthalpy of desolvation per mole of adsorbed monomer, and $\Delta H_{P,P}$ the energy of the interaction of the adsorbed polymer molecules. If the last term is neglected, then

$$-\Delta H(\theta)=-n(\Delta H_{P,A}-\Delta H_{L,P}-\Delta H_{L,A}),$$

i.e. the enthalpy of adsorption is proportional to the number of centres on the surface and to a constant enthalpy contribution (the expression in brackets).

The differential enthalpy of adsorption is

$$D_A=\frac{d\Delta H(\theta)}{dN}=\frac{dn}{dN}(\Delta H_{P,A}-\Delta H_{L,P}-\Delta H_{L,A}),$$

where $N = A/M_M$ is the number of adsorbed polymer molecules in monomer units, A is the amount of the adsorbed polymer in grammes, and M_M the molecular weight of the monomer unit; thus D_A is a measure of the fraction of segments bound to the surface[46]. The enthalpies of adsorption of poly(ethylene glycols) of different molecular weights on aerosil have been determined experimentally. A linear dependence of the enthalpy of adsorption on the extinction coefficient of the band associated with the hydrogen bonds between poly(ethylene glycol) and aerosil (3300 cm^{-1}) was also established. The energy of the binding of poly(ethylene glycol), amounting to 41.4 kJ per mole of SiOH, which corresponds to the energy of the hydrogen bonds, was found from the enthalpy taking into account the density of the SiOH groups on the surface (which is 2.74/100 A^2).

The heat of adsorption data show that, along the initial sections of the isotherms, approximately 50% of the segments are bound, in satisfactory agreement with the estimates of the fraction of bound segments by infrared spectroscopy, and $p = 0.2-0.5$ at saturation. Thus calorimetric measurements yield, in principle, the same conclusions concerning the conformations of the macromolecules in the boundary layers as the other methods used previously[1]. However, calorimetric measurements yield more information about the mechanism of the adsorption and the interaction. The enthalpy of the adsorption per segment estimated from calorimetric data depends on the competing effects of the polymer–adsorbent, polymer–solvent, and solvent–polymer interactions[42].

A strong interaction between the solvent and the surface leads to a lower enthalpy of adsorption per segment than in the case of a non-polar solvent. In order to obtain a definite enthalpy of adsorption in a polar solvent, it is necessary that the degree of binding of the macromolecule be greater than in a non-polar solvent, which leads to a more planar conformation of the adsorbed macromolecule and to a smaller thickness of the adsorption layer.

In principle, when one considers the adsorption of polydisperse polymers, one must also consider the influence on adsorption of the particular level of thermodynamic incompatibility of fractions having different molecular weights, which follows from the dependence of the Flory–Huggins interaction parameter for the fraction χ_{23} or the parameter X_{23} of the new Flory theory on the composition of the mixture of polymer homologues[47]. A partial incompatibility of fractions of different molecular weight leads to the formation of molecular aggregates, which can be adsorbed on the surface independently. This follows from direct adsorption measurements[48], demonstrating the adsorption of aggregates of different structure, for a fairly broad molecular weight distribution, from solutions in a thermodynamically poor solvent.

In this connection one should note that at one time a number of workers[1] estimated the so-called isosteric heats of adsorption. The present state of the problem shows that these estimates cannot be regarded as correct. A change of temperature entails a change in the conformation of the polymer chain and in the interaction of the macromolecules with one another and with the solvent. As a consequence of this, when the temperature is altered, the conditions governing the junction between the macromolecule and the surface are different and the number of bound segments and hence also the overall enthalpy of adsorption per macromolecule (or the number of bound units) are not the same. One should also take into account the different adsorbabilities of high- and low-molecular-weight fractions and in principle the different temperature variations of their solubilities. All this suggests that the required results can be obtained only by the direct experimental determination of the heats of adsorption, as was done for the first time by Killmann et al.[42]

3. Spectroscopic Methods

The structure of adsorption layers has been studied by infrared spectroscopy[49] for linear saturated aliphatic polyesters and polystyrene. When the adsorbent is aerosil, the polyester is bound by hydrogen bonds on adsorption, as expected, which makes it possible to estimate the fraction of bound segments readily by infrared spectroscopy. For polyesters, this fraction is $p = 0.80$, which indicates the formation of layers with a relatively small number of loops. On the other hand, polystyrene does not interact with more than 50% of the surface hydroxyls via its benzene rings. The experimental adsorption isotherms can be described by the equation of the Langmuir isotherm.

Continuation of studies of the adsorption layers of various polymers by ellipsometric methods by Killmann and coworkers[50,51] permitted the subsequent development of a method based on the construction of isotherms for the thickness of the layer, the polymer concentration in the surface layer, and the degree of adsorption as a function of the solution concentration as well as the same quantities at saturation as a function of the molecular weight of the polymer. The influence of the molecular weight and the polarity of the polymer or adsorbent on these characteristics was established and a conclusion was reached concerning the possible conformations of the macromolecules in the adsorbed layer, which corresponds to the features already described and in our view leads to only isolated refinements in relation to specific polymers.

Thus it has been established that the thickness of the adsorption layer is described by the Mark–Houwink relation $d = KM^{\alpha}$, where M is the molecular weight and K a constant. For adsorption in the form of isolated coils, $\alpha = 0.5$ and for molecules extended on the surface, $\alpha \to 0$. An increase of α from 0.15 for low coverages to 0.5 for high coverages confirms the hypothesis that the conformation of the adsorbed chain depends on the solution concentration (degree of surface coverage). The dependence of the mean square thickness of the layer at the maximum solution concentration investigated (5 mg ml^{-1}) on the square root of the molecular weight (straight line) confirms that in the region of high concentrations the molecules are adsorbed in the form of a θ-coil[50,51].

Methods for the estimation of the conformations of adsorbed chains, based on the use of electron paramagnetic resonance (EPR)[52,53] have been developed in recent years together with the infrared spectroscopic method for the determination of the fraction of segments adsorbed on the surface. For this purpose, one uses polymers with a spin label, which gives rise to three lines in the EPR spectrum; their form and width being determined by the rotational correlation time. For a polymer adsorbed at the solid–solution interface, providing the spin label is distributed at random along the chain and does not influence the adsorption process, the differences in the mobilities of the side groups of the chains are clearly manifested in the width of the spectral lines and in their positions. The segments adsorbed in the form of trains on the surface have shorter correlation times than the segments in loops.

The adsorption of the *N*-vinylpyrrolidinone–allylamine copolymer on aerosil has been studied by this method[53]. The label was introduced by the interaction of the polymer via its NH_2 groups with 4-isothiocyanato-2,2,6,6-tetramethylpiperidine oxide (one label for five polymer molecules).

The ratio of the number of segments in the loops to the ratio of the number of segments in the adsorbed trains can be estimated from the EPR data for the linear polymer subject to the assumption made above. However, one cannot then take into account segments with intermediate mobility, i.e. the segments in the loops but close to the surface. Since the complex spectrum can be resolved into two simple spectra, it is suggested that the number of such segments is small compared with the total number of segments. It has been established by this method[52,54] that the conformation of the polymer chain varies from relatively planar to a conformation characterised by the presence of loops with increase of surface coverage of the adsorbent. This follows from the dependence of the fraction of adsorbed segments p on the degree of surface coverage.

Thus the overall pattern revealed by the EPR method is consistent with that already described on the basis of the results of measurements by other methods. However, the following result is of interest. It has been shown that, when an additional portion of pure sorbent is added to the sorbent saturated by the adsorbed polymer, a significant increase of the degree of binding of the segments p, determined by NMR, is observed[53]. This demonstrates the formation of bridges between different sorbent particles bound to the macromolecule, which is important for understanding the mechanism of the interaction of the dispersed particles following the introduction of polymer molecules into the disperse system. The authors suggest[53] that this effect is associated with the fact that some of the segments present initially in the loop are converted into an adsorbed train of segments as a result of the adsorption of added particles on the unoccupied surface. The formation of a bridge implies that some of the molecules pass from an adsorption-saturated particle to an unsaturated particle, which can entail an increase of p.

The application of the EPR method in the study of the influence of the solvent on the conformation of the adsorbed molecule showed that an impairment of the "thermodynamic quality" of the solvent leads to an increase of the fraction of segments in the trains of segments bound to the surface, which conflicts with Hoeve's data[10] showing that the size of the loops increases with "impairment" of the solvent.

The conformations of adsorbed chains have been studied experimentally[54] by high-resolution NMR in adsorption of poly(methyl methacrylate) on silica gel. The method is based on the decrease in the molecular mobility of the adsorbed chains (segmental mobility). Its advantage over infrared spectroscopy is its applicability to the study of stereoregular polymers. Isotactic and syndiotactic polymethacrylates served as the objects of study. The complete disappearance of the signal associated with the segmental mobility, observed by the authors, shows that the polymer forms a large number of contacts with the surface and that the loops formed are relatively short and immobile. Isotactic poly(methyl methacrylate) is adsorbed preferentially relative to the syndiotactic polymer, as shown by data for the adsorption of their mixture.

The NMR method has also been used to determine the molecular mobility in adsorption layers of polystyrene and polycarbonate on aerosil; it is significant that the measurements were performed in the adsorption system itself without separating the adsorbent[55]. The experimental data obtained demonstrated the dependence of the mobility at a given solution concentration on the adsorbent content, which made it possible to regard the structure of the adsorption layers as one formed by adsorbed isolated loops and chain aggregates, in agreement with the concepts developed by the present author[2,3].

4. Colloidal-Chemical Methods

Interesting possibilities for the estimation of the thickness of adsorption layers of polymers arise from the measurement of the $\mathcal{L}$-potential of colloidal particles coated by the adsorbed layer of polymer. However, this method can be applied only to adsorbent particles of colloidal dimensions. When it is used, one measures simultaneously the degree of adsorption of the high-molecular-weight substance and its influence on the electrokinetic potential of the particles[56-58]. It is assumed that the decrease of the $\mathcal{L}$-potential with increasing degree of adsorption of the polymer is due to the displacement of the slip plane to the bulk of the solution as a result of the formation of the polymer layer on the surface and that the adsorption of the polymer does not entail a change in the distribution of charges in the diffuse ionic layer. In this case[59]

$$\tanh\left(\frac{ze\mathcal{L}}{4kT}\right) = \tanh\left(\frac{ze\psi_\delta}{4kT}\right)\exp\left[-\varkappa(\Delta-\delta)\right].$$

On the basis of this equation, it is possible to calculate for each measured electrokinetic potential the distance of the slip plane from the surface, which is assumed to be the thickness of the adsorption layer. In this equation e is the elementary charge, δ the thickness of the Stern layer, ψ_δ the potential at the boundary of the Stern layer for which one adopts[58] the $\mathcal{L}$-potential at the initial (unprotected polymer) sol, and $\varkappa$ the Debye radius.

This method has been developed in detail for polymer-stabilised sols by Kocherga and Baran[60], who determined also the dependence of the thickness of the layers on the degree of adsorption of polymers. According to their data, the thickness of the adsorption layers increases monotonically with increasing degree of adsorption, reaching 100–200 Å, which is in good agreement with other data. The fact that the thickness of the layer depends in the first place on the degree of adsorption and not on the molecular weight of the polymer led to the conclusion that the average length of the adsorption loops also depends little on the molecular weight[60,61]. However, it must be emphasised that the determination of the thickness of the polymer layers on the surface of colloidal particles from electrophoretic measurements constitutes a fairly rough approximation.

At the same time comparison of the thickness of the layers[61] of poly(ethylene oxide) with the dimensions of the macromolecules in solution permits the conclusion that the polymer chains are appreciably deformed on adsorption. The experimental data obtained by this method suggest that the degree of deformation of the coils in the adsorption layer decreases with increasing rigidity of the macromolecular chains[25,60].

IV. CONCLUSION

The problem of the conformations of the macromolecules and of the structure of the adsorption layers is closely related to the elucidation of the mechanism of the adhesion of polymers to solids. However, in this case we are dealing with an adsorption interaction uncomplicated by the presence of a solvent in the system.

The problem of macromolecular conformations in adsorption layers in polymer compositions, i.e. in the absence of a solvent, is very important from the theoretical and practical points of view. Few experimental data have as yet been obtained on the thicknesses of the adsorption layers in the

absence of a solvent and on the conformations of macromolecules in such layers[62-66]. The single theoretical study by Silberberg[67] concerning adsorption in the absence of a solvent is of significant interest. The initial postulate was that adsorption leads to two main consequences—to an increase in the extent of the interfacial zone, where there is a transition from one homogeneous phase to another, and to an appreciable alteration of the conformation of the macromolecules in this region.

The theoretical models of the adsorption considered previously, the most general form of which is that developed by Silberberg, do not predict interfacial zones of considerable thickness. In the usual models of loops of different dimensions the distribution of segments is described by an exponentially decreasing function of the distance from the surface with a characteristic width proportional to the average length of loops. For chains with a large molecular weight, this model predicts that their size is independent of the molecular weight and the observed dependence of the thickness of the surface phase on the molecular weight cannot therefore be explained. For this reason, the model which is more realistic takes into account the influence of "tails" and postulating that the thickness of the layers is determined mainly by the "tails" [19,67] and not by the loops and that the number of segments in the loops is smaller than in the "tails" (this is consistent with the results of the studies by Lal and Stepto described above). The distribution of the segments in the tails should depend on the molecular weight.

Silberberg[67] considered theoretically the distribution of the segments in a pure polymer phase (in the absence of a solvent) in contact with the surface. The treatment is restricted to completely flexible chains whose arrangements correspond to identical energies and are equally probable. It is assumed that, at a distance h from the surface, the macromolecules are not subject to its influence, i.e. their conformations are unperturbed. The molecules in the layer with a thickness h adjoining the surface are then perturbed. By introducing the distribution functions for the density of the segments at different distances from the surface and the distribution functions of the centres of gravity of the macromolecules, the author obtained simple expressions for the number of macromolecules adsorbed by a unit surface ("perturbed") in the form

$$h/PV_0,$$

where P is the number of segments and V_0 the volume of the segment. Among this number, on average PV_0/A_0h segments of each chain are adsorbed on the surface, A_0 being the area per segment on the surface. The fraction of adsorbed segments is then

$$p = V_0^{1/3}/h.$$

Since h is comparable to the mean square radius of rotation at least as regards the order of magnitude, $h \cong V_0^{1/3}P^{1/2}$, it follows that

$$p \simeq 1/P^{1/2}.$$

On the basis of this estimate, Silberberg concluded that the width of the interfacial zone is proportional to the average radius of rotation and that in this region only a small section of the segments are in actual contact with the surface and that the "tails" exert the dominant influence on the thickness of this zone. According to Silberberg, the extent of the interfacial region is a consequence of the fact that the unperturbed macromolecules cannot approach the surface to a distance shorter than the radius of rotation and the remaining space is therefore filled with macromolecules with perturbed conformations. Because of this, the adsorbing surface exerts a significant influence on the form of the distribution functions of the segments and the centres of gravity of the macromolecules. This concept is closely related to the concept of the long-range influence of the surface on the structure of the adsorption layer, developed previously by the present author[1], and therefore confirms theoretically the numerous experimental facts that accumulated in earlier studies[1,68].

The above analysis of experimental data shows that, despite the definite progress achieved in recent years in the study of the structure of adsorption layers, and the development of fairly reliable methods for the estimation of their thickness, the problem of the conformations of the macromolecules at the interface remains open. The present author believes that this situation to some extent reflects that which has arisen in the study of molecular conformations in the amorphous state, where conflicting views exist[69-71]. At the same time it is evident that further investigation of this problem is of primary importance for the physical chemistry of polymeric compound materials.

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Institute of the Chemistry of Macromolecular Compounds, Academy of Sciences of Ukrainian SSR, Kiev