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A Theory of Polymer Adsorption from Solution

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A statistical thermodynamical treatment for polymer adsorption from solution is presented. The canonical partition function for the polymer solution in the presence of a surface or an impermeable interface is formulated on the basis of usual quasi-crystalline lattice model, Bragg-Williams approximation of random mixing, and Pak's simple treatment of liquid. The present theory gives the surface excess Γ_{ex} and the surface coverage ϕ_s^1 of the polymer as a function of the chain length x, the Flory-Huggins parameter χ, the adsorption energy parameter χ_s and polymer concentration v_2. Present theory is also applicable to the calculation of interfacial tension of polymer solution against water. For the idealized flexible polymer, interfacial tensions according to our theory fit good to the experimental data to the agreeable degrees.

Introduction

The adsorption of polymer molecules at an interface from polymer solution is of great importance both in theoretical and practical aspects. It plays an essential role in colloid science, such as adhesion, flocculation, stabilization and destabilization of colloid particles by polymeric additives. One of the important features which are quite different from those of the adsorption of small molecules from monomeric liquid mixtures is that the number of conformations displayed by a flexible

polymer at an interface increases tremendously with chain length of the polymer. Since even in the very dilute solutions the segment concentration near the surface may be very high, the interaction between the segments can not be neglected. In addition, during the adsorption of polymer molecules at a surface, the conformation of the molecule changes considerably, and the initial conformation depends largely on the nature of the solvent, the temperature, the concentration of the solution, and other factors.

The nature of the solvent is one of the most important fac-

tors determining polymer adsorption. It is clear that the conformation of the polymeric chain in the solution depends appreciably on the nature of the solvent. The solvent determines the effective volume, of the polymer molecule in the solution and the asymmetry of the polymeric coil. These factors determine the conditions of contact of the polymer molecule with the surface, the possible orientation of the polymer molecule at the surface, the structure of the adsorption layer, and other parameters.

According to Lee and Pak[1], in order to elucidate the solvent effects in the polymer solution, the polymer solution system has been described by introducing the concept of *"fluidized vacancies or holes"* in liquid.[2-5] In this approach, the holes in the polymer solution are assumed to be nearly dependent on the solvent molecules at moderate concentrations. Thus, it can be assumed that $N_t(V/V_s)/V$, holes are introduced at random into the total volume V, where V_s is the vertual close packed volume of the system which contains N_1 solvent molecules and N_2 polymer molecules. The size of each hole and that of each segment of the polymer are assumed to be molecular size of the solvent molecule.

In this work, we develop a general theory of adsorption from polymer solution by extending the polymer solution theory of Lee and Pak[1].

Theory

A. Formulation of Partition Function. We consider a liquid mixture consisting of N_1 solvent molecules and N_2 polymer molecules in the presence of a clean planar surface or an impermeable interface of area A. For convenience, the canonical partition function $Q(N_1, N_2, V, T, A)$ is written as

$$Q = Q_1 Q_2 \Omega \exp(-U/kT) \tag{1}$$

where Q_1 corresponds to the partition function of the monomer liquid molecules, Q_2 corresponds to that of the polymer molecules in this system, Ω is the combinatory factor which corresponds to the number of ways of arranging N_1 monomers and N_2 polymer molecules, and U is related to the total interaction energy among the molecules and the surface (see *eq* 8).

From the usual quasi-crystalline lattice model of liquid mixtures, the solvent molecule occupies on lattice site and each segment of polymers consisting of x identical segments occupies one lattice site. The surface region is divided into M layers of lattice sites parallel to the surface, designated $i = 1, 2, ..., M$ from the top of the surface.

During the adsorption of the polymer molecules at the surface, there may occur some conformational changes of the polymer molecules. Thus, in general, the chemical or physical nature of the polymer segment in i-th layer is different from that of other layers because of the conformational changes of the polymers near the surface. But, for the sake of simplicity, we assume that the partition function of each segment in all layers except the first layer on the surface is the same with that of the bulk solution. This assumption is similar to BET assumption in the gas phase adsorption theory[6]. In other word, as in the case of BET model, we assume

$$q_1 \neq q_2 = \cdots = q_M = q \tag{2}$$

where q_i is the intrinsic (excluding the surface excess interac-

tion energy) partition function of the polymer segment in i-th layer and q is that of the polymer segment in the bulk solution, respectively. Here, unlike BET model, the surface excess energy term of the partition function of the segment in the first layer is included in energy part U in partition function of the system. Thus, the partition function of the polymer molecules in this system can be expressed as

$$Q_2 = (q_1)^{N_2^s} (q)^{N_2^b} \tag{3}$$

where N_2^s and N_2^b are the numbers of the segments in the surface and the bulk solution, respectively.

The partition of the monomer liquid may be expressed as the form of Pak[5], which has also been used in the polymer solution theory of Lee and Pak[1]. Q_1 is given as

$$Q_1(N_1, V, T) = N_t C_{N_g}(q_s)^{N_s}(q_g)^{N_g}\frac{1}{N_g !} \tag{4}$$

$$\text{where } q_s = \frac{e^{\varepsilon_s/RT}}{(1 - e^{-\theta_1/T})^3} b_s$$

$$q_g = \frac{(2\pi m k T)^{3/2}}{h^3}(V - V_s)b_g e^{\varepsilon_g/RT}$$

$$N_t = N_1(V/V_s), N_s = N_1(V_s/V)$$

$$N_g = N_1(V - V_s)/V, \text{ and } E_g = \varepsilon (V_s/V)^2,$$

respectively, b_s and $\hat{b}_g$ being the corresponding internal partition functions. In the case of preferential adsorption of polymer molecules at the surface, the solvent molecules may be more chemically or physically inert to the surface than the polymer molecules. Thus, V/V_s value in the presence of interacting surface at given condition can be assumed to be constant in the entire system. But, for the cases of strong preferential adsorption of solvent molecules and competitive adsorption of monomeric liquid mixtures, tnere may some conformational changes of the solvent molecules during the adsorption. Therefore, V/V_s value in these cases at given condition may be different from that of initial condition. In these cases, some comprehensive but complicated treatment may be available as presented by Chang and coworkers[7] in the study of the adsorption from normal binary liquid mixtures.

For the combinatory factor Ω, we introduce an additional assumption that configurations of the polymeric chain near the surface do not make differences significantly compared to those of bulk solution during the adsorption. This approximation is probably more valid when x is small, or when the number of surface layers with concentration of i-th layer significantly different from that of bulk solution is small compared to the root-mean-square radius of the polymer. Therefore, the combinatory factor Ω is given as the form of previous polymer solution theory[1].

$$\Omega = (\frac{z-1}{e})^{(x-1)N_2} \frac{(N_t + x N_2)^{(N_1 + N_2)}}{N_2^{N_2}(N_1 t)^{N_1}} \tag{5}$$

where $t = V/V_s$.

According to the quasi-crystalline lattice model, each site has z nearest neighbors, of which lz in the same layer and mz are in each of the adjacent layers, that is, $l + 2m = 1$. The total interaction energy between molecules can be expressed as the sum of contributions from nearest-neighbor pairs of the

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segments.

The volume fractions of the two components in the mixture are defined as

$$\phi_1 = \frac{N_1 t}{N_1 t + x N_2}, \quad \phi_2 = \frac{x N_2}{N_1 t + x N_2} \tag{6}$$

Supposing that there are N_1^i solvent molecules and N_2^i segments of the polymer molecules in the i-th layer, the volume fractions in each layer are then defined as

$$\phi_1^i = {}_t N_1^i / L, \quad \phi_2^i = N_2^i / L \tag{7}$$

where $L = N_1^i t + N_2^i$. Here, the volume fractions defined in this work mean the *"effective volume fractions"* containing *"fluidized vacancies or holes"* as in the case of polymer solution theory[1].

Using the usual Flory-Huggins polymer-solvent interaction energy parameter, we can write the energy part of Q as follows;

$$U = N_1^s t \ u_s^* + N_2^s u_s + kT\chi \sum_{i=1}^{M} N_{12}^i \tag{8}$$

where u_s and u_s^* are the adsorption energies of a segment and a solvent molecule, respectively. N_1^s and N_2^s are the numbers of solvent molecules and segments of the polymers at the surface, i.e., in the first layer. Above equation is similar to the forms which have given by Roe[8], and Scheutjens and Fleer[9]. By making the usual Bragg-Williams approximation of random mixing, the total number of nearest-neighbor contact pairs between a solvent molecule and a polymer segment in energy term is expressed as

$$N_{12}^i = N_1^i (l\phi_2^i + m\phi_2^{i-1} + m\phi_2^{i+1}) \equiv N_1^i <\phi_2^i> \tag{9}$$

Here, $<\phi_2^i>$ has been defined as the *"site volume fraction"* for segments by Scheutjens and Fleer[9], and the *"site volume fraction"* for solvents has also been defined as

$$<\phi_1^i> = l\phi_1^i + m\phi_1^{i-1} + m\phi_1^{i+1} \tag{10}$$

Consequently, $\ln Q$ is obtained as

$$\begin{aligned}\ln Q &= N_1 F(t;T) + \ln Q_2 + (x-1)N_2 \ln((z-1)/e) \\ &+ (N_1 t + N_2) \ln(N_1 t + x N_2) - N_1 t \ln(N_1 t) \\ &- N_2 \ln N_2 - (N_1^s t \ u_s^* + N_2^s \ u_s)/kT - \chi \sum_{i=1}^{M} \bar{N}_{12}^i\end{aligned} \tag{11}$$

where $F(t; T)$ is the parameteric function depending on the solvent parameters an interactions in the polymer solution, and it is expressed as[1]

$$\begin{aligned}F(t;T) &= t \{t^3 \ln t^3 - (t^3-1) \ln(t^3-1) + \sigma \\ &+ (t-1)(\ln t + \gamma + \varepsilon/(t^3 RT))\}\end{aligned} \tag{12}$$

where $\sigma = E_s/RT - 3\ln(1 - e^{-\theta_1/T}) + \ln b_s$

$$\gamma = \ln\left[\frac{(2\pi mkT)^{3/2}}{h^3} \cdot \frac{V_s e}{N_1}\right] + \ln b_g$$

B. Segment Density Distribution. The contributions of the adsorption layers to the net interfacial tension of the

polymer solution can be defined as

$$\gamma_i = \frac{\mu_1^i - \mu_1}{a_1} - \frac{(\mu_2^i - \mu_2)/x}{a_2} \tag{13}$$

where μ_1^i and μ_2^i/x are defined as the chemical potentials of the solvent and the polymer segment in i-th layer, μ_1 and μ_2/x are the chemical potentials of the solvent and the polymer segment in the bulk solution, respectively, and $a_k = (\partial A/\partial N_k)$, $k = 1, 2$. Hence the net interfacial tension is given as the sum of contributions of adsorption layers, that is, $\gamma = \sum_{i=1}^{M} \gamma_i$. This method is similar to that presented by Chang and coworkers[7] in their treatment for monolayer adsorption case of monomeric binary mixtures. Since the total adsorption area is given by

$$A = aL, \tag{14}$$

and $a_1 = a \ l$, $a_2 = a$, the above relation is rearranged as

$$\gamma_i a = \frac{\mu_1^i - \mu_1}{t} - (\mu_2^i - \mu_2)/x \tag{15}$$

where a is the contact area per a solvent molecule.

Before finding the equilibrium segment density distribution set $\{\phi_2^i\}$, we obtain μ_1^i and μ_2^i/x. From $\ln Q$ in eq 11, μ_1^i can be found easily by using the following relation.

$$-\mu_1^i/kT = \left[\frac{\partial \ln Q}{\partial N_1^i}\right]_{N_2^i, V, T, j \neq i} \tag{16}$$

Thus, μ_1^i is obtained as

$$\begin{aligned}-\mu_1^i/kT &= F(t;T) - t\ln\phi_1^i - t(1-1/x)\phi_2^i \\ &- \chi\phi_2^i <\phi_2^i> - u_s^*/kT \ \delta_{1,i}\end{aligned} \tag{17}$$

where $\delta_{1,i}$ is the Kronecker's delta. Similarly, μ_2^i/x is obtained as

$$\begin{aligned}-\mu_2^i/xkT &= \ln q_i + (1-1/x) \ln((z-1)/e) - 1/x \ln(\phi_2^i/x) \\ &+ (1-1/x) \phi_2^i - \chi/t\phi_1^i <\phi_1^i> - u_s/kT \ \delta_{1,i}\end{aligned} \tag{18}$$

where $q_i = q_1$ when $i = 1$, and $q_i = q$ when i is greater than 1.

The chemical potentials of the solvent molecule and the polymer segment in the bulk solution are obtained as

$$-\mu_1/kT = F(t;T) - t\ln\phi_1 - t(1-1/x)\phi_2 - \chi\phi_2^2 \tag{19}$$
$$-\mu_2/xkT = \ln q + (1-1/x) \ln((z-1)/e) - 1/x \ln(\phi_2/x)$$

$$+ (1-1/x) \ \phi_1 - \chi/t \ \phi_1^2, \tag{20}$$

respectively. From the relation 15, we obtain the following set of simultaneous equations determining the equilibrium set of $\{\phi_2^i\}$.

$$\begin{aligned}&\ln(\phi_1^i/\phi_1) - 1/x \ \ln(\phi_2^i/\phi_2) + \chi/t \ \{\phi_1^i <\phi_1^i> - (\phi_1^i)^2\} \\ &+ (\chi_s - \ln(q/q_1))\delta_{1,i} - \chi/t \ \{\phi_2^i - \phi_2^i\} = 0.\end{aligned} \tag{21}$$

for $i = 1, 2, \ldots, M$, where $\chi_s = -(u_s - u_s^*)/kT$.

As a measure of extent of adsorption, we define the surface excess of polymer segment per surface site as follows.

$$\Gamma_{exc} = \sum_{i=1}^{M} (\phi_i^s - \phi_i),$$ (22)

C. Interfacial Tension.

From the given set of equilibrium distribution $\{\phi_i^s\}$, we obtain the following expressions for the contributions of the adsorption layers to the interfacial tension of the polymer solution.

$$a\ \gamma_i/kT = \ln(\phi_i^s/\phi_1) + (1 - 1/x)\ (\phi_i^s - \phi_i) \\ + \chi/t\ (\phi_i^s < \phi_i^s > - \phi_i^2) + u_s^*/kT\ \delta_{i,i}$$ (23)

or

$$a\ \gamma_i/kT - 1/x\ \ln(\phi_i^s/\phi_1) + (1 - 1/x)\ (\phi_i^s - \phi_i) \\ + \chi/t\ (\phi_i^s < \phi_i^s > - \phi_i^2) + (\ln\ q/q_1 + u_s/kT)\ \delta_{1,i}$$ (24)

Therefore, the interfacial tension of the polymer solution is obtained as the sum of γ_i. Here, we can replace u_s^* and u_s by interfacial tensions of pure solvent and pure polymer. Thus, u_s^* and u_s are given as

$$u_s^*/kT = a\ \gamma_1/kT, \quad u_s/kT = a\ \gamma_2/kT$$ (25)

whre γ_1 and γ_2 are the interfacial tensions of pure solvent and pure polymer, respectively.
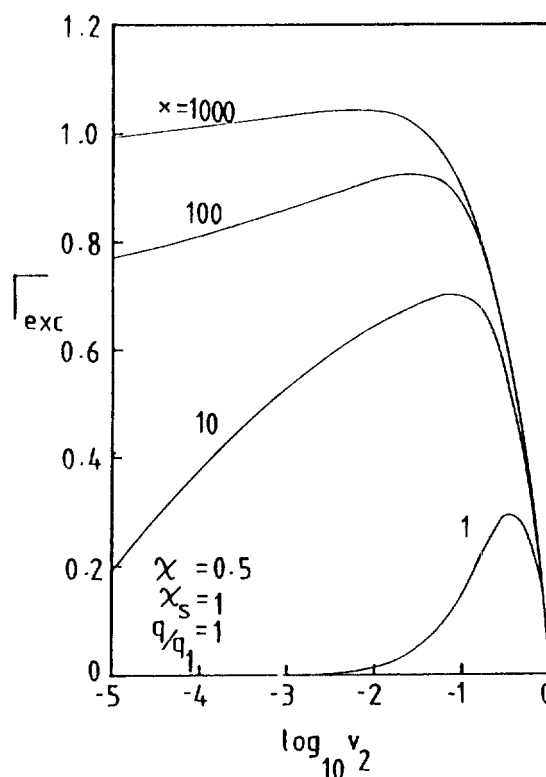
Results and Discussion

In this section, we present some numerical results which elucidate the dependence of some characteristics of the adsorption layer on parameters related to the polymer–solvent–surface system.

The parameters of two solvents in this work, E_s, V_s, ε and θ, are determined by the method presented by Pak[5] and are given in Table 1.

For parameters related to the polymer–solvent–surface system, we choose the segment number x, the polymer–solvent interaction energy parameter χ, the adsorption energy parameter χ_s, the partition function ratio parameter q/q_1 and Flory's equilibrium bulk volume fraction v_2. For the case of the normal polymer solution without interacting surface, parameter χ can be determined from the second virial coefficient of the osmotic pressure at given condition. But, for the case of adsorption, χ can be determined as an adjustable parameter from related experimental data because χ may be changed from its initial value in bulk polymer solution by virtue of concentration distribution in adsorption layers. In addition, as in most theories of the polymer adsorption, χ is treated as a constant parameter at given condition through the entire range of concentrations. The value of V/V, at given condition may be evaluated from the minimum condition of the Helmholtz free energy of the bulk polymer solution.

For adsorption energy parameter χ_s, as mentioned previous-

Table 1. Parameters of Solvents

	θ (°K)	E_s (cal/mole)	ε (cal/mole)	V_s (ml/mole)
benzene	46.57	9627	2797	80.02
cyclohexane	35.68	9450	1869	100.2

Figure 1. The surface excess Γ_{exc} is plotted against the logarithm of v_2 in polymer–benzene–surface system, for $\chi = 0.5$, $\chi_s = 1$ and $q/q_1 = 1$ at 25°C.

ly in *eq* 25, it can be determined from the interfacial tensions of pure solvent and pure polymer if the interfacial tensions of pure components are available. For the case that the interfacial tensions of pure components can not be determined, χ_s may be determined as an adjustable parameter.

For partition function ratio parameter q/q_1, most of results are presented for $q/q_1 = 1$. Since q_1 in which surface excess energy term has been excluded is not quite different from q for most cases, there may not be large discrepancy with real feature of the adsorption layer although it is assumed that $q/q_1 = 1$. This will be illustrated in more details in comparisons of interfacial tensions according to our work with the experimental data.

For lattice parameters l and m, as has been shown by Roe[6], numerical results are quantitatively independent of the lattice type, while only minor differences may occur. In our work, therefore, the lattice type is confined to a hexagonal closed-packed(hcp) lattice: $l = 0.5$, $m = 0.25$.

The solution to the set of simultaneous *eqs* 21 determining the equilibrium concentration distribution is obtained by the method of successive approximation based on the Roe's method[3]. Figure 1 shows surface excess Γ_{exc} of the polymer segments against logarithm of the volume fraction of the polymer in the bulk solution at several values of chain length x. As shown in this figure, the plateau region becomes recognizable at the very dilute concentration of the polymer. It has been well known that the rapid rise to the plateau in the extremely dilute polymer solutions is in fact a particular manifestation of the more general phenomenon that the maximum in Γ_{exc} occurs at low v_2 as the chain length of the polymer

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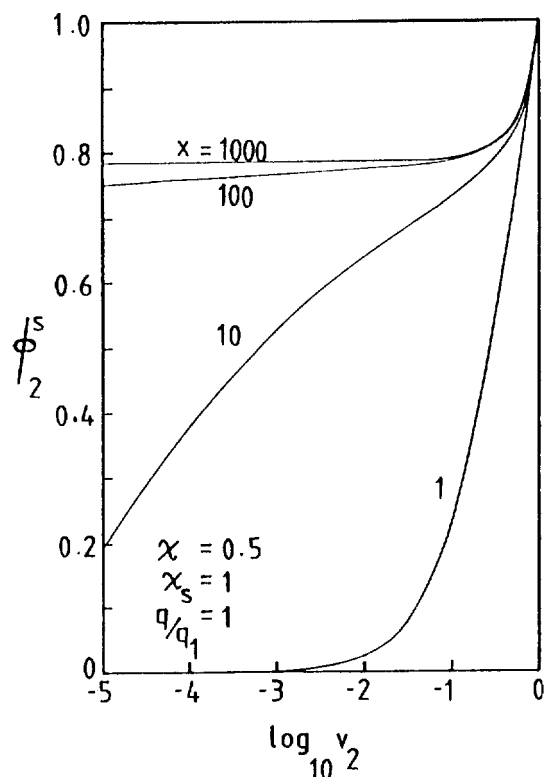*Bull. Korean Chem. Soc., Vol. 8, No. 1, 1987* 23

Figure 2. The surface coverage ϕ_2^s of the polymer is plotted against the logarithm of v_2 in polymer–benzene–surface system at 25°C, for $\chi = 0.5$, $\chi_s = 1$ and $q/q_1 = 1$.

is increased[6]. Comparing surface excess Γ_{exc} of our work to older theories[8,9], Γ_{exc} of our work is small than those of Roe[8] and Scheutjens and Fleer[9] in high molecular weight of solute, while our Γ_{exc} is greater than those of other authors when x = 10 or less. It seems that this feature is mainly caused by the approximation that the segments of the polymer chain are random near the surface, thus each of the segments gives the same contribution to the segment density at any distance from the surface.

Figure 2 shows the dependence of the chain length on the surface coverage ϕ_2^s of the polymer. At higher segment numbers, the plateau is shown at dilute concentration of the polymer. This demonstrates that at low v_2, the surface coverage of the polymer is small, and there is only little effect of the solvent character, but the surface coverage of the polymer increases tremendously with increasing x until a plateau is reached where the surface coverage is independent of chain length and concentration. This is also shown in Figure 3 which gives the dependence of the surface coverage ϕ_2^s on the chain length at constant concentration of the polymer.

Figure 4 shows the dependence of surface excess Γ_{exc} on the adsorption energy parameter χ_s. When χ_s is positive, polymeric chain may adsorbed preferentially at the surface. There is the phenomenon of a surface azeotrope when χ_s is nearly zero. It has also been discussed by Roe[8]. When χ_s is negative, it is shown that there is a phase separation point between the polymer solution and the surface. In this condition, at higher chain length of the polymer, there is no polymer segment on the surface at dilute concentration of the polymer as also shown in Figure 5. Since there is no polymer segment on the surface below the phase separation point at higher chain
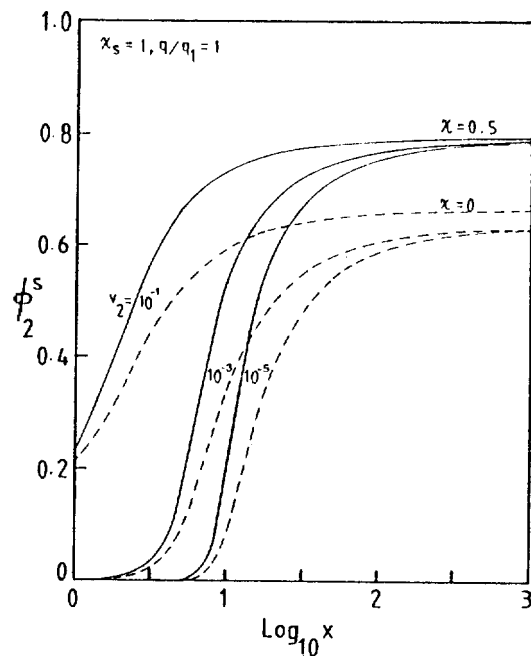

Figure 3. The dependence of surface coverage ϕ_2^s of the polymer on the chain length x of the polymer in polymer–benzene–surface system at 25°C, for $\chi_s = 1$ and $q/q_1 = 1$. The polymer volume fraction v_2 is indicated. Full lines are for a θ solvent ($\chi = 0.5$), dotted lines for an athermal solvent ($\chi = 0$).
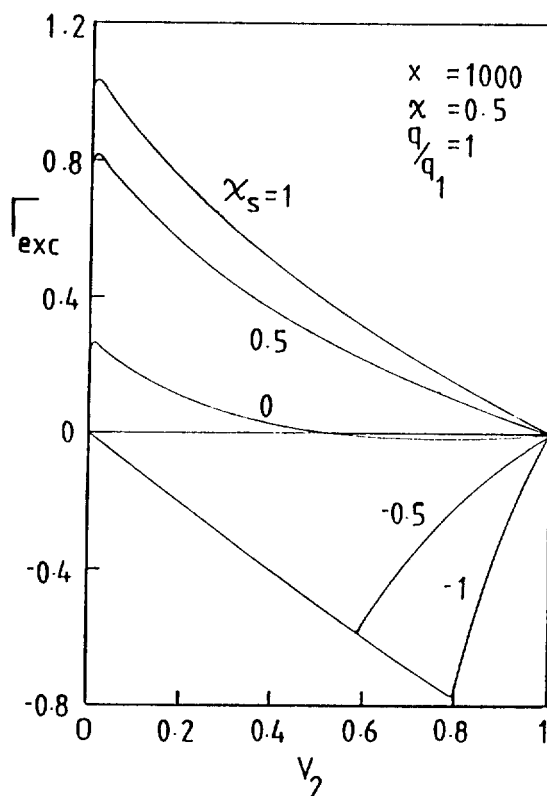

Figure 4. The surface excess Γ_{exc} is plotted against v_2 at various values of adsorption energy parameter χ_s for $x = 1000$, $\chi = 0.5$ and $q/q_1 = 1$ in polymer–benzene–surface system at 25°C. Note the phase separation points for the case of negative χ_s.
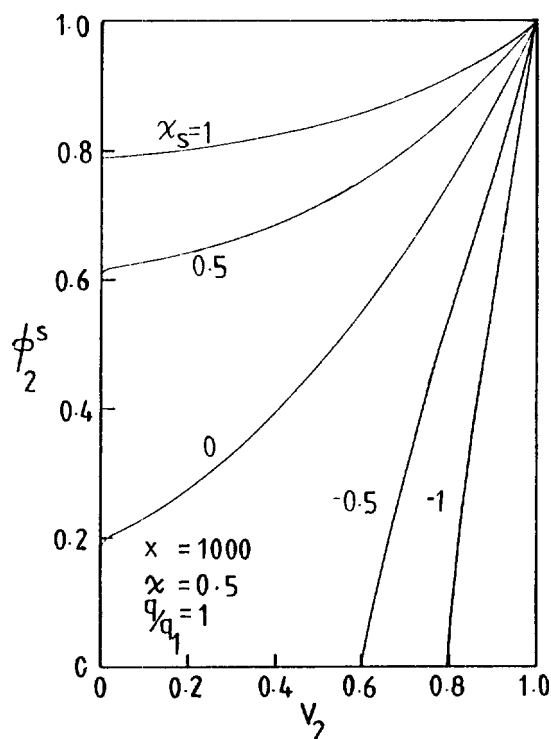
Figure 5. The surface coverage ϕ_2^s of the polymer is plotted against the polymer volume fraction v_2 for several χ_s values in polymer–benzene–surface system at 25°C, for $\chi = 0.5$, $x = 1000$ and $q/q_1 = 1$.
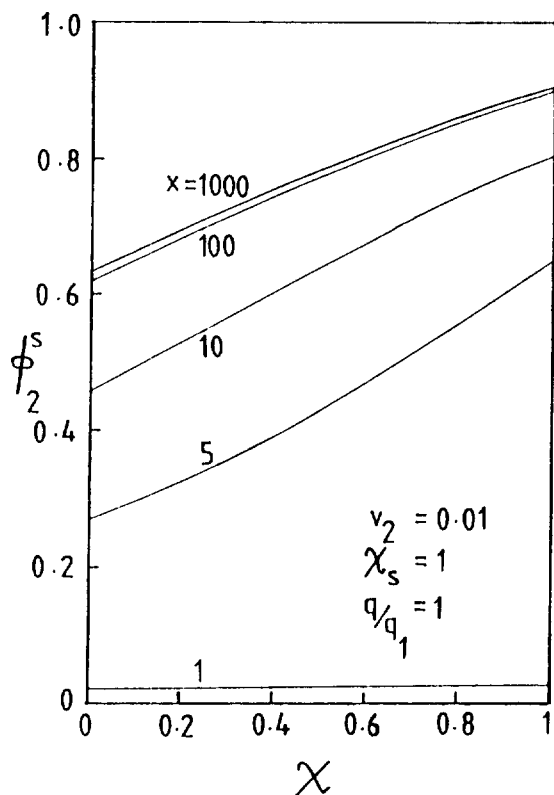
length when χ_s is negative, the polymer molecules are considered to be *"floated"* from the surface by the strong repulsion of the polymer against the surface.

In addition, the polymer–solvent interaction energy parameter χ is one of the important factors which influence the adsorption layer. Figure 6 and 7 illustrate the dependence of the interaction energy parameter χ on the surface coverage ϕ_2^s of the polymer. As shown in these figures, surface coverage ϕ_2^s increases as the chain length of the polymer and as χ increases at constant v_2 in the case of positive χ_s, while ϕ_2^s decreases as x and as χ increases at constant v_2 in the case of negative χ_s. These demonstrate the osmotic action of the solvent by which the polymer coil swells and becomes inflated, and the molecule passes into a state of less probable conformation. It has been well known that the second virial coefficient of the virial expression for the osmotic pressure characterizes the energy of interaction between the polymers and the solvent molecules and, with parameter χ. can serve as the criterion of the solvent power[10]. A decrease in the second virial coefficient, that is, an increase in parameter χ, leads to a decrease in the solvent power, then the solvent becomes poorer. Thus, an increase in parameter χ leads to an increase in surface coverage of the polymer at dilute concentration of the polymer when χ_s is positive. But, at high concentration of the polymer, this demonstration does not always hold. As shown in Figure 8, the dependence of the surface coverage ϕ_2^s on the parameter χ becomes negligible at high concentration of the polymer when χ_s is positive.

For parameter χ_s, it has also an significant effect on the adsorption from the polymer solution as well as the chain length of the polymer. Figure 9 demonstrates that an increase in parameter χ_s leads to an increase in the surface coverage ϕ_2^s at constant concentration of the polymer whether the chain length of the polymer is small or high. But, the surface
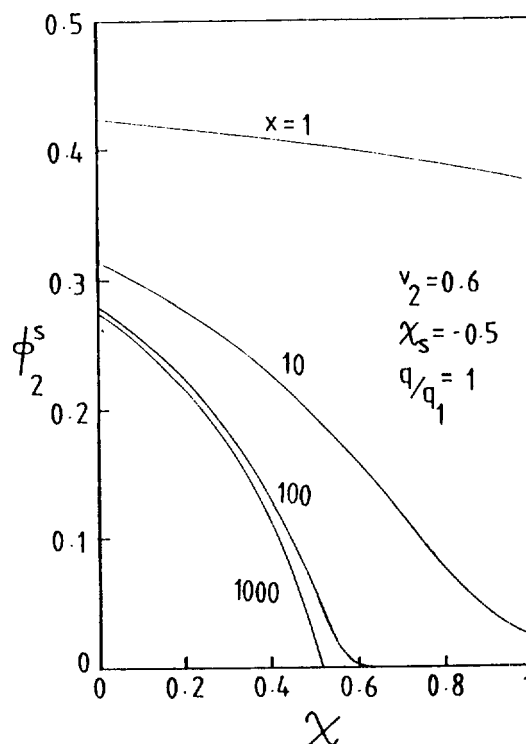

Figure 6. The surface coverage ϕ_2^s is plotted against parameter χ for several values of chain length x in polymer–benzene–surface system at 25°C, for $v_2 = 0.01$, $\chi_s = 1$ and $q/q_1 = 1$.

Figure 7. Similar to Figure 6, but for $v_2 = 0.6$ and $\chi_s = -0.5$
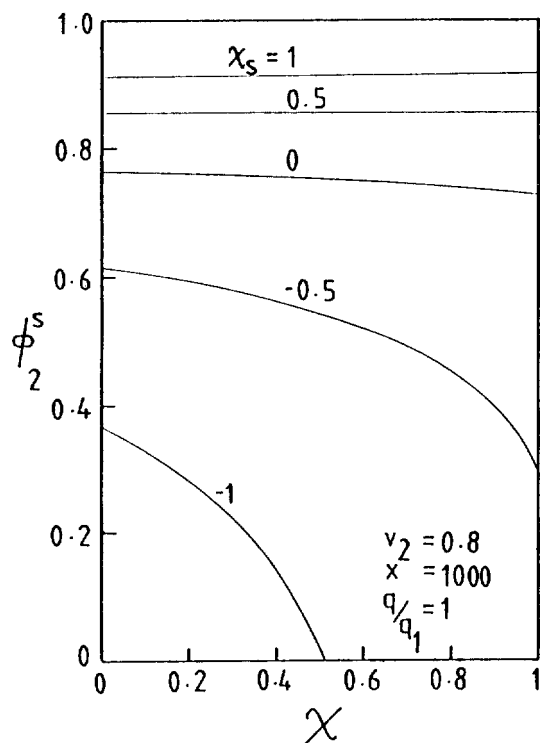
Figure 8. The surface coverage ϕ_2^s is plotted against χ for several χ_s values in the case of concentrated polymer solution ($v_2 = 0.8$) in polymer-benzene-surface system at 25°C, for $x = 1000$ and $q/q_1 = 1$.
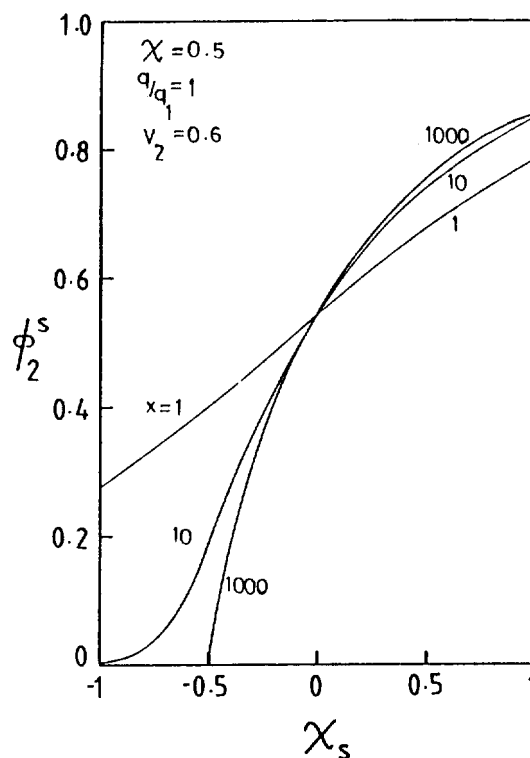
Figure 9. The surface coverage ϕ_2^s is plotted against χ_s in polymer-benzene-surface system at 25°C, for $\chi = 0.5$, $v_2 = 0.6$ and $q/q_1 = 1$.

coverage increases as the chain length of the polymer increases in the case of positive χ_s at constant other parameters, while the surface coverage ϕ_2^s decreases as the chain length of the polymer increases in the case of negative χ_s less than about -0.1.

The interfacial tensions of the polymer solutions against water were determined by Siow and Patterson[11]. These results were analyzed in terms of the Prigogine-Maréchal theory[12], and when χ was adjusted they fit to experimental data which could be obtained in almost all cases.

In our work, the present multilayer theory is compared with the interfacial tension data of those authors. The properties of polymers and solvent used in fitting experimental data obtained from the ones of those authors, and the compact area a is simply obtained from the approximated relation that $a = (V_o/N_o)^{2/3}$, where V_o is the molar volume of the solvent at given condition and N_o is the Avogadro's number. The properties of polymers and solvents are given in Table 2.

Comparisons of interfacial tensions of our work with experimental data from above authors[11] are made in Figure 10. Our multilayer theory fits the interfacial tension data of those authors equally well to the agreeable degrees, using χ as an

Table 2. Properties of Polymers and Solvents

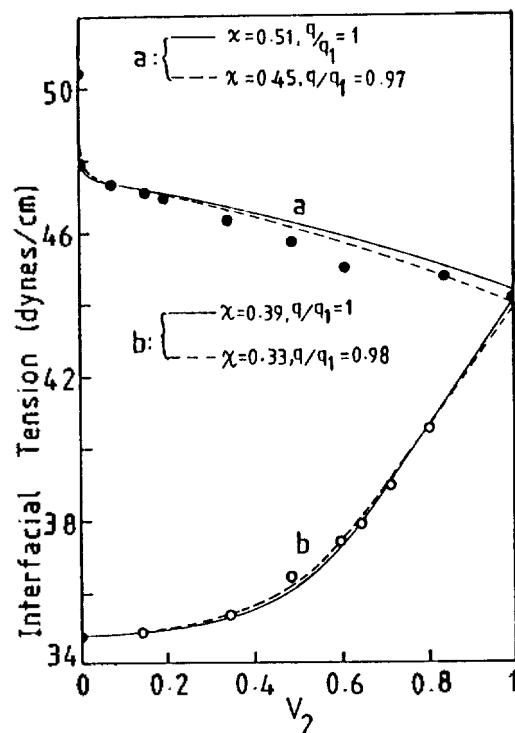|	Interfacial tension (dyn./cm) at 20°C	M_n	a Å²
cyclohexane	50.5	—	31.8
benzene	34.8	—	27.9
poly(dimethyl siloxane)	44.3	5390	—
polystyrene	—	4000	—

Figure 10. Interfacial tensions of solutions poly (dimethylsiloxane)-cyclohexane and -benzene against water at 20°C: a is for the case of its solution in cyclohexane, and b is for the case of its solution in benzene, for parameters chosen to fit the experimental points indicated.
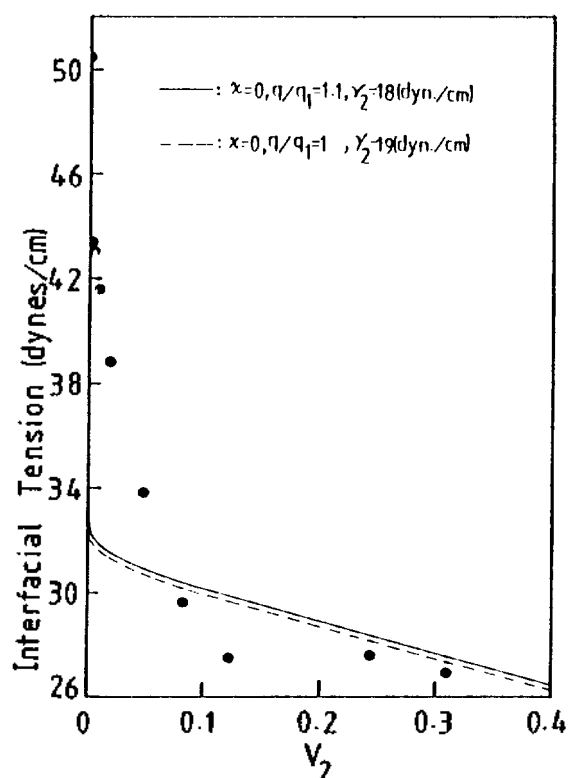
Figure 11. The interfacial tensions of polystyrene solution in cyclohexane against water at 20°C, for parameters chosen to fit the experimental points indicated within the minimum error limit.

adjustable parameter, whether q/q_1 is treated as an adjustable parameter (dotted lines) or assumed to be equal to 1 (full lines).

As mentioned previously in this section, q/q_1 is obtained to be nearly 1 within the agreeable error limit as shown in Figure 10 when q/q_1 is treated as an adjustable parameter, while there are only minor quantitative differences if compared with the case that $q/q_1 = 1$. Thus, in these systems given in this figure, it may be possibly said that there is no significant discrepancy of our theory with experimental data, while there is only a some change of parameter χ adjusted in either cases.

Results of interfacial tension of polystyrene–cyclohexane against water are shown in Figure 11. They are of the preferential polymer adsorption type, but here the interfacial tension curves of our work designated as the full line and the dotted line in this figure are much less satisfactory than other

systems given above, even though q/q_1, χ and γ_2 are determined as adjustable parameters. Figure 11 shows that the drop of interfacial tension at low concentration of the polymer is experimentally much less rapid than predicted and the surface coverage of the polymer at low v_2 is not as completed as predicted. This behavior has also been discussed by above authors[11]. According to them, the less satisfactory results obtained in the polystyrenecyclohexane–water system are mainly due to the greater rigidity of polystyrene in its solution. It has also been shown that a configurational entropy effect is significant in the case of polystyrene[13]. Thus, this effect opposes the adsorption of the polymer due to energetic interactions. Due to the rigidity of polystyrene, the polymeric chain has much less probable configurations near the surface than the idealized flexible polymer. For the case of the rigid polymer, the combinatory factor in our work is not fully available, because the randomness and symmetry of the polymeric coil are much more distroyed than for the idealized flexible polymer. But, for the case of the idealized flexible polymer solution system, our work is still available.

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