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Steric stabilisation of liquid films by adsorption layers of macromolecules

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Abstract. Modern theories of the steric stabilisation of dispersions containing polymers and experimental results of studies of the interaction between adsorption layers of polymers in microscopic liquid films are critically reviewed. The bibliography includes 109 references.

I. Introduction

Polymeric adsorption layers (AL) formed on the surface of particles of a dispersed phase in disperse systems containing polymers control the stability and the structural and mechanical properties of these systems.

Adsorption layers have thicknesses of the order of the size of the macromolecules in the bulk of the solution (a few nanometres). They hinder the approach to the surfaces of particles, and they limit it to the distances at which the forces of intermolecular attraction (van der Waals) lead to an irreversible thinning of the microscopic liquid films (MLF) formed in the contact region between the particles, i.e. to the coagulation or coalescence of the particles.

Thus, since the energy of molecular interaction of the interfaces in disperse systems containing a polymer becomes negligibly small owing to the relatively large thickness of the MLF, and furthermore since the ionic–electrostatic interaction between the electric double layers vanishes at high enough electrolyte concentrations in the system, the main contribution to the energetics of the contact interactions in these systems is provided by the interaction between the AL of macromolecules and by the energy properties of these AL.

The interaction between polymeric AL takes place when the segments of macromolecules are in direct ('steric') contact, and is determined by short-range forces such as hydrogen bonds, hydrophobic interaction, and Born repulsion, and also by the Coulomb interaction between the ionised functional groups in the case of polyelectrolytes and (to a smaller extent) by the molecular forces between the macromolecules themselves in the adsorption layers.

If the energy of the steric interaction between two AL in a liquid film is small (for example, a few kT, where k is Boltzmann's constant and T is the absolute temperature) the disperse system becomes stable by aggregation. In this case the stabilisation of the disperse system is said to be steric.[1,2] Detailed reviews of the theory and of the experimental foundations of the steric stabilisation in these systems have been published.[3–7]

The aim of the present review is to analyse theoretical and experimental studies of the interaction between adsorption layers of macromolecules in microscopic liquid films whilst allowing for nonequilibrium effects in the thermodynamic description of the steric stabilisation of dispersions.

II. Theories of the steric stabilisation of liquid films

Some procedural difficulties are met in the thermodynamic description of the steric interaction between adsorption layers of macromolecules in microscopic liquid films.

One of the problems is the lack of an unambiguous definition of the specific interfacial free energy (interfacial tension) of the phase boundary in the presence of a polymeric adsorption layer whose thickness usually exceeds the radius of action of the molecular forces. In the modern theories of the adsorption of polymers and of interacting adsorption layers of polymers in liquid films[11–23] the interfacial tension σ is expressed as the sum of two components,

$$\sigma = \sigma_s(\varphi_s) + I(\varphi_s, \varphi_b), \quad (1)$$

where φ_b and φ_s are the densities of the polymer in the bulk of the solution and at the contact with the interfacial surface respectively.

The $\sigma_s(\varphi_s)$ component allows for the interfacial tension at distances of the order of the molecular size, and is often expressed as[18,24]

$$\sigma_s(\varphi_s) = \sigma_{s0} + \sigma_1\varphi_s + \sigma_2\varphi_s^2 + \ldots, \quad (2)$$

where σ_1 and σ_2 are the virial coefficients of the expansion, which allow for the interaction between the monomers and the surface, and also between the segments of the macromolecules in the adsorption layer closest to the surface.

The component $I(\varphi_s, \varphi_b)$ describes the contribution to the surface tension of effects associated with a change in the density profile $\varphi(z)$ of the segments close to the interfacial surface. Thus, in order to describe the thermodynamic properties of interfaces (and, even more, their interactions in liquid films) we require information on the density profile of the segments $[\varphi(z)]$ in the adsorption layer, which is a new element, not previously

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considered in the thermodynamics of interfaces and films stabilised by low-molecular surface-active substances (SAS).[25,26]

Hence we should expect the properties of interfaces in liquid films stabilised by polymers to depend on factors such as the molecular mass, the degree of ionisation of the macroions, the hydrophilic–lipophilic balance (HLB) of the molecules, the rigidity of the macromolecular network, and also on the physicochemical factors (pH and ionic strength of the solution, bulk concentration of the polymers, temperature, nature of the solvent, etc.) which affect both the energy of the intermolecular interactions and the conformation of the macromolecules in the adsorption layer.

We should note that tensometry (the main experimental method of determining the energy properties of interfaces stabilised by low-molecular SAS) can no longer characterise unambiguously the energy properties of interfaces when these are stabilised by polymeric AL. Indeed, the measured values of the interfacial tension do not allow for or include the interaction between the segments of the macromolecules in the AL separated from the physical interface by a distance greater than the action radius of the molecular forces. This problem is not found in the measurements of interfacial tension of surfaces stabilised by low-molecular SAS, because the molecules of these SAS are localised within the force field of the interface.

Another problem in the thermodynamic description of liquid films stabilised by polymeric adsorbed layers arises from the indefiniteness of the concept of thermodynamic equilibrium in a system of interacting adsorption layers of macromolecules when interfacial surfaces are brought closer together in a solution of the polymer.

Whereas in the adsorption of low-molecular SAS the equilibrium between the bulk concentration and the concentration in the film is established rapidly, at the contact of adsorption layers of high-molecular SAS the 'true' equilibrium may never be reached (at least, under the conditions of the experiment). de Gennes[19] understood the problem, and suggested that the steric interaction should be calculated for two extreme cases: (1) ideal equilibrium, corresponding to the possibility of reversible adsorption of the macromolecules during the interaction of polymeric adsorption layers, and (2) a limited equilibrium, corresponding to a condition of constant adsorption, reached when the two AL are placed in contact and unchanged thereafter.

However, as will be shown below, the conclusions of the theory of the aggregation stability of a disperse system are strongly influenced by the subjective choice of a hypothesis concerning the type of equilibrium. As was pointed out by de Gennes,[19] with a thermodynamically good solvent, and assuming ideal equilbrium, we must conclude that an attraction exists between polymeric AL, whereas under conditions of limited equilibrium, mutual repulsion between the layers becomes possible. Thus we are faced with the problem of defining and assigning the type of equilibrium in the interaction of AL of macromolecules.

This problem is closely associated with that of determining the extent of the mutual penetration of the AL, when the film thickness is increased, in order to calculate the relative contribution of the entropic and the osmotic effect to the total free energy of interaction of the polymeric AL. This problem could not be solved by using the 'early' theories of the interaction of adsorption layers of macromolecules, such as the Hesselink–Vrij–Overbeek (HVO) theory,[27] because the solution requires a knowledge of the exact form of the density distribution function of the segments of the macromolecule with respect to the distance to the interfacial surface.

At present the most widely used approaches to the construction of a thermodynamic theory of adsorption and of the interaction between adsorption layers of polymers are those developed by Scheutjens and Fleer,[11–17] de Gennes,[18,19] and Klein and coworkers.[20–23]

1. The Scheutjens–Fleer theory

The statistical theory of the adsorption of polymer proposed by Scheutjens and Fleer allows for the effect on the structure of the polymeric AL of interactions between the segments of polymeric molecules and also for those of the interactions between the macromolecules, the solvent molecules, and the interfacial surface. The physical basis of this theory is the postulate that under equilibrium conditions (assuming that the adsorption of polymers is reversible under equilibrium conditions) [17] the conformation of the adsorbed macromolecule is unambiguously determined by the energy of the interaction between the segments of the macromolecules χ and between a macromolecule and the surface χ_s, and also by the length (degree of polymerisation) of the molecule N.

The special feature of this approach is that its authors exploit the concept of the conformational probability of the macromolecule p_c, which is determined in the framework of the quasi-crystalline lattice model by the distribution of segments over the layers of the lattice, by the orientation in space of the bonds between the segments, and by the parameters χ and χ_s (Fig. 1).

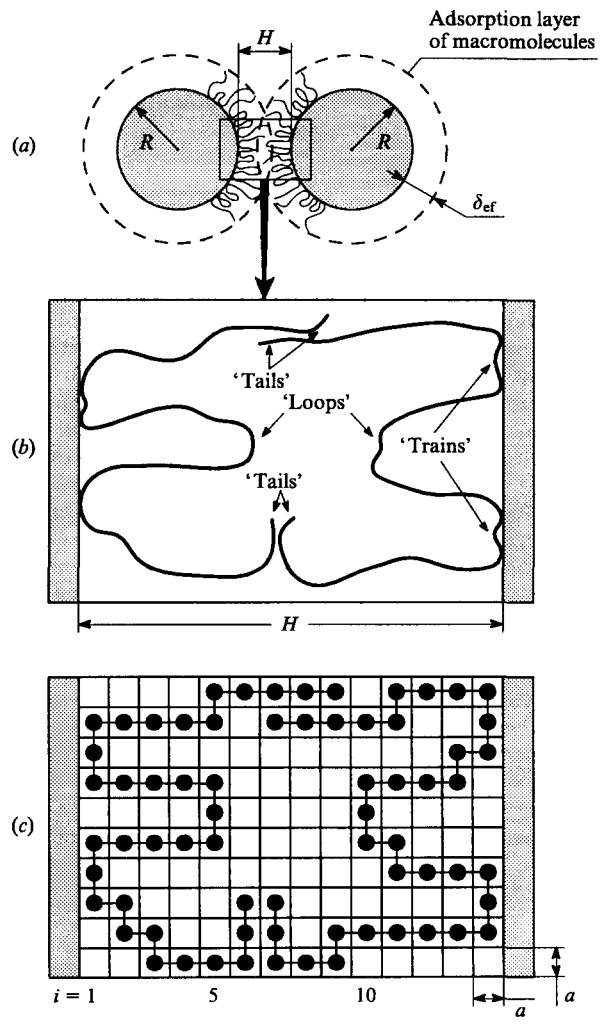


Figure 1. Calculation of the energy of the interaction between adsorption layers of macromolecules in a liquid film. (*a*) Contact of two particles of the disperse phase, of radius R, coated with adsorption layers of the polymer having an effective thickness δ_{ef}; direct steric contact between the two AL takes place in the gap thickness H within the liquid microscopic film; (*b*) the conformation of the interacting adsorbed macromolecules is characterised by 'tails', 'loops', and 'trains'; (*c*) schematic representation of interacting macromolecular chains between two planes in the lattice model used by Scheutjens and Fleer.[13,14]

Assuming that all the states of a segment in a layer of the lattice parallel to the surface are energetically equivalent the authors determined the density profile $\varphi_i = \varphi(z)$ of the segments of the AL in the ith layer of the lattice ($i \approx z/a$, where a is the lattice constant) as the mean probability (weighted over all the conformational states of the macromolecule) of finding the segment in the ith layer of the lattice, i.e.

$$\varphi_i = \varphi_b \sum_c r_{i,c} p_c , \quad (3)$$

where φ_b is the density of the segments in the bulk of the solution and $r_{i,c}$ is the number of segments in the ith layer of the lattice for the given conformation c. The conformational probability p_c of the macromolecule, characterised by the number of segments r_i in the ith lattice layer ($\Sigma r_i = r$), is expressed as

$$p_c = \lambda_0^q \lambda_1^{r-1-q} \sum_{i=1} p_i^{r_i} , \quad (4)$$

where λ_0 is the relative coordination number of the cell in a layer parallel to the surface ($\lambda_0 = 2/3$ for a cubic lattice), λ_1 is the relative coordination number of the cell in contact with the neighbouring layers ($\lambda_1 = 1/6$ for a cubic lattice), q and $(r - 1 - q)$ are the numbers of steps parallel and perpendicular to the surface, and p_i is a weighting factor determined by the configurational entropy and by the parameters χ and χ_s (expressed in units of kT), so that

$$p_i = \frac{\varphi_i^0}{\varphi_b^0} \left\{ \exp\left[-2\chi \left(\langle \varphi_i^0 \rangle - \langle \varphi_b^0 \rangle \right) \right] \right\} \exp(\chi_s - \lambda_1 \chi) \delta_{i,1} , \quad (5)$$

where

$$\langle \varphi_i^0 \rangle = \lambda_i \varphi_{i-1}^0 + \lambda_0 \varphi_i^0 + \lambda_1 \varphi_{i+1}^0 , \quad (6)$$

φ_i^0 is the density of solvent molecules in the ith layer, φ_b^0 is the same density in the equilibrium solution, and $\delta_{i,1}$ is the Kronecker delta function ($\delta_{i,1} = 1$, if $i = 1$; $\delta_{i,1} = 0$, if $i \neq 1$).

A matrix formalism was developed[28] to solve the system of equations (3) and (4): it was based on a calculation of the density profile $\varphi(z)$ of the segments in the vicinity of the surface for noninteracting segments, i.e. when $p_i = 1$ for $i > 1$ and $p_1 = \exp \chi$. In Scheutjens and Fleer's modified matrix formalism[13,14] allowance is made for the effect of interactions between the polymer and the solvent by including in p_i the parameter χ [see Eqn (5)], thus allowing the density profile $\varphi(z)$ of the segments to be calculated as a function of the thermodynamic quality of the solvent.

The new theory offers an additional advantage: it allows the individual contributions to the overall density of the layers of polymer near the interface from its various components to be calculated, i.e. it expresses the density of segments in the form

$$\varphi(z) = \varphi_f + \varphi_t + \varphi_l + \varphi_{tr} ,$$

where φ_f, φ_t, φ_l, and φ_{tr} are the densities of free (nonadsorbed) macromolecules, and the densities of 'tails', 'loops', and 'trains' respectively. This is achieved by introducing a formal calculation procedure which involves using a new method of calculating the probability p_c in Eqn (3):[29-31]

$$\sum_c r_{i,c} p_c = \frac{1}{r p_i} \sum_{s=1}^{r} p(i,s)\, p(i, r - s + 1) , \quad (7)$$

where p_i is given by Eqn (5); $p(i,s)$ and $p(i, r-s+1)$ are the probabilities of finding the sth segment in the ith layer, and the first and subsequent segments of the macrochain occupy all the positions allowed for the given conformation of the macromolecule. Then all the conformations for which neither both chain ends nor one of the intermediate segments are found (even once) in the first layer will correspond to a 'free' (not adsorbed) macromolecule. The corresponding contribution φ_f to the density of the segments can be allowed for by using Eqn (3). The contribution from 'tails' and 'loops' is determined by allowing for the conformations having only one or two contacts with the surface respectively.

The authors carried out numerical calculations of the density profile $\varphi(z)$ and of its components for different values of r (up to 10^4), for several values of the parameter χ (0 for an athermal solvent, 0.5 for a θ-solvent, and 0.7 for a poor solvent), and also for different values of the bulk density of the segments in solution φ_b (Fig. 2). The authors also considered the case of adsorbed ($\chi_s = 1$) and nonadsorbed ($\chi_s = 0$) polymers.

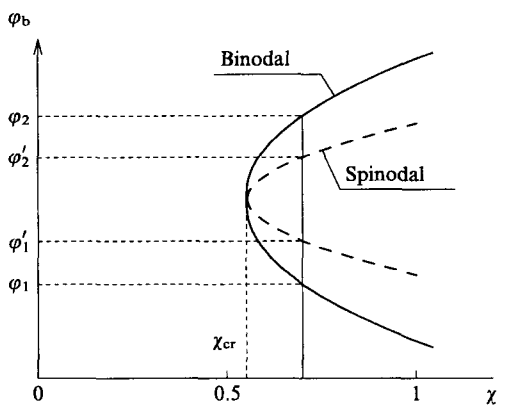


Figure 2. Phase diagram $\varphi_b(\chi)$ for the polymer solution.

For an adsorbable polymer at low coverages φ_s of the surface by adsorbate in a good solvent the proposed theory predicts a 'prone' conformation of the macromolecules on the surfaces, and a density profile $\varphi(z)$ decreasing exponentially with increasing distance from the surface, as expected from the early theories of adsorption known as the 'isolated chain' theories.[32-37] For finite values of φ_b (even quite small, of the order of 10^{-6}) the density profile $\varphi(z)$ takes a specific form, characterised by the presence of a fairly extensive region where the density φ_b is low (Fig. 3). In the layer nearest to the surface the density profile $\varphi(z)$ is determined mainly by the energy of

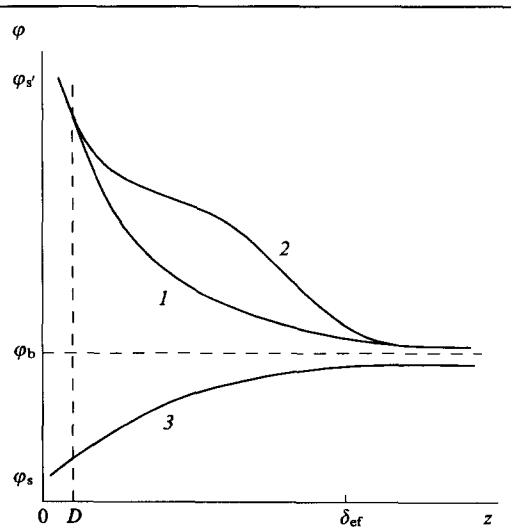


Figure 3. Density profiles of the polymer segments $\varphi(z)$ as a function of the distance to the interfacial surface in a thermodynamically good (*1*, *3*) or bad solvent (*2*) for adsorbed (*1*, *2*) and for nonadsorbed polymers (*3*).

adhesion χ_s, and as the chain length r of the macromolecule is increased the dependence on φ_b is effectively suppressed and replaced by an exponential decrease with increasing distance from the surface. In the more remote layers the density profile is determined essentially by the 'tails'. This is a new element, not considered in the 'isolated chain' theories. It was shown that the root-mean-square thickness δ_{ef} of the adsorption layer in a good solvent is proportional to $M^{0.5}$ (where M is the molecular mass of the polymer). At high adsorptions of the polymer the thickness δ_{ef} becomes comparable with the size of the macromolecular cluster in the bulk of the solution.

A calculation of the density profile of the segments for a thermodynamically poor solvent[16] is of special relevance to the attempt to reconcile the Scheutjens–Fleer theory with other theories (in particular, that of de Gennes[18]). The authors considered the cases of $\chi = 0.7$ ($r = 100$) and $\chi = 0.56$ ($r = 1000$) for $\varphi_b = 10^{-6}$. The problem was that in the transition region of the AL (i.e. in the region between the first layer, with a relatively high density, and the solution, with a relatively low density) the density corresponds to the liquid–liquid phase separation region in the Flory–Huggins diagram (see Fig. 2), i.e. $\varphi_1 < \varphi < \varphi_2$, if the parameter χ exceeds the critical χ_{cr}. For example, for the case of $\chi = 0.7$ ($\varphi_b = 10^{-4}$ and $r = 100$) the binodal concentrations are $\varphi_1 = 1.5 \times 10^{-4}$ and $\varphi_2 = 0.37$; under these conditions the spinodal concentrations are $\varphi_1' = 2.7 \times 10^{-2}$ and $\varphi_2' = 0.27$ respectively, and $\chi_{cr} = 0.605$, i.e. in the transition region of the adsorption layer the condition mentioned above ($\varphi_1 < \varphi < \varphi_2$) is realised. The authors did not observe any anomalous deviations of the density profile $\varphi(z)$ from the corresponding density profile for a thermodynamically good solvent [but we note that for the latter type of solvent the de Gennes theory predicts[20–22] the formation of a plateau in the $\varphi(z)$ profile].

In the case of a nonadsorbable polymer Scheutjens and Fleer[14] determined the density profile $\varphi(z)$ and used it to calculate the energy of the interaction between the surfaces (see Fig. 3).

The interaction energy Δg (referred to one cell of area a^2) is defined as follows in the lattice models for an 'ideal'[19] (or 'full'[13]) equilibrium:

$$\Delta g = kT\left[\left(1-\frac{1}{r}\right)\Gamma + \sum_i \ln\frac{\varphi_i^0}{\varphi_b^0} + \chi\sum_i(\varphi\langle\varphi_i\rangle - \varphi_b^2)\right], \quad (8)$$

where

$$\Gamma = \sum_i(\varphi_i - \varphi_b)$$

is the adsorption of the polymer.

In the case of a 'limited' equilibrium the expression for Δg becomes[13,19]

$$\Delta g = kT\left(\frac{\Gamma_t}{r}\ln\frac{\Gamma_t}{\sum p_c} + \sum_i \ln\varphi_i^0 + \chi\sum_i \varphi_i\langle\varphi_i\rangle\right), \quad (9)$$

where $\Gamma_t = \Sigma\,\varphi_i$.

In the present quasicrystalline lattice model the term containing the parameter χ in the expressions (8) and (9) allows for the interaction between the ith segment and its nearest neighbours. An exact determination of the density profile of the polymer and of the solvent, involving the solution of Eqns (3)–(7), allows for the entropy factor associated with the volume limitation effects.

Most of the calculations were carried out for thermodynamically 'good' solvents under conditions of 'limited' equilibrium, i.e. on the assumption that in the case of adsorbable polymers the macromolecules are not desorbed when the two surfaces come close together. In this case the energy of adsorption associated with one segment is fairly large (1 kT, which corresponds to $\chi_s = 1$). The above results lead to the following conclusions.

In an 'ideal' equilibrium we find attraction between the adsorbed layers for both good and poor solvents, and at all coverages of the surface by polymeric molecules. The authors assume[14,16] that this case is a bad representation of the real state of affairs, and they confine all further discussions to the case of a 'limited' equilibrium.

In a limited equilibrium in poor solvents the close approach of the AL produces attraction, which is replaced by repulsion as the film is additionally thinned. In good solvents attraction occurs at low coverages, but at high coverages only repulsion can be observed. It is pointed out that in the case of a good solvent the attraction is created by 'bridge formation', in which the macromolecule is adsorbed at its end segments on the surfaces of different particles. In a poor solvent a negative osmotic pressure is induced in addition to bridge formation, and leads to attraction between the particles (whereas positive osmotic pressure causes repulsion of the particles stabilised by polymeric adsorption layers).

In the theory of Scheutjens and Fleer great importance is attached to the formation of long 'tails' on the outer side of the adsorption layer at high coverages of the surface by adsorbed molecules. This feature distinguishes the theory from the early theories of steric stabilisation. In spite of the depletion of the outer part of the AL the concentration of the 'tails' is sufficient to produce repulsion when the interfacial layers in the film are brought closer together. The frequently observed film thicknesses substantially greater than double the diameter of the average cluster of macromolecules in solution are attributed to this effect.

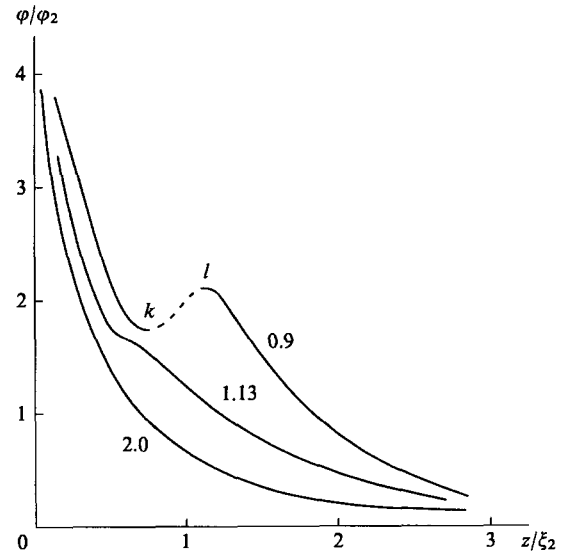


Figure 4. Density profiles of adsorbed layers of polymer in a thermodynamically poor solvent calculated by Eqn (19) for several fixed values of the parameter β^2.

As was pointed out above, in the case of nonadsorbable polymers the local concentration $\varphi(z)$ of segments close to the surface is much lower than the bulk concentration φ_b (Fig. 4). In dilute solutions this 'depletion zone' leads to the development of attraction between the surfaces. However, with a large bulk concentration of the polymer in solution the dislodgment of the macromolecules from the gap between the plates can be hindered, because when the plates are brought closer together the dislodgment should be accompanied by an increase in the free energy of the system (since the macromolecule is being transferred from a region of low bulk concentration of polymer

to a region of high concentration). This produces a coagulation barrier at distances of the order of the size of the macromolecule in solution, similar in shape to the coagulation barrier produced by the electrostatic interaction between electric double layers in the Deryagin–Landau–Overbeek theory. However, in this case the development of a barrier is associated with a decrease in the entropy of the system upon the mutual approach of the surfaces, i.e. the coagulation barrier has an entropic nature.

2. The de Gennes theory

In the theory of the adsorption of polymers proposed[18] by de Gennes the density profile $\varphi(z)$ of segments in the AL is described in terms of the average field approximation in conjunction with the ideas on the theory of polymer solutions developed by Flory and Huggins.[38] For a monodispersed polymer solution having a degree of polymerisation N, described by the Flory–Huggins model with a constant a and a coordination number λ, the free energy of the solution F_0 referred to the volume of one cell of the lattice model can be written as

$$F_0 = kT\left[\frac{\varphi}{N}\ln\varphi - \frac{1}{2}\upsilon\varphi^2 + \frac{1}{6}w\varphi^3 + \ldots\right], \tag{10}$$

where υ and w are the second and the third virial coefficient of the expansion respectively, the first term of the expansion corresponding to the usual Flory–Huggins combinatorial entropy, whereas the second and the third term characterise the interaction between the monomers in solution. The free energy of the system is expressed[39] as

$$F = F_0 + \frac{kT}{24\varphi(z)}\left[a\nabla\varphi(z)\right]^2. \tag{11}$$

The specific interfacial free energy σ is written[18]

$$\sigma = \sigma_s(\varphi_s) + \int_0^\infty \left(\frac{F}{a^3} - \mu_0\varphi + \pi_0\right)dz, \tag{12}$$

where $\sigma_s(\varphi_s)$ is the specific energy of the contact (the energy of adhesion of the first layer of the lattice to the interface), and μ_0 and π_0 are the standard values of the chemical potential and of the osmotic pressure respectively. The integrand expression is the excess of the free energy [referred to unit volume of a solution of density $\varphi(z)$] over a solution having the parameters μ_0 and π_0.

According to Cahn[24] the expression $\sigma_s(\varphi_s)$ in a dilute solution at low coverage of the interfacial surface can be written in the form of Eqn (2) with $\sigma_2 \approx 0$ (since $\varphi_s \ll 1$). Furthermore a weak link between the monomer and the surface is postulated, i.e. it is assumed that $\sigma_1 < kT/a^2$. According to de Gennes[18] this postulate is not inconsistent with the condition of positive adsorption if allowance is made for the multitude of contacts between the polymer and the surface. Thus, in spite of the smallness of the ratio $|\sigma_1|a^2/kT$ in the expression

$$p = A\exp\left[-\theta N\frac{|\sigma_1|a^2}{kT}\right] \tag{13}$$

for the distribution coefficient of the macromolecule units, the large value of N in Eqn (13) ensures a substantial adsorption. (θ is the coverage and A is the preexponential factor introduced by allowing for the increase in entropy produced by the desorption of the macromolecules).

These relationships can be analysed further by determining the density profile of the segments $\varphi(z)$ in the AL [by minimising the interfacial energy σ given by Eqn (12)].[18] The main postulate of the theory is the assumption that the profile $\varphi(z)$ is fully determined by the term $(d\varphi/dz)^2$ in the expression (11). By combining the equality $\varphi(z) = \psi^2(z)$ with expressions (2) and (11), Eqn (12) can be rewritten

$$\sigma - \sigma_{s0} = \sigma_1|\psi_s|^2 + \int_0^\infty \left[\frac{1}{2}L\left(\frac{\psi}{z}\right)^2 + G(\psi^2)\right]dz, \tag{14}$$

where ψ_s is the density of segments in contact with the surface, $L = kT/3a$, $G(\psi^2)$ is a function of the parameter ψ^2, and $\psi_s = \varphi_s^{0.5}$.

Cahn[24] published a detailed analysis of the problem of minimising the functional (14). He showed that the function of state ψ obeys a linear second-order differential equation whose first integral is

$$\frac{1}{2}L\left(\frac{d\psi}{dz}\right)^2 = G(|\psi|^2) - G(|\psi_b|^2), \tag{15}$$

where $\psi_b = \varphi_b^{0.5}$ corresponds to the density of segments in the solution.

The boundary condition on the surface is found by minimising the functional (14), with $\psi = \psi_s$ for $z \to 0$ (see Cahn[24]):

$$2\sigma_s|\psi_s| - L\frac{d\psi}{dz}\bigg|_0 = 0. \tag{16}$$

Expressing (16) as

$$\frac{1}{\psi}\frac{d\psi}{dz}\bigg|_0 = 2\frac{\sigma_1}{L} = \frac{1}{D},$$

we obtain (allowing for $L = kT/3a$)

$$D = \frac{kT}{6a\sigma_1}. \tag{17}$$

Here D is the characteristic thickness of the AL near the surface, where the interaction between the monomer and the wall is substantial.

According to de Gennes's theory of adsorption[18] the structure of the adsorption layer is defined by three regions (see Fig. 3): (1) a near region of thickness D [see Eqn (17)] inversely proportional to the energy of the monomer–surface interaction σ_1; (2) an intermediate region $D < z < \zeta_b$, where the upper limit is the correlation length for the polymer solution; (3) a far region $z > \zeta_b$, in which the density of segments $\varphi(z)$ tends exponentially towards φ_b.

It has been shown[39] that $\zeta_b = a\varphi^{-3/4}$, $\mu_b \sim kT\varphi^{5/4}$, and $\pi_b \sim kTa^{-3}\varphi^{3/4}$. Furthermore, for good solvents in the intermediate region we can write[18]

$$\varphi(z) = \left(\frac{a}{z}\right)^{4/3}.$$

Since the main contribution to $\varphi(z)$ is provided by the 'loops' the effective thickness δ_{ef} of the adsorption layer can be significantly greater than D, and it can approach the thermodynamic radius R_F of the statistical macromolecular cluster. This latter feature is of special interest because it can be checked experimentally. Equally interesting is the expression obtained[18] for the adsorption of the polymer:

$$\Gamma \sim a^{-2}\left(\frac{a}{D}\right)^{1/3},$$

according to which Γ is independent of the degree of polymerisation, i.e. of the molecular mass of the polymer.

The concepts of the de Gennes theory, which had been developed for a good solvent, were extended to thermodynamically poor solvents by Klein et al.[20,22] On the assumption of monomolecular adsorption they determined the profile $\varphi(z)$ of

the adsorption layer of macromolecules by minimising the functional (14) while allowing for the negative sign of the second virial coefficient in Eqn (10).

These authors postulated a small ($\sigma_1 a^2/kT \ll 1$) and irreversible adsorption [$N \gg 1$, see Eqn (13)]. As a result of the adsorption the local concentration of the polymer in the AL exceeds its bulk value in the solution, and it can also exceed the value φ_1 corresponding to the metastable concentration of the polymer on the Flory–Huggins phase diagram (see Fig. 2), and therefore the profile $\varphi(z)$ in the transition region should differ from the profile obtained by de Gennes [18] for a good solvent. In their calculations the authors assumed that the binodal curves (determined from the condition of equality of the chemical potentials in the different phases) and the spinodal curves [determined from the condition of zero osmotic compressibility $a^{-3}\varphi(\partial^2 F/\partial\varphi^2) = 0$] are indistinguishable, and they used the phase curve (spinodal) equation

$$\upsilon(\varphi) = \frac{1}{N\varphi} + w\varphi \,. \tag{18}$$

The region $\varphi_1 < \varphi < \varphi_2$, which includes dilute and semidilute states of the solution, corresponds to phase separation of the system (see Fig. 2). From this standpoint the critical concentration φ_{cr} is given (in terms of N and w) by the expression

$$\varphi_{cr} = (Nw)^{-0.5} \,,$$

where the critical temperature T_{cr} exceeds the temperature of the given state of the system. By using the correlation length $\zeta = a(3\upsilon\varphi/2)^{-0.5}$ (see Klein and coworkers [21,23]), or $\zeta = a\varphi^{0.75}$ (see Babak [7]), and also the new coordinates $y = (\varphi/\varphi_2)^{0.5}$ and $x = z/\zeta_2$, we can minimise the functional σ in Eqn (14) and obtain the expression

$$\left(\frac{dy}{dx}\right)^2 = \alpha y^6 - \gamma y^4 + \beta^2 y^2 + b \,. \tag{19}$$

Here $\alpha = 1$ (Refs 18 and 20) or $\alpha = w\varphi_2^{0.5}$ (Ref. 7), $\gamma = 2$ (Refs 21 and 23) or $\gamma = 3\upsilon/\varphi_2^{0.5}$ (Ref. 7), $\beta^2 \simeq 2\gamma(\ln\varphi_b)/(\ln\varphi_1)$, b is a constant adjustable parameter [chosen by using the condition $y \to y_s \gg 1$ for $x \to 0$, where $y_s = (\varphi_s/\varphi_2)^{0.5}$].

By using the numerical values $\varphi_1 \simeq 2 \times 10^{-4}$ and $\varphi_2 \simeq 0.2$, reported by Klein,[40–42] and also $w \simeq 0.2$ and $\upsilon = w\varphi_2 \simeq 0.04$, and $\gamma \simeq 0.3$, it is easy to prove [7] the existence of a critical value of the parameter β_{cr}^2 [$\beta_{cr}^2 = 1.125$ for the numerical values used above, below which Eqn (19) has no real solution]. For $\beta_{cr} > \beta$ the calculated density profiles tend to become S-shaped when β decreases (Fig. 4). For $\beta = \beta_{cr}$ the $\varphi(z)$ curve has a point where $d\varphi/dz = 0$. For $\beta < \beta_{cr}$ we find a region (the part of the curve between the points k and l) for which Eqn (19) has no real solution. This region can be interpreted as a region of 'condensation' of the polymeric molecules,[7] where the molecules are spontaneously densified from a thickness z_l to z_k. If this interpretation is legitimate we may conclude that in a poor solvent a bulk concentration $\varphi_{cr\,b}$ can be defined above which direct 'condensation' of the macromolecules can take place, producing a continuous increase in the adsorption of the polymer with time.

The critical value of the bulk concentration of the polymer $\varphi_{cr\,b}$, corresponding to the instability region of the AL, is related to the concentrations φ_1 by the expression [40]

$$\varphi_{cr\,b} \simeq \varphi_1^{\upsilon} \,,$$

where $\upsilon \simeq \beta_{cr}^2/2\gamma$. It follows that at polymer concentrations above $\varphi_{cr\,b} \approx 10^{-7}$ multimolecular adsorption can be expected. Thus, in real system there is no equilibrium between the AL and the solution in the case of poor solvents, though phase separation in the bulk may not take place if $\varphi_b < \varphi_1$.

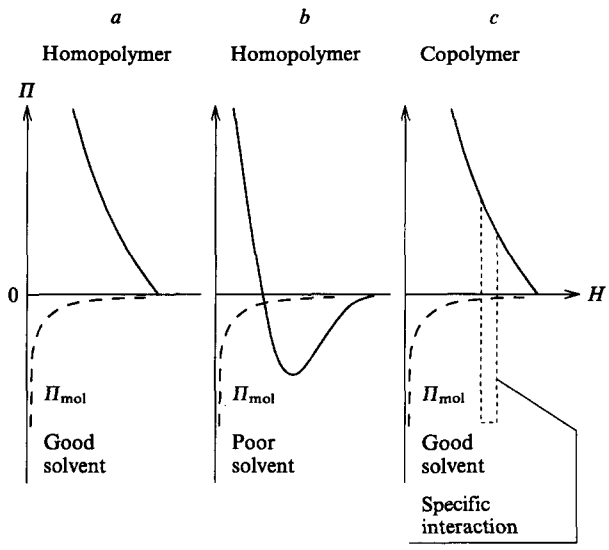


Figure 5. $\Pi(H)$ disjoining pressure isotherms for a plane-parallel liquid film stabilised by adsorption layers of a homopolymer in a good (*a*) and in a poor solvent (*b*), and for a copolymer in a good solvent (*c*).

de Gennes [19] studied the contact between two parallel surfaces in a solution of a polymer in a good solvent and determined the dependence of the disjoining pressure $\Pi(H)$ on the width of the gap (H) between the plates. To this end he used Eqn (14), and expressed its first integral as

$$\frac{1}{2}L\left(\frac{\partial\psi}{\partial z}\right) = G(|\psi|^2) - \tilde{G}(|\psi_{H/2}|^2) \,, \tag{20}$$

where $\tilde{G}(|\psi_{H/2}|^2)$ is an integration constant chosen from the condition $d\psi/dz|_{H/2} = 0$. By using the boundary condition (16) he determined unambiguously the distribution function of the equilibrium profile $\varphi(z)$, and also the function $\sigma(z)$, from which the disjoining pressure was calculated;

$$\Pi = -\frac{\partial\sigma}{\partial z} \,.$$

The main conclusions of the theory of de Gennes [19] relating to thermodynamically good solvents can be formulated as follows: (1) in the case of an 'ideal' equilibrium (i.e. when the adsorption is reversible) a force of attraction is observed beween the surfaces; (2) in the case of a 'limited' equilibrium (i.e. for a constant adsorption of the polymer) a force of repulsion between the surfaces is observed for all values of the distance H. Thus, in relation to these topics the conclusions of the theories of de Gennes [19] and of Scheutjens and Fleer [13,14] are fully consistent.

When applying the results of theoretical studies of adsorption and of the interaction between adsorbed layers of polymers to real dispersions containing polymers the difference in interacting conditions between parallel platelets and spherical particles should not be forgotten.[19] Whereas in the approach of infinite parallel surfaces the desorption of macromolecules from the surfaces is hindered, leading to mutual repulsion of the surfaces, at the contact between spherical particles the macromolecules can migrate away from the region of increased pressure at the centre of the contact and move towards the periphery of the contact region. In the latter case the local adsorption Γ at the centre of the contact zone can decrease, thus inducing mutual attraction between the particles. Similarly, at the contact between liquid interfaces, for which the lateral mobility of the macromolecules is greater than on solid surfaces, we may find that other conditions being equal emulsion particles experience attraction whereas the solid particles of sols experience repulsion.

Furthermore, the brief contacts of particles in Brownian motion may generate mutual repulsion, whereas in the deposits from suspensions or emulsions the desorption of the macromolecules is more likely, leading to mutual attraction of the particles.

Thus the problem of the aggregation stability of dispersions stabilised by polymeric AL in thermodynamically good solvents in still unsolved. It is directly related to a more complex problem: how can the degree of equilibration (or the reversibility of the adsorption) be estimated under actual experimental or technological conditions?

The interaction between platelets in a solution of a polymer in a thermodynamically poor solvent was studied by Klein and coworkers,[20-22] who used the computation schemes proposed by de Gennes[19] supplemented by an additional condition: a negative value of the second virial coefficient v in the expansion (10). In particular, it was shown[22] that the type of interaction between AL of macromolecules is determined by parameters which characterise the bulk properties of the polymer solution, for example by parameters of its phase separation diagram (see Fig. 2), and also by the unperturbed radius of the polymer cluster in solution and by the third virial coefficient w of the expansion (10). One of the consequences of this conclusion is that, in the range of parameters corresponding to mutual attraction between two AL in contact, the adsorption of macromolecules at the boundary with the bulk solution should increase indefinitely with time, and the thicknesses of the AL should also increase indefinitely.[7] We note that Scheutjens and Fleer[14-16] criticised the suggestion[22] that the phase separation diagram of polymers can be used to describe the interaction between AL of macromolecules in a polymer solution.

3. Interaction between adsorption layers of polyelectrolytes

Lyklema et al.[17] have pointed out that the adsorption theories developed to explain the steric stabilisation of dispersions by nonionic macromolecules with flexible chains can be extended (in principle) to copolymers and polyelectrolytes by adding to Eqn (5) the term: $\exp(y_i - y)$ (where $y = e\phi/kT$, and ϕ is the electrostatic potential in the solution), in order to allow for the specific (electrostatic) interaction. However, a statistical theory of the adsorption of polyelectrolytes has not yet been developed.

Hesselink's theory of the adsorption of polyelectrolytes[43,44] is often quoted in the discussion of experimental results. It is an approximate theory, because the exponential dependence of the density of segments upon distance from the surface $\varphi(z)$ is postulated rather than established. Furthermore the theory makes the following assumptions: low concentration of polyelectrolytes in solution (which allows the intermolecular interactions in solution to be neglected), and high ionic strength of the solution [which allows the effect of ionic electrostatic forces between charged functional groups upon the distribution $\varphi(z)$ to be neglected]. This theory establishes the interrelation between the parameters of the adsorption layer of polyelectrolyte (layer thickness, extent of adsorption, density of charges on the interfacial surface) and the physicochemical parameters (degree of dissociation of the macroion, ionic strength of the solution, concentration of the polyelectrolyte, molecular mass, surface charge density, etc.).

The conclusion of Hesselink's theory, that the adsorption of a polyelectrolyte decreases as the degree of dissociation of the macroion is increased, is attributed to a decrease in the electrostatic component of the energy of adsorption. The effect is also explained by an increase in the hydrodynamic radius of the polymer cluster with increasing charge. According to Hesselink's theory a lowering of the Debye screening length (for example, by increasing the ionic strength of the solution) should result in an increased adsorption of the polyelectrolytes (PE): this prediction is confirmed experimentally by a study[46,47] of the effect of pH and of the concentration of sodium chloride on the surface activity of poly(acrylic acid) (PAA) at the solution–air interface. In particular it has been shown that for ionisation levels of the macroion $\alpha \geqslant 0.2$ (i.e. at pH $\geqslant 4$) the PAA becomes surface-inactive because of the increase in solubility of the polyacid with increase in α.

Hydrophobic interactions play an important role in the conformation of polyelectrolytes and in their adsorption at the oil–water inteface.[2,48-52] Hydrophobic binding favours the formation of a more convoluted and rigid conformation of the macroion. The interaction between the hydrophobic (residual acetate) functional groups of poly(vinyl alcohol) and the water–oil interface increases the surface activity of the macromolecule by lowering the free energy in response to the accumulation of hydrophobic groups in the oil phase.[50,51] Increasing the content of acetate groups in the copolymers of acrylic acid and vinyl acetate leads to the formation of gel-like layers at the interface, and therefore also to an increase in the stability of the emulsion films towards rupture (coalescence).[8,9,52-57] The effect of hydrophobic and of electrostatic interactions on the conformation of natural PE (proteins, polysaccharides, etc.) under given physicochemical conditions can be used to explain (at least, qualitatively) the special aspects of their adsorption at phase boundaries.[58-60]

A working theory of the steric stabilisation of dispersions of polyelectrolytes has not yet been developed, in spite of the wide technological use of these materials as stabilisers (especially in mixtures with nonionic polymers).[56,61,62] The difficulty of describing the specific interactions in terms of statistical theories is responsible for this state of affairs, as well as the long-standing interest of researchers in this area in the opposite effect of PE on disperse systems (i.e. in aggregative destabilisation effects such as flocculation and coagulation). However, studies of stabilisation based on the work of La Mer[63,64] and Gregory[65,66], now form a substantial part of the work of Baran,[67] Audebert and coworkers,[68-71] and others.

III. Experimental study of the interaction between adsorption layers of polymers

The most serious problem in the interpretation of experimental results on the properties of AL of polymers and on the interaction between AL is the lack of a criterion for recognising and controlling the thermodynamic equilibrium in disperse systems containing polymers. Because of the finite diffusion time of the macromolecules from the solution to the surface, and of the slowness of the conformational rearrangements of an adsorbed molecule (in particular, at relatively high bulk concentrations of the polymer in solution) we can define a time beyond which the rate of the transition processes falls to zero (i.e. ceases to be an experimentally determinable quantity). This time is of the order of hours or days. The probability of reaching what has been called the 'equilibrium' state of these systems decreases still further if structure formation processes can take place in the AL as a result of the specific interactions between the macromolecules.

Another difficulty met in the experimental study of the properties of AL is the correct choice of a model substance (both for the polymer and for the surface) for difference studies of the effect of physicochemical factors on the adsorption of polymers. In particular, uncontrolled polydisperseness of the polymer samples is reported[67,72] to introduce serious distortions into the results of adsorption measurements, because of the difference in surface activity between macromolecules with small and with large molecular masses. Most probably the adsorption of macromolecules on immobile surfaces (vessel walls, mica laminae, or quartz surfaces in the modelling of contact interactions)[20-23,41,42,52,73-85] or on colloidal deposits[67] is markedly different from their adsorption on the particles of sols undergoing Brownian motion, partly because of the difference in the accessibility of the surface to the molecules and partly because of the hydrodynamic effects produced by the motion of the particles. The effect of the method of measuring adsorption on the result of the measurement has been examined in depth.[67]

1. Measurement of the thickness and of the density profile of adsorption layers of polymers

As was pointed out above, modern theories of the steric stabilisation of disperse systems by polymer layers[11-13] attach great importance to the structure of the AL of macromolecules in their outer side (oriented towards the solution). The layer, formed by 'tails' (and to a smaller extent by 'loops'), makes a relatively minor contribution to the density profile $\varphi(z)$ of the adsorption layer, but its role in the stabilisation of the disperse phase is dominant. The stabilising power of this layer is associated with the mutual repulsion of 'tails' and 'loops' at their steric contact (see Fig. 1*a*).

Unfortunately, only a small number of experimental methods of determining the density profile or the thickness of the outer part of the AL is available at present. Among the methods most recently reported we should include the low-angle neutron diffraction method,[86] and also the measurement of contact interactions between molecularly smooth mica surfaces[20,74,83] or between liquid interfacial surfaces (air bubbles or oil drops approximately 1 mm in diameter) in aqueous solutions of polymers.[84] However, other indirect methods have also been a valuable source of information on the structure of AL. Detailed analyses of all these methods have been published.[5,7,67]

Many systematic studies of the effect of various physico-chemical factors on the thickness of AL of polymers have been reported.[41,42,52,53,74,79-84,87-95] All these works concluded that the effective thickness of the AL is substantially greater than the root-mean-square distance between the ends of the statistical macromolecular cluster ($2R_F$), or than double the hydrodynamic radius R_h of the macromolecule, in keeping with the ideas proposed in the steric stabilisation theories[11-23] on the structure of the AL (i.e. on the mutual repulsion between 'tails' and 'loops' of the macromolecular chains in the liquid film).

The experimental determination of the dependence of the effective thickness of the AL on the molecular mass of the polymer is of great importance because its results can be compared with calculations based on the steric stabilisation theories.

In particular, the following dependence was obtained[88] for AL of poly(vinyl alcohol) (PVA) on particles of polystyrene latex:

$$\delta_{ef} = M^{\beta},$$

where $\beta = 1.14$ in the range $8000 < M < 67\,000$. On the other hand, a study of aqueous emulsion layers stabilised by PVA gave[93] $\beta \simeq 0.2$. This suggests a weak dependence of δ_{ef} on M. It was also stated[93] that the thickness of an adsorption layer of poly(ethylene oxide) on a solid surface, measured ellipsometrically, corresponds to a value of the β coefficient of 0.4, which differs from the value (0.5) predicted by the theories of Hoeve[29] and of Scheutjens and Fleer.[11,14] Kawaguchi et al.[93] interpret this result on the basis of the de Gennes theory,[18] developed for thermodynamically good solvents, by assuming that the size of the 'tails' is comparable with the size of the macromolecule R_F in the bulk of the solution, and that the density profile is described by the function $\varphi(z) \sim z^{-4/3}$, which is valid for the bulk of the solution. By determining δ_{ef} by the expression

$$\delta_{ef} = \int_0^{R_F} z\varphi(z)\mathrm{d}z$$

and putting $R_F \sim M^{0.6}$ (see de Gennes[18]) they obtained the value of 0.4 for β quoted above.

It should be noted that according to de Gennes[18] the adsorption Γ should be independent of the molecular mass M of the polymer. In this respect the reported[93] $\delta_{ef}(M)$ dependence [which is effectively a $\Gamma(M)$ dependence, having been measured ellipsometrically] is incompatible with the de Gennes theory for good solvents.[18] Therefore it is relevant to note the comment[18] that an increase in the adsorption Γ with M can be expected if the adsorbent surface has a mosaic structure with extended 'active' centres (such as dislocations) which can bond to the segments of the macromolecule with a relatively large energy.

The effective thickness of AL of poly(ethylene oxide) on a mica surface in a thermodynamically good solvent (an aqueous 0.1 mol dm^{-3} KNO_3 solution and toluene) was measured by Klein and Luckham[23] by the contact interactions method. The result ($\beta = 0.43 \pm 0.02$) differed from de Gennes' prediction of $\beta = 0.6$, but allowing for the experimental error it is consistent with the theory of Scheutjens and Fleer.[11,14] It has been reported[23] that the agreement with the de Gennes theory[18] is improved by making a correction for the rigidity of the dynamometer used to detect the instant of contact between the two AL. Klein et al.[22] showed that in a thermodynamically poor solvent (polystyrene in cyclohexane) $\beta \leqslant 0.5$. In particular, when calculating the dependence of the thickness δ_{ef} of the adsorption layer on the molecular mass of the polymer in the limit of $f_a^* \to 0$ (where f_a^* is the maximum force, leading to the dislodgment of a particle) these workers obtained the relationship $\delta_{ef} \sim M^{0.5}$ whereas for a finite value of the adhesion force the relationship was $\delta_{ef} \sim M^{0.3}$, which is not inconsistent with any of the adsorption theories.

As regards the effect of the quality of the solvent on the adsorption and on the thickness of the adsorption layer it is usually found that worsening the solvent increases the adsorption of nonionic polymers from aqueous solutions on hydrophobic surfaces.[70] This is attributed to the decrease in size of the macromolecules, to their aggregation, and to the increase in the adsorption energy. In particular, an increase in the adsorption of polymers on hydrophobic surfaces (PVA on polystyrene, and polyvinylpyrrolidone on silica) has been observed upon worsening the quality of the solvent.[90,92,97] The same workers noted a decrease in the thickness of AL of the polymers δ_{ef} when a worse solvent was used, which contradicted Klein's experimental data[22] on the adsorption of poly(ethylene oxide).

In a study[52] of the contact interactions between mica sheets and drops of heptane ($\sim$1 mm in diameter) in aqueous solutions of polymers it was found that although the thickness of the undeformed AL of macromolecules [poly(acrylic acid) (PAA) and copolymers of acrylic acid and vinyl acetate with different contents of acetate groups] exceeded the size of the average macromolecular cluster in the bulk of the solution it increased monotonically with R_F (for example, upon increasing the pH or decreasing the ionic strength of the solution).

A special study[83] by the contact interactions method of the effect of the time of formation of adsorption layers of PVA on a molecularly smooth mica surface in aqueous solutions upon the thickness δ_{ef} of undeformed AL showed that this thickness increases with time at a rate of $\sim 10^{-4}$ nm s^{-1} (the δ_{ef} value doubling in approximately 48 h). Under these conditions structuring effects (gel formation processes) develop within the AL, as shown by the increase in the effective viscosity of the layers (a decrease in their rate of thinning).[8]

Structural changes in the adsorption layers of PVA, dependent on time and leading to an increase in the refractive index of the thin liquid layers, were observed[97] at the contact of a silicone sphere and a solid surface in a solution of PVA, but the authors were unable to draw any firm conclusions as to the nature of this phenomenon. In the experiments of Sonntag and coworkers,[76,85] and of Rabinovich et al.,[73,98] who studied the contact interactions between crossed filaments in solutions of PVA, the change in thickness of the AL could not be determined because the method can measure the absolute deformation of the AL but not their thickness.[47] A study[2,91,99] of foam and emulsion films stabilised by adsorption layers of PVA, and in particular of the dependence of their thickness on the difference in hydrostatic pressure ΔP, allowed the disjoining pressure (or its

steric component) to be expressed as a function of the film thickness, thus making it possible to calculate the thickness of the undeformed adsorption layers of PVA in the limit of $\Delta P \to 0$. The time-changes in the properties of the films observed in these experiments were interpreted as a consequence of the failure of the transition processes to go to completion, which complicated the experiment and compelled the hold time of the interfaces prior to film formation (i.e. the time of formation of the adsorption layers of polymer) to be fixed arbitrarily between 0.5 and 2 h. Thus in these experiments no attempt was made to study the effect of the formation time of the adsorption layers of PVA on their thickness or on the adsorption. Estimates of the thickness of AL of polymers formed on the surface of particles in sols and suspensions have a much lower precision than the direct measurements.[5,67] In particular, even an integral characteristic such as the adsorption of the polymer depends on the chosen measurement method (rate of displacement, method of precipitation of the dispersion, etc.).[67]

Thus our analysis of experimental studies aimed at measuring the thickness of the adsorption layers of polymers or their density profile has shown that the conclusions of the steric stabilisation theories of Scheutjens and Fleer[11-17] and of de Gennes[18,19] on the structure of AL of polymers (the presence of 'tails' and 'loops' in the outer part of the AL, oriented towards the solution, and making an important contribution to the steric stabilisation of the dispersions) is essentially confirmed both for nonionic polymers and for polyelectrolytes. However, we should stress the fact that experimental tests of the dependences predicted by these theories (for example, of the dependence of the thickness of the AL on the molecular mass of the polymer) have given contradictory results. There is very little information on the properties of AL of polymers in thermodynamically poor solvents, and no experimental approaches towards solving this problem have so far been developed. In particular it has been shown[83] that the thickness of adsorption layers of PVA on a molecularly smooth mica surface increases monotonically with time, in spite of the fact that aqueous solutions of electrolytes are moderately good for this polymer ($\chi = 0.45-0.48$).[5] Evidently, in polymers with thermodynamically poor solvents the increase in the thickness of the AL should be even more marked. Therefore experimental methods of studying the properties of AL of polymers should allow for possible time-changes of the parameters of the AL (thickness, rheological properties, etc.), and they should be designed to measure these changes.[52]

2. Steric repulsion between adsorption layers of polymers

According to the thermodynamic theories of steric stabilisation[11-23] an increase in the thickness of liquid films stabilised by AL of polymers produces an increase in the free energy of the repulsion between these AL (Fig. 6). The direct determination of this energy as a function of the film thickness H is a difficult problem. This accounts for the small number of publications on this topic. We shall consider only the experimental methods which allow the pressure P to be measured as a function of the contact pressure force (in the case of a contact between solid surfaces), or of the difference in hydrostatic pressure ΔP (in the case of liquid films).

The first measurements of the repulsive force f_p between bent mica plates in a polymer solution [an aqueous solution of poly(ethylene oxide), PEO, with a molecular mass of the order of 150 000] as a function of the width of the gap between the plates (H) were reported by Israelachvili et al.[74] These workers found that after a 2 h exposure to the solution the thickness of the film (double the thickness of the undeformed AL) reached 300 nm, and that in this region the force of repulsion increased exponentially as H was decreased. In the 10-150 nm region the force f_p depended on the rate of compression of the plates, and showed hysteresis phenomena (the thickness of the AL after loading was not restored to its initial value). Lastly, in the region < 5 nm a steep increase in the repulsive force was observed: it was accompanied by removal of the polymer from the gap and the appearance of a cohesive force as a result of 'bridge formation'.

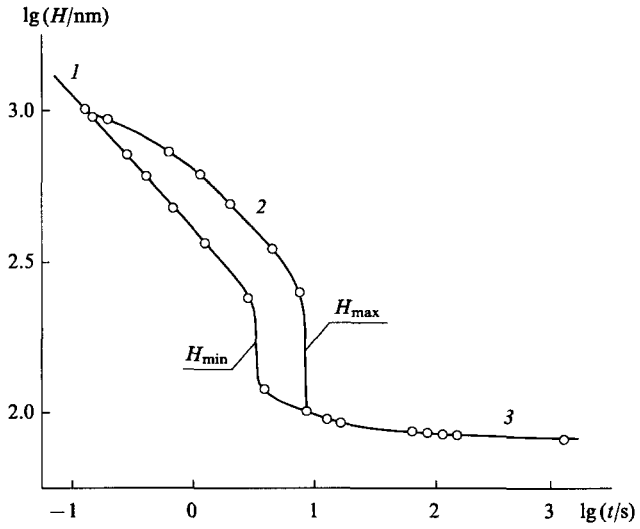


Figure 6. Kinetic curve for the thinning of a water film stabilised by a copolymer of acrylic acid and vinyl acetate containing 74% of acetate groups.[53]

The main conclusions from the work of Israelachvili et al.[74] can be formulated as follows: (1) the adsorption of PEO in a moderately good solvent (Flory-Huggins parameter $\chi = 0.45-0.48$)[100] is multimolecular, since a continuous increase in the thickness of the AL was observed; (2) a gel-like structure is formed in adsorption layers of PEO, with an elastic deformation time (after compression) exceeding the characteristic relaxation time of the sample, thus leading to hysteresis effects; (3) the achievement of film thicknesses $H < 5$ nm in the experiments indicates the absence of contaminants such as dust and microgel particles in the PEO solution.

Klein and Luckham,[41] using a similar apparatus, repeated the measurements of the deformation properties of AL of PEO in an aqueous solution of KNO_3 (0.1 mol dm^{-3}). The PEO samples had molecular masses of 4×10^4 and 1.6×10^5, and the formation time of the AL of polymers was 16 h (as opposed to 2 h, used by Israelachvili et al.[74]). Their main conclusions[41] were: (1) the adsorption of PEO on a mica surface is monomolecular; (2) the adsorption of PEO is irreversible, i.e. the so-called 'limited' equilibrium is established between the polymer solution and the AL (whereas Israelachvili[74] stipulated a 'full' equilibrium since macromolecules are removed from the gap when its thickness is reduced to < 5 nm); (3) the possibility of forming a gel-like structure in the AL is denied; (4) though mica plates were compressed as far as $H \simeq 6$ nm no adhesion between the AL of the polymer was detected (in contrast to the report[74] of the development of a cohesive force between the adsorbed layers of PEO at gap thicknesses < 5 nm).

Klein and Luckham[41] noted the good agreement between the results of measurements of the interaction energy of AL of polymers and those given by the steric stabilisation theory developed by de Gennes[19] for thermodynamically good solvents. The specific free energy of repulsion as a function of the film thickness $\Delta F(H)$ was found by the expression $\Delta F(H) \sim f_p/R$, where R is the radius of curvature of the surface. On the assumption that in the region of weak overlapping of the AL ($H \approx 80$ nm) the mutual repulsion effect between the AL is associated with an increase in the osmotic pressure in the contact region, with $\Delta F(H) \sim V\pi$, where $V = 2\delta - H$ (δ is the thickness of the undeformed AL, π is the excess osmotic pressure), the authors expressed π in terms of the density profile

$\varphi(H)$ of the segments in the contact region [stated[19] to obey the expression $\varphi(H) \sim \exp(-H/2\zeta)$, where ζ is the correlation length], and

$$\pi \sim \upsilon\varphi^2(H) \sim \exp\left(\frac{-H}{\xi}\right).$$

Then,

$$\Delta F(H) \sim (2\delta - H)\exp\left(\frac{-H}{\xi}\right),$$

and the parameter $\Delta = \partial[\lg \Delta F(H)]/\partial(\lg H) = -H/(2\delta - H) - H/\zeta$. In the region of slight overlapping of the AL the inequality $H \leqslant 2\delta$ applies, and the parameter Δ is negative, with $\Delta \to -\infty$ for $H \to 2\delta$. Exactly this law for the changes in Δ was observed[41] for a good solvent in the region of slight overlapping of the adsorption layers of PEO.

Conversely, in the region of strong overlapping of the AL, i.e. for $H < 10$ nm, the following dependence is observed (on the assumption of a constant adsorption of the polymer):[19]

$$\varphi(H) \sim H^{-1},$$

whence we find

$$\pi \sim \varphi^2 \sim H^{-2},$$

which leads to the expression

$$\Delta F(H) \sim H^{-1},$$

which was formulated experimentally.

Klein and Luckham[41] also discovered a hysteresis on the $\Delta F(H)$ curve during a heating–cooling cycle, the parameter $\Delta F(H)$ being smaller during unloading than during loading and remaining always positive (i.e. adhesion between the AL was not observed).

The present writer has reported[83] measurements of the time-dependence curves $H(t)$ of films of aqueous soutions of PVA while compressing mica sheets with gradually increasing forces (f_p). A sudden increase in f_p produces a thinning of the film at a measurable rate even after 10^3 s of observation, though the deformation is mostly completed in 100–200 s after the application of the constant force f_p. After a sudden decrease in the force f_p to a new constant value the thickness of the film relaxes to the previous value in a period of $\sim 10^3$ s in the case of adsorption layers of PVA formed over a time $t_f > 10^5$ s. No relaxation was seen for $t_f < 10^3$ s. As has been pointed out,[52] the experimental $\Delta F(H)$ dependences are not well correlated with the theoretical dependences $\Delta F(H) \sim (2\delta - H)\exp(-H/\zeta)$ and $\Delta F(H) \sim H^{-1}$ for a weak and a strong overlapping of the adsorption layers respectively in a thermodynamically good solvent.[19] The best concurrence is found for AL formed in times $t_f > 10^4$ s, with weak overlapping of the AL, by formally choosing the parameters $\delta = 80$ nm and $\zeta = 7$ nm. We note that the value $\delta = 80$ nm greatly exceeds the value $\delta = 35$ nm, which corresponds to the contact interaction force $f_p \simeq 10^{-8}$ N, i.e. to the precision of the measurement of force in these experiments.

It was also pointed out[52,83] that for an extent of overlapping corresponding to a film thickness $H > 40$ nm (and $t_f \sim 10^4$ s) the $\Delta F(H)$ curves are satisfactorily described on the basis of the HVO theory † (see Ref. 27). Those papers also discuss an attempt to describe the deformation of adsorption layers of PVA by rheological methods based on a simplified solution of the Hertz contact problem[101,102]

$$\frac{f_p}{R} = 0.75E\left(\delta - \frac{H}{2}\right)^{5/2}(R+\delta)^{1/2}, \qquad (21)$$

† More exactly, on the basis of a variant of the HVO theory which assumes an exponential distribution of the density of segments with increasing distance from the surface.

where E is the effective elastic compression modulus of the AL of polymer.

It has been shown that none of the theoretical curves drawn by using Eqn (21) describes the experimental dependence over the whole region of overlap of the adsorption layers. However, by formally assuming that the layer is not uniformly thick the appropriate elastic modulus can be calculated by Eqn (21) for each value of the thickness δ. The following values of E/Pa were obtained for adsorption layers of PVA having $c_{PVA} = 0.1\%$, $c_{KCl} = 10^{-2}$ mol dm^{-3}, and $t_f \geqslant 2.2 \times 10^4$ s: 4.2×10^3, 2.0×10^5, 2.5×10^6 for δ values of 50, 30, and 20 nm respectively.

Thus we have to consider a gradient of the elastic properties of AL of polymers, probably generated by the density gradient of the the polymer segments near the surface or by the gradient in the bulk density of the number of contacts between the segments, responsible for the formation of a gel-like structure within the AL.

The studies by Klein and Luckham,[20,41] of the polystyrene–cyclohexane system were aimed at the interactions between AL of polymers in thermodynamically poor solvents. They stress the presence of an equilibrium minimum on the $\Delta F(H)$ curve [or the $\Pi(H)$ curve, see Fig. 5*b*], having a depth of 10^{-3} J m^{-2}. A strong repulsion arises between the AL when mica sheets are squeezed together.

A group of experimental papers[89,91,99] describes studies of the steric interaction between AL of polymers in free emulsion and foam films. In this work the thickness of the films H was determined interferometrically as a function of the difference in hydrostatic pressure ΔP (which is equal, under equilibrium conditions, to the disjoining pressure in the film). In particular, it was found[91] that the dependence of the disjoining pressure Π on the deformation is linear up to values of $\Delta H/H \simeq 0.3$ when the film is compressed under hydrostatic presure, which is markedly different from the dependence $\Pi \sim \exp(-H/\zeta)$ predicted for good solvents at low coverages by the AL.[19]

The steric interaction between adsorption layers of polymers in microscopic foam or emulsion films (about 100 μm in size) located between air bubbles or liquid droplets in a solution of the polymer has been widely discussed[52,53,96,103]. In particular, it has been shown that when a load is suddenly applied as a constant compressive force f_p between two liquid or gaseous particles with a radius of ~ 1 mm three characteristic regions can be distinguished on the curve which describes the thinning of the liquid film [$H(t)$] between the particles (see Fig. 6). In the first region ($H \sim 1$ μm) the form of the approaching surfaces remains spherical (as shown by the interference image of the film in reflected light), and the thinning of the film can be described by Taylor's equation for the flow of a medium of constant velocity η out of the gap between two undeformed spheres of radius R (see Ref. 52).

$$-\frac{dH}{dt} = \frac{4f_p H}{3\pi R^2 \eta}. \qquad (22)$$

The parameter η calculated by formula (22) is satisfactorily consistent with the bulk viscosity of the polymer solutions.[52,53]

In the second region ($H < 1$ μm) we observe a compression of the spherical surface of the drops and the formation of lenticular thickenings ('dimples') at the centre of the circular films, from which the polymer solution flows through a gap of thickness H_{min} towards the periphery of the film.

Lastly, when the compression of the 'dimple' is almost complete we come to the third stage of thinning of the film, taking place against a background of steric interactions between AL of macromolecules with a variable effective viscosity and a velocity of the order of 10^{-2}–10^{-1} nm s^{-1} (see Refs 52 and 53). The deformation of the element of the flat film has been described by using the rheological model of Kelvin, consisting of elastic (E_K) and viscous elements (η_K) connected in parallel,

according to which

$$\Delta P = E_K \varepsilon + \eta_K \frac{d\varepsilon}{dt}, \quad (23)$$

where $\varepsilon = (H_0 - H)/H_0$ is the relative deformation of the film, H is its thickness, and H_0 is the effective thickness of the undeformed film, i.e. the thickness of the film for $\Delta P = 0$. By solving Eqn (23) we obtain the expression

$$H(t) = H_0\left[1 - \frac{\Delta P}{\eta_K}\tau\left(1 - \exp\frac{-t}{\tau}\right)\right], \quad (24)$$

in which $\tau = \eta_K/E_K$. In spite of the fact that Eqn (24) does not describe the experimental curves for the third stage of thinning of the film $H(t)$ a formal application of this equation to the separate parts of the $H(t)$ curve can determine the rheological parameters E_K and η_K as a function of the film thickness.

It has been shown [52,53] that the elastic modulus of the adsorption layers of PVA can vary between 100 and 500 Pa, suggesting a relatively low value of the density of segments for film thicknesses between 90 and 75 nm. According to the steric stabilisation theories [11-23] relatively low values of the elastic modulus (and therefore also of the free energy of mutual repulsion between the AL of macromolecules) are typical of a bulk density of segments not much greater than the bulk density of the polymer in solution, and may be attributed to the entropic component of the disjoining pressure associated with the limitation imposed on the volume of the macromolecules (in terms of the HVO theory [27]).

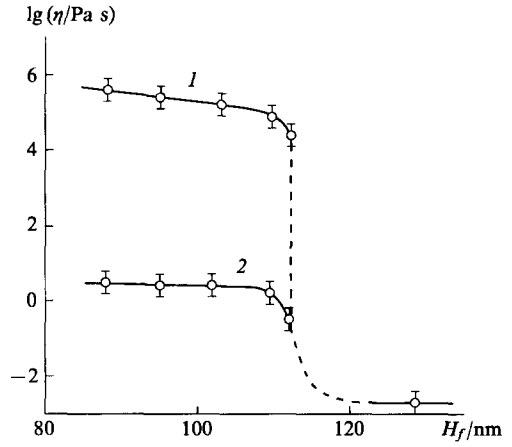


Figure 7. Dependences of η_K (*1*) and η_0 (*2*) for a water film stabilised by PVA upon its thickness H_f.

A characteristic feature of the dependence of the viscosity η_K upon the thickness H of the film is the sudden increase in η_K over a relatively narrow range of film thickness (Fig. 7). The H_0 value can be interpreted as the thickness of the film formed by almost undeformed adsorption layers of the polymer. The effective value of the viscosity η_0 calculated by the expresssion

$$\eta_K = \frac{3}{2}\frac{r_0^2 H_0}{H^3}\eta_0,$$

which corresponds to the plane-parallel disc model, also increases in this range of film thickness but only by 2-3 orders of magnitude (see Fig. 7). Unfortunately, the estimated value of η_0 thus obtained does not justify any unambiguous conclusions on the structure of the steric contact region between AL of macromolecules. For example, the above estimate of η_0 can be obtained by assuming the presence in the central region of the film of a layer of dispersion medium ~ 10 nm thick flowing almost freely.[52] By assuming 'tails' and 'loops' of the macromolecules (which impart a positive disjoining pressure to the film) can penetrate into this layer we are compelled to allow for the hydrodynamic resistance of the segments to the outflow of the liquid medium, i.e. to postulate that the thickness of the layer in which the flow of the liquid is fast can be much greater than 10 nm.

Babak and Monissova [53,96] reported the first attempt to determine the specific free energy of the interaction $\Delta F(H_f)$ in a film of thickness H_f stabilised by polymers. They used the expression

$$\Delta F(H_f) \simeq \Delta P(H_{\min} - H_f), \quad (25)$$

where H_{min} is the minimum thickness of the idealised profile, which can be obtained by extrapolating the profile of the surface of constant average curvature to the region of the bulk meniscus on the intermediate region of the film.[26] It was shown that the positive quantity $\Delta H_{\min} - H_f$ is not greater than 4-6 nm, which sets the following upper limits for $\Delta F(H_f)$: 4×10^{-7} J m^{-2} for PVA [96] and 1.5×10^{-7} J m^{-2} for PAA.[53] The values thus obtained for $\Delta F(H_f)$ are consistent with those predicted by the steric stabilisation theory for the interaction between AL of polymers in liquid films.

3. Adhesion between adsorption layers of polymers in liquid films

The development of adhesion between AL of macromolecules in thermodynamically poor solvents is predicted by all the steric stabilisation theories [11-19] and is confirmed by direct measurements of the cohesive forces between the mica plates in polymer solutions.[20-23]

In the case of thermodynamically good solvents the steric stabilisation theories predict mutual repulsion between AL of polymers at high coverages and on the assumption of a limited thermodynamic equilibrium (constant adsorption of the polymer in the region of steric contact between the two AL in the film, i.e. no desorption of macromolecules upon compressing two AL). Under full thermodynamic equilibrium these theories predict mutual attraction between AL in good solvents.

Direct measurements of the attachment forces between AL of polymers in good solvents are inconsistent. As was pointed out above, Klein and Luckham [41] failed to detect any cohesive forces between adsorption layers of PEO. On the other hand Israelachvili et al.[74] observed large adhesion forces for AL of the same polymer upon bringing mica surfaces within 5 nm of each other. Rabinovich and coworkers [73,85,98] reported the absence of adhesion between adsorption layers of PVA formed on the molecularly smooth surfaces of quartz fibres. Large adhesion forces were detected between adsorption layers of PVA on a mica surface,[8,52,78,83] and also on other solid or liquid interfaces.[104,105] Some of these studies [8,52,57,106] included a systematic examination of the effect of different physicochemical factors on the force of adhesion between two air bubbles or heptane drops in aqueous solutions of PVA.

Concentrated emulsions of oil (heptane) in water, stabilised by PVA, acquire a finite plastic shear strength P_s (see Refs 8, 9, 52, 57) after sedimentation in a centrifuge. We shall assume that the plastic strength can be calculated from the expression

$$P_s \simeq n\bar{f}_a^*. \quad (26)$$

Here n is the surface density of broken contacts in the shear plane, equal to $\approx 1/\bar{R}^2$ ($\bar{R}$ is the average radius of the emulsion drops), $\bar{f}_a^*$ is the average adhesion force between drops of emulsion, given (according to the theory of adhesion of liquid particles [107]) by the expression

$$\bar{f}_a^* = \pi v_a R \Delta F_a, \quad (27)$$

where ν_a is a parameter dependent on the capillary pressure and on the shape of the profile of the disjoining pressure, varying between 0.5 and 1, and $\Delta F_a = \Delta F(H_f)$ is the specific free energy of adhesion in a liquid emulsion film of thickness H_f, formed between emulsion drops. Using Eqns (26) and (27) gives the expression [8,9]

$$P_s \simeq \frac{\Delta F_a}{\bar{R}}. \tag{28}$$

Calculations of ΔF_a by means of Eqn (27) from measured values of the plastic strength of concentrated emulsions give values of the order of (-10^{-5}) to (-10^{-4}) J m^{-2} (see Refs 8–10, 52, 57).

It should be noted that the plastic strength of very concentrated emulsions is measured at a small but finite relative shear velocity. Under these conditions the breaking of the adhesion contacts between the emulsion drops and the formation of new contacts take place in a finite time. Thus the adhesion force f_a^* calculated by Eqn (26) cannot be assumed to be an equilibrium adhesion force, just as the ΔF_a value calculated by Eqn (28) is not an equilibrium value of the specific free energy of adhesion. We can expect (as is found in practice) [52,78,83] a decrease in the cohesive force between emulsion drops on lowering the shear rate, i.e. on lowering the velocity of the breaking load applied to the drops

$$f_a = \frac{df_a}{dt}.$$

On the rheological curve this region corresponds to creep. The creep phenomenon itself is characteristic not only of disperse systems stabilised by AL of polymers (interacting through short-range forces, including hydrophobic interactions produced by hydrogen bonds), but also of very concentrated dispersions with contacts of the coagulation type between particles, interacting through molecular and electric forces.

When the size of the particles is decreased, i.e. when the potential energy of the interaction between particles is lowered to a level comparable with kT, the breaking of the adhesion force between particles is caused by thermal fluctuations and becomes controlled by probability laws.[108] The same is true of the breaking of the adhesion contact between two AL of macromolecules, when the discrete bonds between 'active' functional groups are not broken simultaneously upon the application of a disjoining pressure. Under these conditions we can expect the force of adhesion between particles coated with AL of polymers to depend on the rate of application of the disjoining pressure P_a, decreasing as dP_a/dt is decreased.

The effect was discovered in measurements of the cohesive force between two mica sheets in a solution of PVA while increasing the disjoining load at a controlled rate to the value $f_a^* \leqslant 10^{-5}$ N s^{-1} (see Refs 52, 78, 83). Furthermore, in these experiments the authors measured the time t_a needed to break down the adhesion contact after the application of a constant pulling force to the particles, and they noted that t_a decreases as f_a^* increases (Fig. 8). The following expression was used [108,109] to describe the dependence $t_a(f_a)$ on the assumption that a thermal fluctuation mechanism is applicable to the breaking of the adhesion contact between the surfaces:

$$t_a = t_0 \exp\left[\frac{E_a - \gamma P_a}{kT}\right], \tag{29}$$

where t_0 is a constant parameter, E_a is the activation energy for bond breaking, γ is the activation volume of the bond breaking, and $P_a = f_a/A$ is the detachment pressure (A is the area of contact).

The value thus obtained ($\gamma \simeq 500$ nm^3) has been interpreted [52,78,83] as the volume assigned to one acetate group in the macromolecule of PVA (the content of residual acetate groups in the sample of PVA used in this work was $\sim 1\%$).

It has been pointed out that the volume γ is smaller by a factor of 100 than the volume of one molecule, and approximately 100 times greater than the volume assigned to one hydroxyl group. We also note that the activation energy E_a obtained from the temperature dependence of the force of adhesion f_a^* between adsorption layers of PVA is $(0.1-0.4) \times 10^{-20}$ J (see Refs 8, 52), i.e. it is a quantity of the order of kT, which is in keeping with the suggested thermal fluctuation character of the breaking of the adhesion bond between AL of the polymer.

There have been repeated references [9,52,57] to the practical problems met in the measurement and in the determination of the specific free energy of the interaction $\Delta F(H_f)$ between the AL of polymers resulting from the short-range forces between the bonds which are not broken simultaneously, and also from the long-range elastic compression forces between the AL during compression. In particular, during the compression of two AL in the film the corresponding work of elastic compression of the macromolecules can be arbitrarily assigned to the dividing surface of the liquid film, and it can be assumed that the interfacial tension σ_0 is increased by an amount $\Delta F(H_f)$, which can be found for the profile of the film by using Eqn (25). A positive sign of $\Delta F(H_f)$ corresponds to long-range forces of mutual repulsion between the phase boundary surfaces in the film, containing elastically compressed AL. Under these conditions if specific interactions between the AL of macromolecules (hydrophobic interactions, hydrogen bond formation, electrostatic interaction between oppositely charged functional groups) are taking place in the region of steric contact, leading to a decrease in the free energy, the shape of the film profile can be almost unaffected by this decrease in the free energy because of the short-range influence of these interactions. In experiments aimed at the direct measurement of the contact interaction forces in the compression cycle of mica plates [41,74,83] or of quartz fibres [73,85,98] the decrease in free energy could not be detected against the background of long-range repulsive forces between the elastically compressed AL of macromolecules.

However, dilution of the samples produces an elastic expansion of the macromolecules in the AL as a result of the short-range specific interactions, which formally converts these interactions into 'long-range' interactions since the deformed macromolecules in the AL produce a deformation of the interfacial surface and give the characteristic 'neck' shape to the film profile: in other words, a finite contact angle is created. The formal application of formula (25) in this case leads to negative values of $\Delta F(H_f)$. However, the magnitude of this effect, i.e. the value of the negative energy $\Delta F(H_f)$, will depend on the relationship between the rate of change of the external interaction and the rate of the relaxation processes in the AL of polymers. Since the specific interactions are short-range forces

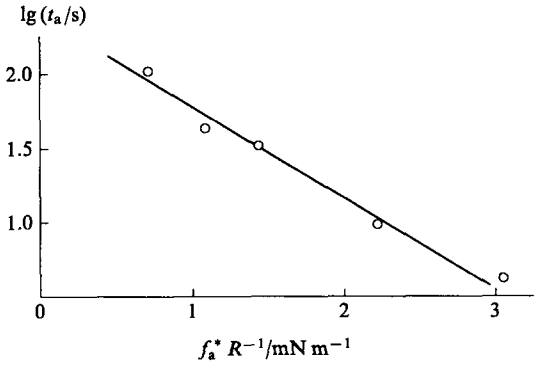


Figure 8. Dependence of the breaking time t_a of the contact between mica sheets in an aqueous solution of PVA upon the pull force f_a^*/R (see Babak [83]).

and cannot be assigned to the dividing surfaces of the film their contribution is arbitrarily shown as a broken line[8,9,52] on the disjoining pressure isotherm (Fig. 5*c*).

IV. Conclusions

The new ideas[8-10,52,57] on the mechanism of the interaction between AL of macromolecules clearly point to the need to devote proper attention to the kinetic factors in experimental studies of the steric interaction between the AL of polymers: these factors include the ageing time of the AL (i.e. the time of formation of the AL), the time of formation of the steric contact between two AL, the rate of application of the pull force when breaking the adhesion contact between the AL, etc. This state of affairs arises because in the stabilisation theories[11-19] the problem of choosing between a 'limited' and a 'full' equilibrium in a system of two interacting AL (see Introduction) is solved arbitrarily, since there are no rational criteria for choosing the type of equilibrium which best describes the steric interaction between AL of polymers. However, the conclusions suggested by the theory as to the stability of sterically stabilised dispersions are strongly affected by the type of equilibrium, since (as was pointed out above) in the case of thermodynamically good solvents these theories predict the formation of adhesive forces between AL of polymers on the assumption of a 'full' equilibrium but not on the assumption of a 'limited' equilibrium.

Evidently the best approach in these circumstances is to assume that, when the time of formation or of steric contact between AL of polymers is increased, a 'limited' equilibrium will tend towards a 'full' equilibrium, thus creating adhesion forces between the particles coated with AL and suppressing the aggregative stability of the dispersions. Similarly, lowering the rate of application of the pull force creates conditions favouring a 'full' equilibrium between the interacting AL of macromolecules, and the adhesive force between particles will be lowest when the equilibrium is most evident. In the limit of a 'full' equilibrium the force of adhesion between polymer particles coated with AL in a thermodynamically good solvent will vanish, as predicted by the steric stabilisation theories.[11-19]

The above concepts were used as a foundation for the interpretation of the results of measurements of the rheological properties of very concentrated emulsions stabilised by adsorption layers of PVA. The development of plastic strength in the emulsions stabilised by this polymer, for which aqueous solutions of electrolytes are thermodynamically good solvents, and also the increase of this strength with time of centrifuging,[9,57] can only be explained by allowing for the finite time needed for the transition of the system from a 'limited' to a 'full' equilibrium. Allowing (in terms of the steric stabilisation theories) for the kinetic factor which characterises the achievement of a 'full' equilibrium by a system of two interacting AL of macromolecules, which can be determined experimentally, should bring the steric stabilisation theories closer to the description of actual nonequilibrium processes in disperse systems containing polymers.

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