

POLYMERS AT INTERFACES AND THE INTERACTIONS IN COLLOIDAL DISPERSIONS

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Abstract—Solutions of different polymers in the same solvent are incompatible as a rule and show phase separation when they are mixed. If incompatibility is also to be observed in systems where one of the polymer components is replaced by colloidal particles, sterically stabilized by a cover of polymer chains, will be discussed in this lecture.

After a discussion of the applicability of statistical thermodynamical criteria for colloid stability we focus attention on the potential of average force between two particles, $V(r)$, and the second virial coefficient, B_2 .

First it is shown from general arguments that $V(r)$ and B_2 always decrease in magnitude upon addition of particles identical to the particle pair considered. The decrease is particularly large for high molecular weight polymers.

Subsequently, the analysis is extended, with the help of simple models, to mixtures of polymer colloid and polymer. It is predicted that B_2 should decrease and may become negative when the molecular weight and concentration of the polymer are sufficiently large. For high molecular weight polymer this is of the order of a per cent or less. More polymer is needed for low molecular weights.

The destabilization is intimately connected with the expulsion of polymer from the interstitial spaces between approaching particles because of "volume restriction"- and "osmotic" effects.

The predictions are in accordance with some experiments that were available. Finally the applicability of light scattering as an experimental tool in these stability problems is stressed. Results are also given of the incompatibility of two polymers in a single solvent in which one of the polymers is masked i.e. does not scatter light.

1. INTRODUCTION

When two dilute solutions of different polymers in the same solvent are put together, generally a cloudy mixture is formed that upon standing separates into two phases. The homogeneous system in which both polymer species are uniformly dispersed is clearly *unstable*. One says that the polymers are *incompatible*. In our laboratory we have been working on this phenomenon and in this lecture I will discuss the experimental methods and some results later on.

First, however, I would like to discuss a question that is of more interest for the *colloid* scientist.

At present an increasingly important class of colloidal dispersions is stabilized by polymer chains attached to the particle surfaces in one or another way. In Fig. 1, I have sketched a scale of possibilities ranging from linear polymer molecules (type A) to uncovered particles (type F). Now one may ask: what will occur upon mixing of

different dispersions of the types A-F; are those species also "incompatible"? In this lecture I will attempt to make some theoretical predictions. For simplicity the discussion will be restricted to mixtures of A (or B) with A-F.

1.1. Incompatibility and coacervation

Some 30 yr ago, Dobry and Boyer-Kawenoki¹ showed in experiments with many polymers and solvents that, with a few exceptions, incompatibility is the rule.

This can be explained by the observation that the entropy of mixing of a solution containing large chains is only small, whereas the energy of mixing is of the same order of magnitude as in a low molecular weight mixture. Slight differences in the interactions between polymer segments are thus sufficient to give phase separation. The effective interactions between different polymer segments are usually unfavorable so that after phase separation has occurred the different phases contain mainly the separate polymer components. In fact the opposite case—in which the effective interactions are favorable—was investigated earlier especially by Bungenberg de Jong and Kruyt^{2,3}. They observed all mixing of two solutions of macromolecules carrying ionized charges of opposite sign, gives a phase separation in which one of the phases contains predominantly the macromolecular "complex" and the other phase is very dilute. They called it (*complex*)*coacervation*. The term *coacervation* is still used frequently for phase separations of this sort. Entering into the question of incompatibility in the more general types of polymeric dispersions (A-F) leads us in the first place to the more general question as to how far thermodynamic (stability) criteria can be used for the problem of colloid stability in general.

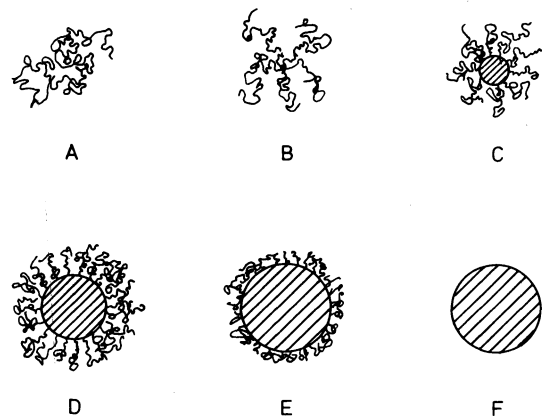


Fig. 1. Types of polymer colloids (A = linear macromolecule; B = star macromolecule; C, D, E = cores, sterically stabilized by attached macromolecules; F = naked core).

2. STABILITY OF COLLOIDS

In the early days of colloid science it was felt that thermodynamic criteria of stability could not be applied to colloids. This was quite clear from observations of irreversible flocculations in hydrophobic colloids. But

even for systems as mentioned above, i.e. the instability of a solution containing two macromolecules with opposite charges (hydrophobic colloids), Kruyt and Bungenberg de Jong² found it expedient not to identify this with phase separation in the classical thermodynamical sense. That is why they coined the term "(complex) coacervation"; coacervation meaning here: "grouping together".

At present, however, it is felt that this view is too restrictive. Thermodynamic criteria are used successfully to describe solutions of polymers and polyelectrolytes, including phase separation.

But also in hydrophobic colloids at least the effective forces between the colloidal particles can be described in (statistical) thermodynamical terms, and the way in which they manifest themselves in stable states can be studied, e.g. by measuring (Donnan) osmotic pressure or light scattering.

However, consideration of unstable states in hydrophobic colloids requires more care. This can be illustrated with the (now) classical picture in which the free energy of interaction (or potential of average force) between two particles, $V(r)$, is determined by electrical double layer repulsion and van der Waals attraction forces. Generally, $V(r)$ has two minima separated by a maximum, depending on the surface potential of the particles and the electrolyte content in the surrounding solution (see Fig. 2).

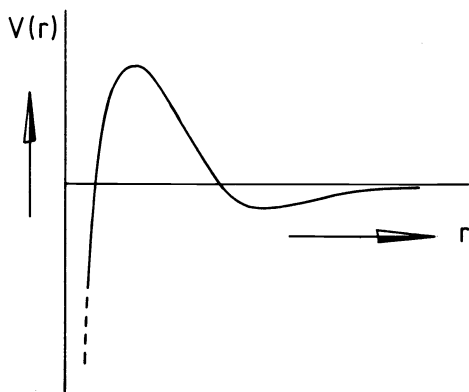


Fig. 2. Schematic plot of the potential of average force, $V(r)$, for electric double layer repulsion plus van der Waals attraction forces.

If the maximum is too small or absent two interacting particles may reach the primary minimum in which they are in close contact. In this state of close proximity the minimum in $V(r)$ can be very deep so that a spontaneous escape is very improbable and subsequent irreversible processes as sintering, recrystallization etc. can take place, making it impossible to redisperse the particles by simply changing the conditions of the surrounding solution. The main description of instability here is the kinetics of the irreversible flocculation process. This does not mean that in this case thermodynamics cannot be used for partial processes. It will depend, however, on the time scale in which these processes occur⁴ and thus on the specific properties of the system under study.

When the maximum in $V(r)$ is high enough, two interacting particles cannot reach the deep, primary minimum and cannot come in close proximity. The particles feel a repulsive force at a finite distance between their surfaces, the magnitude of this distance depending on the surface potential of the particle and in particular on the thickness of the double layer.

When the depth of the secondary minimum, preceding the maximum is smaller than the thermal energy kT , the particles feel effectively only the repulsion due to the steep rise in $V(r)$ and the system will be stable. In certain important cases, however, where the size of the particles is large enough, the secondary minimum can also become deep enough to trap the second particle for some time. (In this process no activation barrier has to be crossed as usually occurs in flocculations in the primary minimum.)

In this case the occurrence of subsequent, irreversible processes is less obvious than in the former one although there is an important exception in the case of emulsions where subsequent breaking of the intervening liquid layer between the particles may take place after which coalescence of the two particles occurs.

Now, when the particles always keep their individuality in all the processes the system undergoes, there is no formal difference between such a colloidal suspension and a low molecular liquid. This was stated clearly for the first time by Einstein⁵ in his treatment of osmotic pressure and Brownian motion of suspended particles. It was worked out further in particular by McMillan and Mayer,⁶ Onsager⁷ and Hill.⁸ In this picture the particles act as "supramolecules", whereas the liquid solution between the particles merely acts as a background medium, the properties of which only enter in an indirect way in that they determine the properties (magnitude and range) of the (effective) interactions between the particles. The effective interactions have a free-energy character. Formally the pair potential between two molecules, $U(r)$, has to be replaced by the potential of average force, $V(r)$, of two particles.

This has far-reaching implications for the study of these systems because the whole machinery of (statistical) thermodynamics of liquids can be invoked. Recently Snook and van Megen⁹ used a Monte Carlo technique and Richmond¹⁰ used the Percus-Yevick equation to calculate the radial distribution function, $g(r)$, at higher particle concentrations for $V(r)$ as in Fig. 2.

Ottewill¹¹ will report in this conference on light scattering experiments from which $g(r)$ was obtained. At present some "coacervates" are recognized as separated phases. In systems containing anisometric particles so-called "tactoids" have been known for a long time although it is not certain if phase separation is due here to the secondary minimum alone. But also in systems containing spherical particles phase separations of this type have been reported e.g. by van den Tempel¹² in emulsions. Phase separation of another type, due to repulsive ordering, have been reported by Krieger^{13,14} and Hachisu.^{15,16}

These considerations are not new. Martynov and Muller¹⁷ recently discussed certain properties of aggregate-equilibria in particulate systems. They coin the names infra-gas, infra-liquid and infra-solids for these systems. We would prefer the prefix "supra" instead of "infra". Also Long, Osmond and Vincent¹⁸ discussed some equilibrium aspects of weak flocculation.

The point we want to stress, however, is that this approach may become of particular significance for the increasingly important class of colloidal dispersions stabilized by macromolecules (as depicted in Fig. 1). The attached polymer chains can be very efficient in keeping the particle surfaces separated at a finite distance. Theory¹⁹ suggests that $V(r)$ has one minimum comparable with the secondary minimum in the classical double layer and steeply rises at smaller r (see Fig. 3). These types of $V(r)$

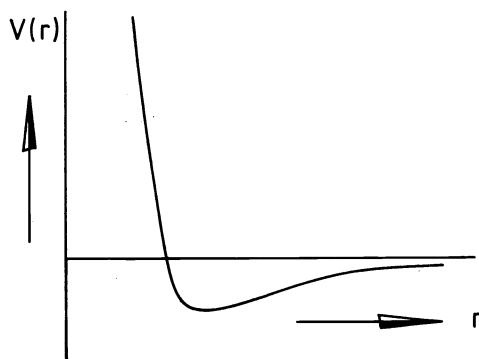


Fig. 3. Schematic plot of the potential of average force, $V(r)$, for sterically stabilized particles with repulsive "volume restriction" forces plus repulsive (or attractive—depending on solvent quality—) "osmotic" forces plus attractive van der Waals' forces.

have the same shape as pair potentials in simple liquids, although there can be important differences in the depth and the width of the potential well. In liquids the depths are in the order of kT and the widths are comparable with the size of the molecules. For the larger colloidal particles the depths may be many times kT and the widths, although large with respect to atomic dimensions, may be very small with respect to the particle size.

Let us now see what mechanisms in steric stabilization contribute to $V(r)$.

2.1. Volume restriction and osmotic effects

In a previous paper¹⁹ on the theory of the steric stabilization of dispersions, two mechanisms were considered by which polymer chains attached to the particle surface can keep the particles in suspension.

(a) Polymer chains attached to a particle surface lose configurational entropy when they approach the (surface of a second) particle. This was called: "volume restriction effect".

(b) When the layers of attached polymer chains on the two particles interpenetrate, the higher polymer segment concentration between the particles will lead to a local "osmotic pressure" in many cases counteracting the approach.

Up to now these mechanisms were considered for particles dispersed in a simple, low molecular weight solvent. The question now arises what will occur if one adds polymer molecules (A/B) to the solvent. We think that similar mechanisms will operate.

(a) added polymer molecules lose configurational entropy when they penetrate the (narrow) space between two interacting particle surfaces

(b) segments of added polymer molecules will interact with the segments of the attached chains

Both mechanisms will promote the expulsion of added polymer from the space between the particles, when the solvent is not poor. Effect (a) will be most effective when the size of the polymer molecules is larger than the thickness of the polymeric layer around the particles (type E and F) and effect (b) in the opposite situation.

2.2. Potential of average force and second virial coefficient

Our theoretical discussion will be concentrated on the potential of average force, $V(r)$, and the second virial coefficient, B_2 , of suspended particles of the types A–F in a solvent containing polymers of the type A/B, where

$$B_2 = \frac{1}{2} \int_0^\infty [1 - e^{-V(r)/kT}] 4\pi r^2 dr. \quad (1)$$

We will first look at the simplest situation and investigate how $V(r)$ of a particle pair and B_2 as given by eqn (1) will change when one adds particles that have identical properties as the pair considered. This is a special case that can be treated in a general way and gives insights of a much wider scope.

3. MIXTURES OF MARKED AND UNMARKED PARTICLES

Consider a mixture of two kinds of particles, 2 and 3, in a low molecular weight solvent, 1, which plays only a role as a background medium with a constant chemical potential. We stipulate that all the physical properties of 2 and 3 are identical, except that one of them is marked in one or another way for convenience.

The main question is: how are the effective interactions between particles of type 2 affected by the presence of particles of type 3? More particularly we will discuss the following process.

Take a system of particles 3 in which one considers a macroscopic (geometrical) volume V . How will the number of particles 3, N_3 , in V change when one adds particles 2 in V and keeps them there and how will the pressure, P , change?

In other words: how large is the "adsorption", $\Gamma \equiv (\partial n_3 / \partial n_2)_{\mu_3}$, of particles 3 "on" particles 2 and how large is $(\partial P / \partial n_2)_{\mu_3}$? Here $n_i = N_i / V$ and μ_i is the chemical potential of component i . The device is really a Donnan osmotic cell having a membrane permeable to 1 and 3 but not to 2. Although such a membrane does not exist it is sometimes possible to obtain the same kind of information from light scattering (see section 7).

3.1. Thermodynamic route

For the chemical potentials one may write

$$\mu_2/kT = \text{const.} + \ln n_2 + f(n_i) \quad (2)$$

$$\mu_3/kT = \text{const.} + \ln n_3 + f(n_i). \quad (3)$$

Here n_i is number density (number of particles per unit volume) of component i and $n_i = n_2 + n_3$. These equations merely express that all the non-ideal terms in the chemical potentials depend on the total number density, n_i , only which is obvious because we stipulated that all the interactions of 2 and 3 are identical. Information of $f(n_i)$ can be obtained from experiments or from a theory. So, from the osmotic pressure, P , (of either 2 or 3 in 1) one obtains

$$dP/kT dn_i = n_i, \quad d\mu/kT dn_i = 1 + n_i df/dn_i = 1 + n_i f' \quad (4)$$

where we write: $f' = df/dn_i$.

To obtain $(\partial P / \partial n_2)_{\mu_3}$ we use the following thermodynamic relation (see e.g. Guggenheim²⁰)

$$(\partial P / \partial n_2)_{\mu_3} = (\partial P / \partial n_2)_{n_3} - \frac{(\partial P / \partial n_3)_{n_2} (\partial \mu_3 / \partial n_2)_{n_3}}{(\partial \mu_3 / \partial n_3)_{n_2}}. \quad (5)$$

Substituting the eqns (2–4) one then obtains

$$\frac{1}{kT} \left(\frac{\partial P}{\partial n_2} \right)_{\mu_3} = \frac{1 + n_i f'}{1 + n_3 f'} = 1 + \frac{n_2 \left[\frac{1}{kT} \frac{dP}{dn_i} - 1 \right]}{n_2 + n_3 \frac{1}{kT} \frac{dP}{dn_i}}. \quad (6)$$

This equation reveals that the effective interactions between the particles 2 are damped out when n_3 increases. So when $(1/kT) dP/dn_i > 1$ and $n_3 \gg n_2$ one has

$$\frac{1}{kT} \left(\frac{\partial P}{\partial n_2} \right)_{\mu_3} \rightarrow 1. \quad (7)$$

Let us consider more particularly the second virial coefficient of component 2 (in 3), $B_2(n_3)$, as a function of n_3 . The second virial coefficient is defined by

$$\frac{1}{kT} \left(\frac{\partial P}{\partial n_2} \right)_{\mu_3} = 1 + 2B_2(n_3)n_2 + \dots \quad (8)$$

With eqn (6) one finds

$$2B_2(n_3) = \left(\frac{\frac{1}{kT} \frac{dP}{dn_i} - 1}{n_3 \frac{1}{kT} \frac{dP}{dn_i}} \right)_{n_i=n_3}. \quad (9)$$

Also this equation reveals several interesting features. When $(1/kT) dP/dn_i \gg 1$, e.g. when n_3 is large, then

$$2B_2(n_3) \rightarrow \frac{1}{n_3} \quad (10)$$

which is small. When $(1/kT) dP/dn_i = 1$, $B_2(n_3) = 0$. The "adsorption" of component 3 "on" component 2, $\Gamma = (\partial n_3 / \partial n_2)_{\mu_3}$ can be obtained in a similar way

$$\Gamma = (\partial n_3 / \partial n_2)_{\mu_3} = - \frac{(\partial \mu_3 / \partial n_2)_{n_3}}{(\partial \mu_3 / \partial n_3)_{n_2}} = - \frac{n_3 f'}{1 + n_3 f'}, \quad \text{or} \quad (11)$$

$$\Gamma = - \frac{n_3 \left[\frac{1}{kT} \frac{dP}{dn_i} - 1 \right]}{n_2 + n_3 \frac{1}{kT} \frac{dP}{dn_i}}. \quad (12)$$

This equation reveals that for $(1/kT) dP/dn_i > 1$ and $n_3 \gg n_2$

$$\Gamma \rightarrow -1 \quad (13)$$

a result one would expect. In particular for $n_2 \rightarrow 0$ one obtains

$$\Gamma^0 = - \left(\frac{\frac{1}{kT} \frac{dP}{dn_i} - 1}{\frac{1}{kT} \frac{dP}{dn_i}} \right)_{n_i=n_3}. \quad (14)$$

With eqn (9) it follows that

$$\Gamma^0 = -2n_3 B_2. \quad (15)$$

Identical equations are obtained when one uses a statistical approach (see appendix 1).

Let us now make use of eqns (9 and 14) in two simple cases: hard spheres and polymer molecules.

3.2. Hard spheres

For the compressibility we use the accurate, but not exact equation of Carnahan and Starling.²¹

$$\frac{dP}{kT dn} = 1 + 8\phi \frac{[1 - \frac{1}{4}\phi]}{(1 - \phi)^4}. \quad (16)$$

Here n is either n_2 or n_3 and ϕ is the volume fraction of the spheres

$$\phi = (1/6)\pi\sigma^3 n \quad (17)$$

where σ is the sphere diameter.

The second virial coefficient of spheres 2 among (identical) spheres 3 and the adsorption of spheres 2 on an (identical) sphere 2 is given in Figs. 4 and 5.

One observes that $B_2(\phi_3)$ levels off at increasing ϕ_3 and is reduced to 30% of its value at $\phi_3 = 0$ when $\phi_3 \approx 0.4$.

Also the (negative) adsorption is asymptotic to the value -1 , and is about -0.95 for $\phi_3 \approx 0.4$.

3.3. Polymer molecules

For our illustrative purposes we use the (approximate) Flory-Huggins theory²² (although one could use experimental values) for the osmotic pressure (against solvent, 1).

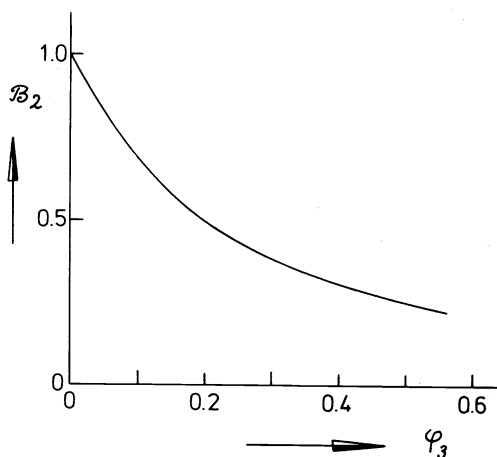


Fig. 4. Reduced second virial coefficient $\beta_2 = B_2 / ((2/3)\pi\sigma^3)$ of hard spheres, 2, in the presence of identical hard spheres, 3, as a function of the volume fraction, ϕ_3 , of the hard spheres, 3. With $\phi_3 = (1/6)\pi\sigma_3^3 n_3$, where $\sigma_3 =$ hard sphere diameter and $n_3 =$ number density of 3.

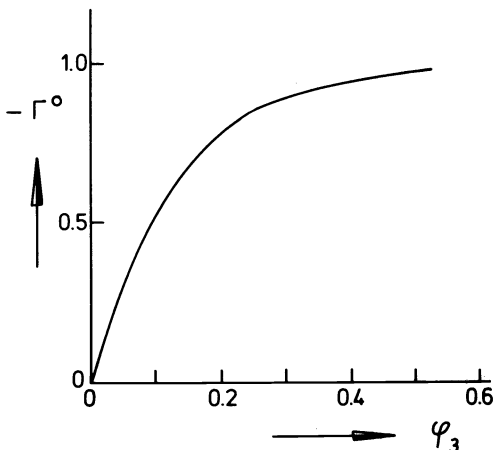


Fig. 5. Adsorption, Γ^0 , of hard spheres, 3, by an identical hard sphere, 2, as a function of the volume fraction, ϕ_3 , of the hard spheres, 3.

$$\frac{\omega_1 P}{kT} = -[\ln(1-v) + \left(1 - \frac{1}{m}\right)v + \chi_{12}v^2] \quad (18)$$

where ω_1 is the volume of a solvent molecule, m is the number of segments in the chains; v the volume fraction of polymer, and χ_{12} the solvent-polymer interaction parameter, which is taken to be constant here.

Analogously as before one obtains:

$$\frac{2B_2(v_3)}{m^2\omega_1} = \frac{\Psi_3 + 1 - 2\chi_{12}}{1 + mv_3[\Psi_3 + 1 - 2\chi_{12}]} \quad (19)$$

and

$$\Gamma^0 = \left(\frac{\partial v_3}{\partial v_2}\right)_{\mu_3} = -\frac{[\Psi_3 + 1 - 2\chi_{12}]mv_3}{1 + mv_3[\Psi_3 + 1 - 2\chi_{12}]} \quad (20)$$

where $\Psi_3 = v_3(1-v_3)^{-1}$. Calculated results are given in the Figs. 6 and 7 for $m = 2000$ and $\chi_{12} = 0.45$ (moderate solvent).

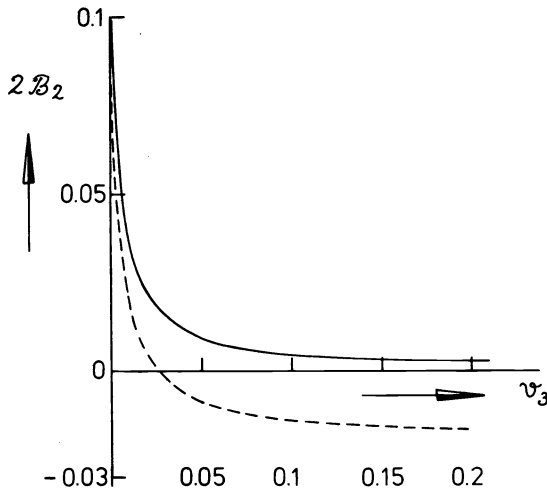


Fig. 6. $2B_2 = 2B_2/(m^2\omega_1)$ of polymer molecules, 2, in the presence of identical polymer molecules, 3, as a function of the volume fraction, v_3 , of polymer 3 (—). Also in the presence of different polymer molecules, 3, with $\gamma_{22} = \gamma_{33} = 0.10$ and $\gamma_{23} = 0.11$ (-----) (see section 5). $v_3 = \omega_3 n_3$, where ω_3 is the volume of a polymer molecule, 3, and n_3 the number density.

It is clear that the damping of the effective interactions takes place here at much smaller concentrations than for hard spheres. It is apparently the concentration range where the individual polymer molecules begin to penetrate each other.

According to eqn (1) it is an integral of $V(r)$ that decreases. What does this mean for $V(r)$ itself? For hard spheres, $V(r)$ is very simple for $n_3 \rightarrow 0$:

$$\begin{aligned} V(r) &= +\infty & \text{for } 0 < r < \sigma \\ V(r) &= 0 & \text{for } r \geq \sigma. \end{aligned} \quad (21)$$

Because $V(r)$ in the interval $0 < r < \sigma$ does not change upon adding other spheres, $V(r)$ must become sufficiently negative in the interval $r \geq \sigma$ to make B_2 smaller. (It turns out, in fact, that $V(r)$ and $g(r)$ become oscillating functions.)

For polymer molecules $V(r)$ is probably a monotonously decreasing function (if $\chi_{12} < 0.5$) for the whole

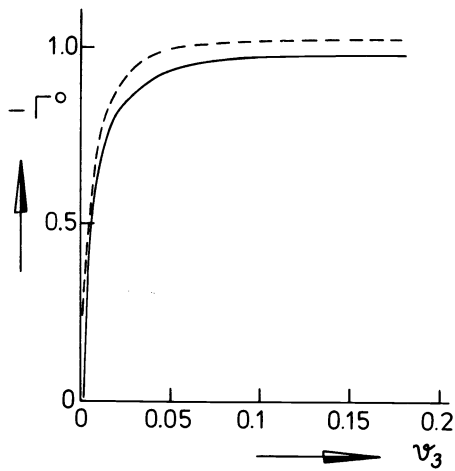


Fig. 7. Adsorption, Γ^0 , of polymer molecules, 3, on an identical polymer molecule, 2, as a function of the volume fraction, v_3 , of polymer 3 (—). Also in the presence of different polymer molecules, 3 (-----) (see Fig. 6).

interval $r = 0 \rightarrow \infty$. Addition of other polymer molecules probably also decreases $V(r)$ monotonously.

Although B_2 decreases upon adding particles of the same kind, its *sign* will not alter. One may anticipate, however, that, say, e.g. a positive B_2 may become negative when the added particles are *different*. To understand when this may occur we investigated more closely how $V(r)$ and $B_2(\phi_3)$ change due to "volume restriction" and "osmotic" effects. We will consider a simple model of volume restriction, i.e. the interaction between hard, spherical particles.

4. VOLUME RESTRICTION EFFECTS

4.1. Interactions in mixtures of hard spherical particles

Consider the effective interaction of a pair of spheres of diameter σ_2 in a dilute suspension of spheres of diameter σ_3 . The pair potential of two hard spheres (i, j) is given by

$$U_{ij}(r) = \infty \quad \text{for } r < \bar{\sigma} \quad (22)$$

$$U_{ij}(r) = 0 \quad \text{for } r \geq \bar{\sigma}$$

$$\bar{\sigma} = \frac{1}{2}(\sigma_2 + \sigma_3). \quad (23)$$

At $n_2, n_3 \rightarrow 0$ the potential of mean force, $V(r)$, between particles, 2, is equal to $U_{22}(r)$. How will $V(r)$ change when n_3 is finite (and $n_2 = 0$)? This can be solved in a simple way if n_3 is small. In Fig. 8 it is shown how a particle 3 can only partially penetrate the space between the pair.

This implies that the thermal impact forces on the pair from the "outside" are only partially compensated by those from the "inside".

The pair of particles 2 feels an effective force, $K(r)$, driving them together. This force is simple to calculate if n_3 is so small that seldom more than one particle, 3, interacts with the pair. In that case $K(r)$ is proportional to $n_3 kT$. A simple calculation shows that

$$K(r) = -\pi\bar{\sigma}^2[1 - \frac{1}{4}(r^2/\bar{\sigma}^2)]; \quad \sigma_2 \leq r \leq 2\bar{\sigma}. \quad (24)$$

The potential of average force is

$$\begin{aligned} V(r) &= \int_r^{2\sigma_2} K dr = -\frac{4}{3}\pi\bar{\sigma}^3 \left[1 - \frac{3}{4}\rho + \frac{1}{16}\rho^3\right] n_3 kT \\ \rho &= r/\bar{\sigma}; \quad \sigma_2/\bar{\sigma} \leq \rho \leq 2. \end{aligned} \quad (25)$$

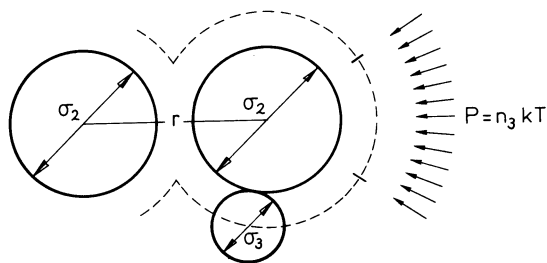


Fig. 8. Interaction of hard spheres, 3, with a pair of hard spheres, 2. Excluding surface (-----). The arrows indicate the *non-compensated* pressure exerted by the spheres 3 on a sphere, 2. Its component along the horizontal axis, integrated over the indicated surface area (l-----) gives the effective force $K(r)$.

One observes that $V(r)$ is negative in this interval, having a minimum value, $-\frac{5}{12}\pi\bar{\sigma}^3 n_3 kT$, at $r = \bar{\sigma}$ and zero at $r = 2\bar{\sigma}$. [$V(r) = 0$ for $r \geq 2\bar{\sigma}$ in this approximation and ∞ for $r < \bar{\sigma}$.]

Equation (25) can be rewritten as

$$V(r)/kT = -\left(1 + \frac{\sigma_2^3}{\sigma_3^3}\right) \phi_3 \left[1 - \frac{3}{4}\rho + \frac{1}{16}\rho^3\right] \quad (26)$$

where $\phi_3 = (1/6)\pi\sigma_3^3 n_3$ is the volume fraction of 3.

The second virial coefficient of particles of kind 2 follows by substituting eqn (26) into eqn (1)

$$B_2(\phi_3) = \frac{2}{3}\pi\sigma_2^3 \left[1 - \frac{3}{8}\left(1 + \frac{\sigma_3^3}{\sigma_2^3}\right) I(\alpha; \sigma_3/\sigma_2)\right] \quad (27)$$

$$I(\alpha; \sigma_3/\sigma_2) = \int_{\rho=\sigma_2/\bar{\sigma}}^{\rho=2} \left[\exp\left\{\alpha\left(1 - \frac{3}{4}\rho + \frac{1}{16}\rho^3\right)\right\} - 1\right] \rho^2 d\rho \quad (28)$$

$$\alpha = \left(1 + \frac{\sigma_2^3}{\sigma_3^3}\right) \phi_3. \quad (29)$$

Integral, I, must be calculated numerically except for $\alpha \rightarrow 0$, when it becomes

$$I = \frac{1}{3}\alpha \left[1 - s^3 \left(1 - \frac{9}{16}s + \frac{s^3}{32}\right)\right] \quad (30)$$

$$s = \sigma_2/\bar{\sigma}. \quad (31)$$

For example for $\sigma_3 = \sigma_2$, the eqns (27, 30) give

$$B_2(\phi_3) = \frac{2}{3}\pi\sigma_2^3 \left[1 - \frac{17}{4}\phi_3\right] \quad (32)$$

which is in accordance to the eqns (9, 16).

These equations are valid if n_3 is sufficiently small. At larger n_3 the effect of "crowding" of spheres 3 around the pair has to be taken into account.

A good approximation is provided by the "scaled particle" theory²³ and the Percus-Yeovick equation.²⁴

We will not pursue this because Lebowitz and Rowlinson²⁴ have shown that liquid-liquid phase separations are improbable in hard sphere mixtures.

Our simple treatment shows, however, the origin of the effective attraction forces in these systems.

In the next section we will consider how similar volume

restriction effects can play a role in some types of polymer colloid mixtures.

4.2. Mixtures of hard spheres and polymer molecules

For the interaction of a polymer molecule and a hard sphere one expects an effective repulsion, partly because a polymer molecule in proximity to the sphere surface has to adopt less probable conformations, which decreases the entropy, and also because of increased local segment densities (volume restriction and osmotic effects). (We assume, of course, that no adsorption of the polymer takes place.) In a θ solvent the "osmotic" effect vanishes.

When the sphere is larger than the polymer molecules, one could, crudely, assign to the sphere-polymer molecule interaction a hard sphere repulsion starting at $r < \sigma_{23}$. We expect a similar interaction between a polymer molecule and a pair of spheres.

The volume restriction effect has been worked out by Richmond and Lal for a random flight chain between two parallel plates (see Appendix 3 and Ref. 40). The pressure exerted by one polymer molecule confined between two plates is much smaller than kT when $(2r_g)^2/h^2 \ll 1$, and much larger than kT when $(2r_g)^2/h^2 \gg 1$, where r_g is the radius of gyration of the chain and h the distance between the plates. So one would expect that σ_{23} should be assigned a value $\frac{1}{2}\sigma_{22}$ plus a number of the order of r_g .

Also two polymer molecules may exert a repulsion on each other (when $\chi_{12} < 0.5$) due to the "osmotic" effect, to which one, crudely, could assign a hard sphere interaction at $r < \sigma_{33}$.

Usually, $\sigma_{23} > \frac{1}{2}(\sigma_{22} + \sigma_{33})$, where $\sigma_{22} = \sigma_2$, the sphere diameter. In this way one obtains a model system, known as the "non-additive" hard sphere model in the theory of liquids, with the pair potentials:

$$\begin{aligned} U_{22} &= \infty & r < \sigma_{22} \\ U_{22} &= 0 & r \geq \sigma_{22} \\ U_{33} &= \infty & r < \sigma_{33} \\ U_{33} &= 0 & r \geq \sigma_{33} \\ U_{23} &= \infty & r < \sigma_{23} \\ U_{23} &= 0 & r \geq \sigma_{23}. \end{aligned} \quad (33)$$

Even for this system, $V(r)$ is not simple to formulate. Let us consider therefore the special case when $\sigma_{33} = 0$. This would resemble a polymer at the θ -point.

(a) *Mixtures with $\sigma_{33} = 0$.* It will be clear that the equations of section 4.1. apply, *not* now restricted to very small n_3 .

This opens the possibility for B_2 to become *negative* if n_3 is large enough. Some calculated results are shown in Fig. 9. One observes, e.g. that for $\sigma_3/\sigma_2 = 2$ to $1/4$, $B_2 = 0$ at $\phi_3 \approx 0.1-0.3$ and $B_2/(\frac{2}{3}\pi\sigma_2^3) = -10$ at $\phi_3 \approx 0.8-1.0$. The relatively small variation in these numbers is caused by the fact that for the larger values of σ_3/σ_2 , the width of the potential well increases but its depth decreases and vice versa.

The absolute values of ϕ_3 suggest that 10-100% of the volume of the solution must be occupied by polymer clouds in order to have a sufficiently negative B_2 to give phase separation.

(b) *Mixtures with $\sigma_{22} = \sigma_{33}$ and $\sigma_{23} = 1.2\sigma_{22}$.* A negative value for B_2 is not a guarantee that phase separation will occur at higher values of n_2 . It is therefore of interest that Melnyk and Sawford²⁵ investigated the case of $\sigma_{22} = \sigma_{33}$ and $\sigma_{23} = 1.2\sigma_{22}$ in great detail. From computer simulation

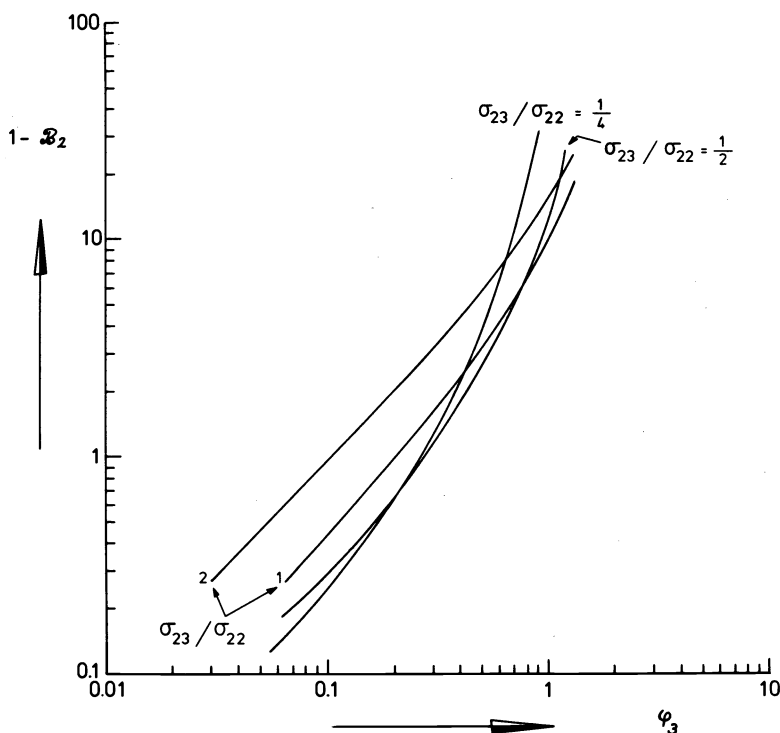


Fig. 9. Contribution, $1 - \beta_2$, to the reduced second virial coefficient, $\beta_2 = B_2/((2/3)\pi\sigma_{22}^3)$, caused by component 3, as a function of the volume fraction of component 3, for several ratios σ_{23}/σ_{22} . ($\sigma_{22} = \sigma_2$; $\sigma_{33} = 0$; $\sigma_{23} > 0$).

and from perturbation theory they found that fluid–fluid phase separation takes place with a critical point at $n_2 = n_3$ and $(n_2 + n_3)(\pi/6)\sigma_{22}^3 = 0.221$, i.e. at a total volume fraction of 22%.

These theoretical considerations suggest indeed that destabilization because of “volume restriction” may occur. The absolute values of ϕ_3 indicate that relevant concentrations for the higher molecular weight polymers would be a few percent or less.

We will now turn our attention to the “osmotic effect”.

5. “OSMOTIC EFFECT”

We will first look at the simplest case, i.e. a mixture of polymer molecules (both of type A/B in solvent). Experiments on such mixtures will be reported in section 7. section 7.

5.1. Mixtures of polymer molecules

We use the theory of Flory and Huggins^{22,26,27} because of its simplicity, despite its known shortcomings. For the free energy of mixing per unit volume, g , of a ternary mixture of polymer 2, polymer 3 in solvent 1, one has

$$g/kT = \sum_1^3 n_i \ln v_i + \beta/\omega_1. \quad (34)$$

Here $v_i = n_i\omega_i$ is the volume fraction of component i occupying a (constant) volume, ω_i , per molecule. $v_1 + v_2 + v_3 = 1$. Furthermore, β is a free energy excess function depending on v_2 and v_3 at constant temperature, T . Because eqn (34) is used in its differentiated forms, it is convenient to formulate the interaction parameters that occur in β by means of the derivatives, $g_{ij} = \partial^2 g / \partial v_i \partial v_j$. We write, ($i = 2, 3$)

$$g_{ii} = \frac{kT}{\omega_1} \left(\frac{1}{m_i v_i} + \frac{1 - v_1}{v_1} + \gamma_{ii} \right); \quad g_{ij} = \frac{kT}{\omega_1} \left(\frac{1 - v_1}{v_1} + \gamma_{ij} \right) \quad (35)$$

where the γ_{ij} 's are taken constant; $m_i = \omega_i/\omega_1$.

Expressed in the χ -parameter notation, $\gamma_{ii} = 1 - 2\chi_{1i}$, $\gamma_{23} = 1 + \chi_{23} - \chi_{12} - \chi_{13}$. Using the equations of section 3.1 one obtains (see Appendix 2) the second virial coefficient of polymer 2,

$$\frac{2B_2(v_3)}{m_2^2 \omega_1} = \frac{\gamma_{22} + \Psi_3}{1 + m_3 v_3 (\gamma_{33} + \Psi_3)} - \frac{m_3 v_3 [\gamma_-^2 + \gamma_{23}^2 - \gamma_+^2 + 2\Psi_3(\gamma_{23} - \gamma_+)]}{1 + m_3 v_3 (\gamma_{33} + \Psi_3)} \quad (36)$$

and similarly for the “adsorption” of 3 on 2 at $\phi_2 = 0$,

$$\Gamma^0 = (\partial v_3 / \partial v_2)_{\mu_3} = - \frac{m_3 v_3 (\gamma_{23} + \Psi_3)}{1 + m_3 v_3 (\gamma_{33} + \Psi_3)} \quad (37)$$

where $\Psi_i = v_i(1 - v_i)^{-1}$; $\gamma_+ = \frac{1}{2}(\gamma_{22} + \gamma_{33})$; $\gamma_- = \frac{1}{2}(\gamma_{22} - \gamma_{33})$.

To unravel eqn (36) let us look at some limiting cases.

(a) when polymer 3 is absent,

$$\frac{2B_2}{m_2^2 \omega_1} = \gamma_{22} = 1 - 2\chi_{12} \quad (38)$$

which is the familiar result.

(b) when the polymers 2 and 3 are physically identical,

$$\frac{2B_2(v_3)}{m_2^2 \omega_1} = \frac{\gamma_{22} + \Psi_3}{1 + m_2 v_3 (\gamma_{22} + \Psi_3)} \quad (39)$$

in accordance with eqn (19).

(c) the full eqn (36) shows the same kind of damping effect on B_2 as the eqns (19, 39) do in the denominator. It also shows that B_2 may become negative, if the term between the brackets is positive. This is so when $\gamma_{23} > \gamma_+$, which is equivalent with the condition that $\chi_{23} > 0$, which seems to be the rule in dilute solutions.

For illustrative purposes we have drawn curves of B_2 and Γ^0 in Figs. 6 and 7 for $\gamma_{22} = \gamma_{33} = 0.10$; $\gamma_{23} = 0.11$ and $m_2 = m_3 = 2000$.

The physical picture of the interactions can be described as follows. In a neutral to good solvent, polymer molecules resist overlap with other polymer molecules, because the segments exert an effective repulsion on each other, either explained as separate entropy and energy effects or as an overall effect of an excluded volume of the segments on the chain configuration. This is clearly shown by the *negative* value of Γ . Thus if one enforces (by any device, e.g. an osmotic cell, see section 3) an increase in the segment density of component 2 in a certain region of the solution, V , segments of component 3 will diffuse out of V , thus relaxing the increase in segment density and hence the applied stress.

This explains the damping effect on B_2 and $V(r)$. The relaxation is less effective for small kinetic units (low m_3) and for small v_3 . The effects are enhanced when the effective repulsion between unlike segments is larger than the average repulsion between like segments ($\gamma_{23} > \gamma_+$).

The Flory-Huggins equation is rather poor for calculating a second virial coefficient because it assumes a uniform dispersion of segments which does not occur at low v_2 .

In the better theory of Flory and Krigbaum^{22,28} (for two-component solutions) the Flory-Huggins equation is applied *locally* to the overlap region between two interacting polymer molecules. In this way they obtained a B_2 that contains the parameter $\gamma_{22} = 1 - \chi_{12}$ in eqn (38), multiplied by a coil size factor which slowly decreases with increasing coil size. In a better theory eqn (36) should also be supplemented with several such factors reflecting the coil sizes of 2 and 3. When, however, v_3 is so large that the intermingling of the segments of 2 and 3 is more complete, a *single* factor reflecting the coil size of 2 alone should be sufficient to supplement eqn (36).

5.2. Polymer colloids (A-E) with added polymer (A/B)

Also in this case the "osmotic" effect of overlapping clouds of segments, attached to the particle surfaces, is characterized (for a low molecular weight solvent) by the factor $\gamma_{22} = 1 - 2\chi_{12}$ multiplied by a factor depending on the extension and shape of the overlapping segment clouds, as a function of the interparticle distance.¹⁹ So, in principle, the same mechanism will operate as described in section 5.1., i.e. expulsion of (segments of) polymer 3 from the overlap region and a decrease of the repelling force between the particles. When the intermingling of the segments 2 and 3 is good one could, as a first approximation, replace the factor γ_{22} by those found in either (39) or (36).

6. DESTABILIZATION OF POLYMER COLLOIDS BY ADDED POLYMER

Two mechanisms were proposed in the previous sections that predict a destabilizing action of polymer added to a polymer colloid: a "volume restriction"—and an "osmotic" effect.

Both will occur simultaneously and it is difficult at this stage to give a quantitative account of their relative importance. (One must also consider that in itself the

decomposition of the total interaction into two superimposable effects is a simplification, that is only justified when the segment-segment interactions are small.²⁹ We disagree with Evans and Napper³⁰ that the "osmotic" effect already encompasses the "volume restriction" effect. This would mean that at the θ -point a chain would not resist compression which is clearly not true.)

Both effects increase with increasing molecular weight and concentration of the added polymer. Quite small concentrations (order of per cents) should be effective with high molecular weight polymers. It is not feasible here to make a general scheme of predictions. In order to make judgements the following parameters are of importance. The size of the polymer molecules with respect to the particle core size and the thickness of the protecting chains. The surface density of the protecting chains. The solvent quality with respect to added polymer, attached chains and particle surface.

Some of these factors are also of crucial importance for the *adsorption* of polymer which we assumed to be absent.

Finally we have to remember that other forces like van der Waals attraction and electric double layer repulsion may play an important role, especially in aqueous solutions.

6.1. Experimental evidence

(a) *Creaming rate of latex.* We have not yet made a systematic literature search, but we found an older paper of Vester³¹ on the increase of the creaming rate of Hevea latex upon the addition of "strongly" hydrophilic colloids (several natural plant polymers, as pectin) and also Na-poly(acrylate).

He found an increased creaming rate upon adding 0.2–1% polymer to a 40% latex suspension. The larger sized polymers (larger $[\eta]$) were most effective. He also obtained separated phases with a sharp boundary. At smaller latex concentrations clustering was observed and sometimes the formation of separated, rather viscous liquid droplets with a low interfacial tension. All these phenomena were *reversible*.

(b) *Flocculation of sterically stabilized latex.* Recently, Li-In-On, Vincent and Waite³² found that aqueous latex dispersions, sterically stabilized by poly(ethylene oxide) (PEO) chains did flocculate above a certain, critical concentration of added PEO. The critical concentrations decreased from 55 to 27% with increasing molecular weight of the PEO ($M_3 = 200-4000$), in accordance with our prediction. Possibly the damping effect of the added PEO alone suffices to decrease the steric repulsion effectively, so that the long range van der Waals forces between the latex particles will induce flocculation. Also the γ_{ij} 's between the segments could be somewhat different because of the small chain lengths. Osmotic measurements on high molecular weight PEO with low molecular weight PEO plus water as membrane-permeable-solvent could give more insight in these interactions. For the observed partial redispersion of the latex at still higher concentrations of added PEO we do not have a ready explanation.

(c) *Microemulsion with added polymer.* We did some preliminary experiments and mixed a clear 50% microemulsion of water in benzene (stabilized with oleic acid and hexanol) with a 2% solution of high molecular weight poly(styrene) ($M_3 \sim 2 \times 10^6$) in benzene (containing some hexanol) and obtained a turbid mixture that separated after a day into two clear (benzene containing) separated phases with a small interfacial tension. The smaller, upper phase

was rather viscous and contained apparently most of the poly(styrene).

7. LIGHT SCATTERING OF A MIXTURE OF POLYMER COLLOIDS

Consider a mixture of two polymeric colloids 2, 3, in a solvent, 1. From the multicomponent theory of light scattering³³ one obtains for the scattering of the mixture over that of the pure solvent

$$R_0 = (2\pi^2 n^2 / \lambda_0^4) (1 + \cos^2 \theta) kT \times \left[\left(\frac{\partial n}{\partial c_2} \right)^2 \left(\frac{\partial c_2}{\partial \mu_2} \right)_{\mu_3 \mu_1} + \left(\frac{\partial n}{\partial c_3} \right)^2 \left(\frac{\partial c_3}{\partial \mu_3} \right)_{\mu_2 \mu_1} + 2 \left(\frac{\partial n}{\partial c_2} \right) \left(\frac{\partial n}{\partial c_3} \right) \left(\frac{\partial c_2}{\partial \mu_3} \right)_{\mu_2 \mu_1} \right] \quad (40)$$

Here, R_0 is the relative scattering (Rayleigh ratio) of the solution over that of the solvent, n and λ_0 are the refractive index of the solution and the wavelength in vacuo of the light used; c_i is the concentration in mass per unit volume and μ_i is the chemical potential of component i . θ is the scattering angle. This equation only applies for $\theta \rightarrow 0$ and when multiple scattering is negligible. The last condition implies either that the refractive indices of the colloidal particles must be comparable with that of the solvent or that their dimensions are small with respect to the wavelength of the light used, which are rather severe restrictions. There are, however, a number of cases where this applies (e.g. polymer solutions; latex particles in oil).

Let us now consider the (important) special case where $\mu_3 = 0$, so that the light scattering of this component is masked. Then eqn (40) can be written as follows

$$(2\pi^2 n^2 / \lambda_0^4) (1 + \cos^2 \theta) \left(\frac{\partial n}{\partial c_2} \right)^2 c_2 / R_0 \approx \frac{1}{kT} \left(\frac{\partial P}{\partial c_2} \right)_{\mu_3 \mu_1} \left[1 + 2 \frac{\partial n / \partial c_3}{\partial n / \partial c_2} \left(\frac{\partial c_3}{\partial c_2} \right)_{\mu_3 \mu_1} \right]^{-1} \quad (41)$$

with $(\partial P / \partial c_2)_{\mu_3 \mu_1} = c_2 (\partial \mu_2 / \partial c_2)_{\mu_3 \mu_1}$.

Thus by choosing component 3 and λ_0 so that $\partial n / \partial c_3 = 0$, one may determine the otherwise inaccessible quantity, $(\partial P / \partial c_2)_{\mu_3 \mu_1}$ directly, and by choosing another λ_0 for which

dn/dc_3 is different from zero one may also, in principle, determine the "adsorption" $\partial c_3 / \partial c_2$ as well. We will this on a system containing poly(styrene)(PS,2) and poly(isobutylene)(PIB,3) in toluene. The dn/dc of PIB ≈ 0 .

7.1. Experiments

I will show some of our experimental work performed by Dr. van den Esker for his thesis.³⁴ Full details will be published elsewhere.³⁵ The following polymer pairs were used in toluene:

- (I) PS($M_w = 0.194 \times 10^6$) + PIB($M_w = 0.156 \times 10^6$)
- (II) PS($M_w = 0.526 \times 10^6$) + PIB($M_w = 0.670 \times 10^6$)
- (III) PS($M_w = 2.40 \times 10^6$) + PIB($M_w = 2.44 \times 10^6$).

The mixtures showed phase separations.

A binodal at 21°C is shown in Fig. 10 for pair II. Figure 11 shows a light scattering experiment (Zimm-plot) at $v_3 = 0.0100$ and $\lambda_0 = 436$ nm, where $dn/dc_3 \approx 0$.

The slope of the $\theta = 0$ line, which is proportional to the second virial coefficient of PS in PIB, is large and negative in accordance with the fact that the mixture shows phase separation at higher PS concentration (see Fig. 10) and as expected from our discussion in section 5.1.

At the point where the extrapolated line crosses the horizontal axis, the light scattering becomes very large (critical opalescence). At the corresponding c_2 , $(\partial P / \partial c_2)_{\mu_3 \mu_1}$ goes to zero. From similar Zimm-plots at other PIB-concentrations one thus may obtain a collection of v_2, v_3 -pairs where $(\partial P / \partial c_2)_{\mu_3 \mu_1} = 0$. They constitute the so-called spinodal curve, of which a few points are given in Fig. 10. In our notation of the free energy of mixing, eqn (34), the spinodal is given by

$$g_{22}g_{33} = g_{23}^2 \quad (42)$$

where $g_{ij} = \partial^2 g / \partial v_i \partial v_j$.

Using the eqns (35), this gives

$$\left(\gamma_{22} + \frac{v_2 + v_3}{v_1} + \frac{1}{m_2 v_2} \right) \left(\gamma_{33} + \frac{v_2 + v_3}{v_1} + \frac{1}{m_3 v_3} \right) = \left(\gamma_{23} + \frac{v_2 + v_3}{v_1} \right)^2 \quad (43)$$

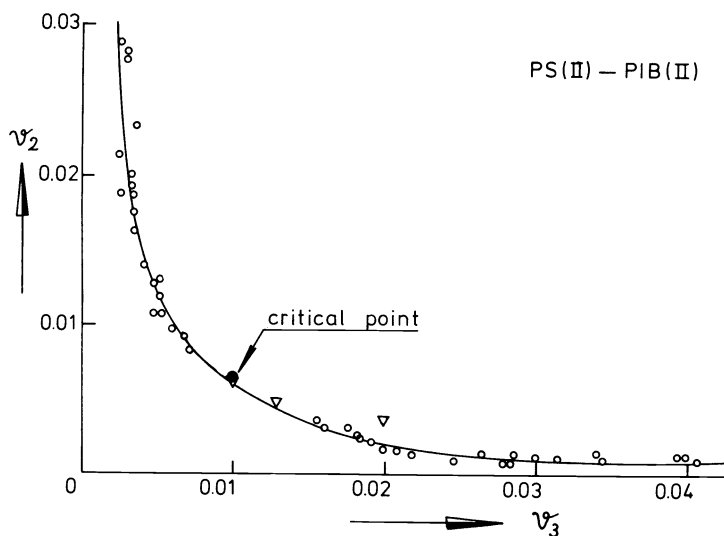


Fig. 10. Binodal (O) and spinodal (∇) points in the system PS(II)-PIB(II) - toluene. Critical point (●); $t = 21.0^\circ\text{C}$.

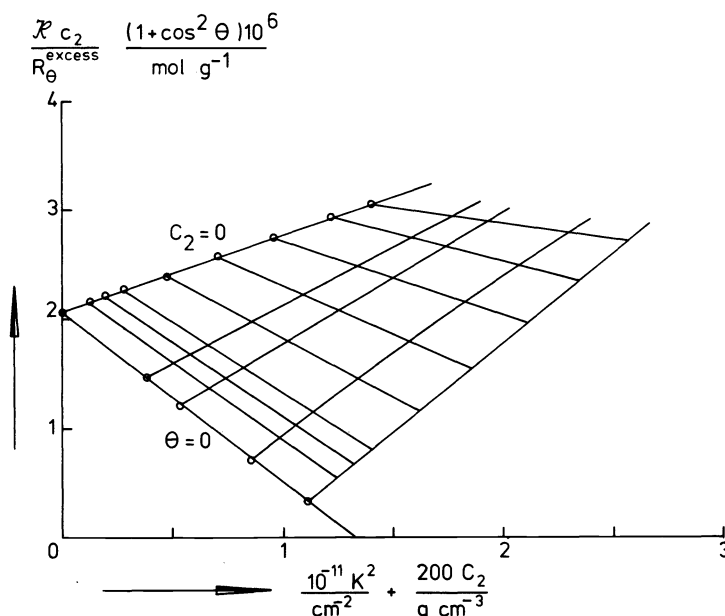


Fig. 11. Zimm-plot of PS(II) in PIB(II) + toluene; $v_3 = v(\text{PIB}) = 0.01$; $dn/dc_3 = 0$; $\lambda_0 = 436 \text{ nm}$; $K = 2\pi^2 n^2 (dn/dc_2)^2 / (\lambda_0^4 N_{AV})$. $R_\theta^{\text{excess}} = R_\theta(\text{comp. 1} + 2 + 3) - R_\theta(\text{comp. 1} + 3)$.

This makes it possible to obtain values for γ_{23} when the spinodal compositions are substituted and γ_{22} and γ_{33} are given. Results are shown in Table 1. An equation similar to (43) can be formulated for the *binodal* in which phase compositions must be substituted. It turns out, however, that this procedure is much less accurate. In this way the light scattering method is superior.

From Table 1 one observes that the values of γ_{23} , like those of γ_+ and γ_- , depend on the molecular weights which shows a deficiency in the Flory-Huggins formulation.

The second virial coefficients as a function of the PIB-concentration are plotted in Fig. 12. Values calculated from eqn (36) with the corresponding γ_{ij} 's at the critical

concentrations are also shown. One observes that the decrease of A_2 is indeed larger for the higher molecular weight pairs, and for larger v_3 , although the latter dependence is not quantitative. Comparison with the lower curve in Fig. 6 shows that we are in the range just below the horizontal axis. Kuhn, Cantow and Burchard³⁶ and Kuhn and Cantow³⁷ reported second virial coefficients of PS in benzene containing masked PMMA over a large concentration range. The shape of the A_2 vs v_3 curves is indeed similar as that of the lower one in Fig. 6.

They found that the v_3 -values at which $A_2 = 0$, $v_3(a_2 = 0)$, increase with M_3 , the molecular weight of PMMA, in accordance with eqn (36). The relation is not quantitative,

Table 1. Second virial coefficient, $A_2 = B_2 N_{AV} M_2^{-2}$, of PS in PIB + toluene, as a function of the volume fraction, v_3 , of PIB. v_2 (spin.) if the volume fraction of PS where the light scattering goes to infinity. γ_{23} is the parameter of the PS/PIB interactions. $\gamma_+ = \frac{1}{2}(\gamma_{22} + \gamma_{33})$; $\gamma_- = \frac{1}{2}(\gamma_{22} - \gamma_{33})$

System	$v_3 \times 10^2$	$-2A_2 \times 10^4$ ($\text{mol cm}^3 \text{ g}^{-2}$)	$v_2 \times 10^2$ (spin)	γ_{23}	γ_+	γ_-
	0	-9.80				
PS(I)	1.32	1.21	1.88	0.138		
	1.91	3.54	1.41	0.134		
+	2.43†		1.23†		0.101	0.033
	2.43	5.10	1.12	0.134		
PIB(I)	3.02	7.26	0.85	0.137		
	3.53	8.36	0.68	0.141		
PS(II)	0	-7.52				
	1.00†	3.14	0.62†	0.104	0.086	0.030
+	1.30	4.08	0.48	0.105		
PIB(II)	2.00	4.90	0.36	0.108		
PS(III)	0	-4.86				
	0.30	1.00	0.46	0.077		
	0.44†		0.24†		0.072	0.030
+	0.41	1.38	0.27	0.079		
	0.51	1.88	0.22	0.079		
PIB(III)	0.60	2.46	0.16	0.081		
	0.68	3.20	0.13	0.083		

†Critical concentrations.

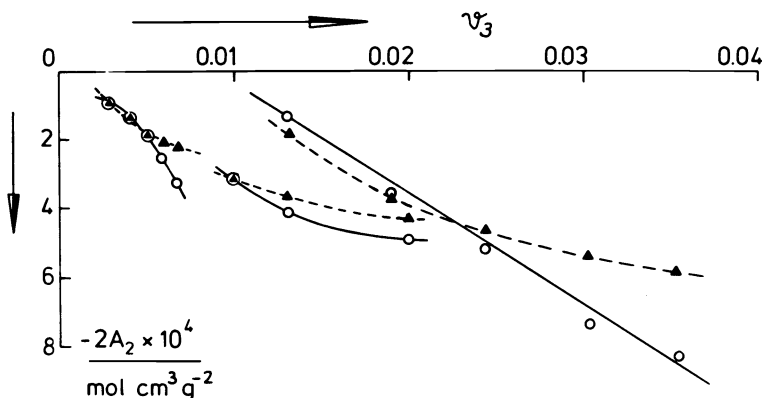


Fig. 12. Second virial coefficient, $A_2 = B_2 N_A v M_2^{-2}$, of PS in PIB + toluene. From left to right: system III, II, I. $V_3 = v(\text{PIB})$.

however. Equation (36) predicts that approximately: $v_3(A_2 = 0) \sim M_3^{-1}$, whereas they found $v_3(A_2 = 0) \sim M_3^{-0.72}$. They also observed that $v_3(A_2 = 0)$ is independent of M_2 , the molecular weight of PS, which is in accordance with eqn (36), but also with out expectation (see section 5.1) that an improved theory will give the same result if v_3 is large enough.

We also attempted to measure the adsorption of PIB on PS, $\Gamma = (\partial c_3 / \partial c_2)_{\mu_3, \mu_1}$, by performing light scattering experiments at $\lambda_0 = 546 \text{ nm}$ where $\partial n / \partial c_3$ is small but finite ($\approx +0.08 \text{ cm}^3/\text{g}$) (see eqn (41)).

We found rather large, negative adsorptions of $\Gamma \sim -2$ to -3 gram PIB per gram PS for all three pairs. Values calculated from eqn (37) are also negative but about 50% smaller in magnitude. This conclusion is based on the rather inaccurate value of $\partial n / \partial c_3$.

7.2. Concluding remarks

We have found that light scattering experiments can give very useful information on the osmotic compressibility of one polymer component at constant chemical potential of the other polymer component and in principle also about the adsorption of one component on the other if one of the components can be chosen in such a way that the light scattering is (nearly) masked.

This could also be applied on, say, (cross linked) latex particles in a non-polar liquid of nearly the same refractive index (to reduce secondary scattering) containing a (nearly) masked polymer component. We are planning such experiments in the near future, in order to test our theoretical predictions about the destabilizing effect of added polymer on the dispersed latex.

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APPENDIX 1

Second virial coefficient and radial distribution function

The second virial coefficient is given by the eqn (8)

$$B_2 = \frac{1}{2} \int_0^\infty [1 - e^{-V(r)/kT}] 4\pi r^2 dr. \quad (A1-1)$$

Here $V(r)$ is the potential of average force, i.e. the work that has to be done (isothermally) to bring two particles 2 (at $n_2 \rightarrow 0$ embedded in identical particles, 3, plus solvent, 1) from infinity to a distance of separation r (between their centers). $V(r)$ is closely connected with $g(r)$, the radial distribution function, as follows⁸

$$e^{-V(r)/kT} = g(r). \quad (A1-2)$$

Thus,

$$B_2 = -\frac{1}{2} \int_0^\infty [g(r) - 1] 4\pi r^2 dr. \quad (A1-3)$$

In our case where the properties of 2 and 3 are identical (except for a marking) there is only one $g(r)$, which depends on $n_i = n_2 + n_3$. The integral in eqn (A1-1) is connected with the isothermal compressibility of the whole system according to the theorem of Ornstein and Zernike³⁸ which states that

$$1 + n_i \int_0^\infty [g(r) - 1] 4\pi r^2 dr = kT \frac{dn_i}{dP}. \quad (A1-4)$$

Substituting this equation into eqn (A1-3) gives for $n_i = n_3$

$$B_2 = \frac{1}{2n_3} \left[1 - kT \frac{dn_3}{dP} \right] \quad (A1-5)$$

which is identical with eqn (9). A similar derivation follows for Γ . The average number density of particles, 3, around a fixed value for 2, is for $n_2 \rightarrow 0$

$$n_3 g(r) = n_3 e^{-V(r)/kT}. \quad (A1-6)$$

The integrated deviation of this number density from the average one, n_3 , is Γ^0 ,

$$\Gamma^0 = n_3 \int_0^\infty (e^{-V(r)/kT} - 1) 4\pi r^2 dr. \quad (A1-7)$$

Comparing this with eqns (A1-2, 4) gives

$$\Gamma^0 = kT \frac{dn_3}{dP} - 1 \quad (A1-8)$$

which is identical with eqn (14). A similar reasoning was used by Benoit *et al.*³⁹ to calculate B_2 of deuterated PS in PS.

APPENDIX 2

Osmotic compressibility in polymer mixtures

(a) We have to formulate the osmotic compressibility,

$$(\partial P / \partial n_2)_{\mu_1, \mu_3} = n_3 (\partial \mu_2 / \partial n_2)_{\mu_1, \mu_3} \quad (A2-1)$$

in terms of the free energy of mixing per unit volume, $g = G/V$, as given by the Flory-Huggins eqn (34) where $V = \omega_1 N_1 + \omega_2 N_2 + \omega_3 N_3$, with constant ω_i , for an incompressible system.

(b) Consider the process of adding $\omega_2 dN_2$ cm³ of comp. 2 and simultaneously subtracting $\omega_1 dN_1$ cm³ of comp. 1 (at constant N_3) so that V remains constant. The chemical potential for this process is:

$$\omega_2^{-1} (\partial G / \partial N_2)_{V, N_3} = (\Delta \mu_2 / \omega_2) - (\Delta \mu_1 / \omega_1) \quad (A2-2)$$

where $\Delta \mu_i$ is the excess chemical potential (of mixing) of

component i . Whereas the l.h.s. of (A2-2) is equal to $(\partial g / \partial \phi_2)_{\phi_3} = g_2$, we have for the chemical potential of the exchange process,

$$g_2 = (\Delta \mu_2 / \omega_2) - (\Delta \mu_1 / \omega_1). \quad (A2-3)$$

(c) Then one may write

$$(\partial \mu_2 / \partial n_2)_{\mu_1, \mu_3} = \omega_2 (\partial g_2 / \partial v_2)_{\mu_1, \mu_3} = \omega_2 (\partial g_2 / \partial v_2)_{g_3} \quad (A2-4)$$

where the condition: μ_1, μ_2 are constant, is replaced in the exchange process by: g_2 is constant. Further²⁰

$$(\partial g_2 / \partial v_2)_{g_3} = g_{22} - g_{23}^2 / g_{33} \quad (A2-5)$$

where $g_{ij} = (\partial (\partial g / \partial v_i)_{v_j} / \partial v_j)_{v_i} = \partial^2 g / \partial v_i \partial v_j$, $i, j = 2, 3$. Substituting the eqns (35) into (A2-5) leads then with eqn (8) to eqn (36).

APPENDIX 3

Polymer molecules between two flat plates

Richmond and Lal⁴⁰ calculated the free energy of a single polymer molecule with radius of gyration, r_g , confined between two parallel plates separated by a distance h , and the pressure exerted by this molecule on the plates. They give explicit equations for two limiting cases $(2r_g)^2/h^2 \ll 1$ and $(2r_g)^2/h^2 \gg 1$. The (Helmholtz) free energy, F , of N independent molecules can be written as follows

$$(F/kT) = N \ln(N/V) + Nf(h) \quad (A3-1)$$

where $V = h \cdot A$, A = area of the plates and

$$f(h) \approx 2\pi^{-1/2} (2r_g/h), \quad \text{for } (2r_g)^2 \ll h^2 \quad (A3-2)$$

and

$$f(h) \approx \ln(\pi^2/8) + \pi^2 (2r_g/h)^2, \quad \text{for } (2r_g)^2 \gg h^2. \quad (A3-3)$$

The pressure is given by

$$P/kT = -(\partial F/kT \partial V)_{N, A} = (N/V)(1 - h df/dh) \quad (A3-4)$$

which is positive for both formulations of f . In our case, however, we are interested in the pressure on the plates when the molecules are in equilibrium with a reservoir of molecules with chemical potential, μ^u . This can be found as follows,

(a) The chemical potential between the plates is

$$\mu = (\partial F / \partial N)_{N, A} = \{\ln(N/V) + f + 1\} kT \quad (A3-5)$$

and outside the plates ($f = 0$),

$$\mu^u = \{\ln n^u + 1\} kT \quad (A3-6)$$

where n^u is the number density outside the plates. At equilibrium $\mu = \mu^u$, thus

$$N/V = n^u e^{-f}. \quad (A3-7)$$

Then, from eqn (A3-4), we find the pressure from the molecules between the plates

$$P/kT = n^u e^{-f} (1 - h df/dh). \quad (A3-7)$$

From this we subtract the pressure, $P^u = n^u kT$, exerted on the outside,

$$(P - P^u)/kT = n^u [e^{-f} (1 - h df/dh) - 1]. \quad (A3-8)$$

For small f , eqn (A3-2), one finds

$$(P - P^u)/kT \approx -\frac{1}{2} n^u f^2. \quad (A3-9)$$

Observe, that this pressure (difference) is negative, which means

the plates feel an effective *attraction*, in accordance with the "volume restriction" effects found earlier. For large f , e^{-f} in eqn (A3-3) becomes very small so that

$$(P - P^*)/kT \rightarrow -n^*$$
(A3-10)

(b) A more formal route goes as follows. Calculate $(\partial P/\partial h)_{\mu, \lambda}$, from

$$(\partial P/\partial h)_{\mu} = (\partial P/\partial h)_N - (\partial P/\partial N)_h (\partial \mu/\partial h)_N (\partial \mu/\partial N)_h^{-1}$$
(A3-11)

all at constant A. From the eqns (A3-1) and (A3-4),

$$h(\partial P/kT\partial h)_{\mu, \lambda} = (N/V)[h^2(df/dh)^2 - 2h df/dh - h^2 d^2f/dh^2].$$
(A3-12)

The same equation follows upon differentiation of eqn (A3-8) after h .