

Steric Stabilisation and Flocculation by Polymers

Th. F. TADROS

*ICI Agrochemicals, Jealotts Hill Research Station,
Bracknell, Berks. RG12 6EY, U.K.*

(Received November 26, 1990)

ABSTRACT: The theories of steric stabilisation and the main parameters that control stability are briefly reviewed. This is followed by description of the methods that can be applied for studying steric interactions. Of these viscoelastic measurements offer an indirect, but simple method, for studying inter-particle interaction. The storage modulus (G') volume fraction (ϕ) results could be compared with the force-distance curves obtained from direct measurements. The effect of addition of free polymer to sterically stabilised dispersions, i.e. depletion flocculation, was investigated using rheological measurements. The latter was applied to calculate the energy of separation E_{sep} between the particles in a flocculated structure. E_{sep} was compared with the free energy of depletion G_{dep} that was calculated using Asakura and Oosawa as well as Fleer, Scheutjens and Vincent's theories.

KEY WORDS Sterically Stabilised Dispersion/Measurement of Steric Forces/Depletion Flocculation.

Natural and synthetic polymers are versatile materials for the control of stability/flocculation of dispersions. Polymers are used as stabilisers in many industrial applications of which we mention pharmaceuticals, agrochemicals, cosmetics, dyestuffs, paper coatings and ceramics. Of particular use is the use of polymers for stabilisation of concentrated dispersions, i.e. those with high volume fraction ϕ , in media with high electrolyte concentration and for stabilisation of non-aqueous dispersions. The general application of polymers (and nonionic surfactants) for stabilisation of dispersions is usually referred to as steric stabilisation.

The interaction between two particles containing an adsorbed polymer layer depends on the adsorption and conformation of such molecules at the solid/liquid interface. This is determined by the total amount of polymer adsorbed Γ , the number of segments in close contact with the surface, i.e. the trains, and the extension of the polymer layer at the solid/liquid interface. The extension of the polymer is usually described by the segment density distribution $\rho(z)$ or the adsorbed layer thickness δ . The key factors in designing polymeric stabilisers is to understand the interaction with the surface, the interaction with the solvent and the conformation of the polymer chain at the solid/liquid interface. This is beyond the scope of the present review. We will assume that the reader is familiar with such concepts and start with a summary of the theories of steric stabilisation and the parameters that

control the stability of dispersions. This is followed by a brief description of the methods that can be applied for studying steric interaction. Particular attention will be paid to the viscoelastic measurements that offer an indirect method for studying interaction between adsorbed or grafted polymers in particulate dispersions.

The third part of this overview will deal with the effect of addition of free (non-adsorbing) polymer to sterically stabilised dispersions, i.e. depletion flocculation. The latter has been investigated in concentrated dispersions using rheological techniques. As a model of sterically stabilised dispersion, polystyrene latex containing grafted poly(ethylene oxide) was used, to which poly(ethylene oxide) (PEO) or hydroxy ethyl cellulose (HEC) with various molecular weights were added. A comparison between the energy of separation between the particles in a flocculated structure, E_{sep} , calculated from rheology and the free energy of interaction due to depletion, G_{dep} , will be made.

THEORIES OF STERIC STABILIZATION AND CONTROL OF DISPERSION STABILITY

Theories of steric stabilisation

For simplicity, we will consider two parallel plate macroscopic bodies with adsorbed polymer layers of thickness δ . Let us now consider the interaction free energy ΔG_s , as a function of distance of separation between the macroscopic bodies h . There are basically two main approaches to treat the interaction in such a system. The first and more chemical approach^{1,2} considers ΔG_s to consist of two (supposedly) additive contributions, namely ΔG_m ("mixing" or "osmotic" term) and ΔG_{el} ("elastic", entropic or "volume restriction" contribution). The second and more modern approach considers ΔG_s as a configurational term, treating the interaction between segments as an excluded volume effect³⁻⁷. Scheutijens and Fleer⁸ introduced a somewhat similar approach for evaluating ΔG_s . Below a summary of the classical and more modern approaches will be given.

In the classical approach ΔG_s is arbitrary taken to be the sum of ΔG_m and ΔG_{el} , i.e.,

$$\Delta G_s = \Delta G_m + \Delta G_{el} \quad (1)$$

where ΔG_m is the free energy of mixing of polymer segments and solvent molecules in the overlap region calculated from the Flory-Krigbaum theory^{9,10}, assuming the segment density distribution function to be given by random flight statistics. ΔG_{el} is a configurational entropy term resulting from the reduction in the number of possible configurations of the chains (again calculated assuming random flight statistics) by the opposing surface.

The total free energy of interaction ΔG_s obtained by Hesselink *et al*¹ for two parallel flat plates coated by steric layers is given by the expression,

$$\Delta G_s = 2 (2 \pi / 9)^{3/2} \nu^2 kT (\alpha^2 - 1) \langle r^2 \rangle M(d) + 2 \nu kT V(d) \quad (2)$$

The first term is the mixing free energy and the second term is the elastic free energy. ν is the number of chains adsorbed per unit area, α is the expansion factor whereas $\langle r^2 \rangle^{1/2}$ is the room mean square (rms) end to end distance of the chain in free solution.

The distance dependent mixing and elastic functions $M(d)$ and $V(d)$

could be evaluated from the segment density distribution function. Both numerical and analytical solutions for $M(d)$ and $V(d)$ were given by Hesselink *et al.*¹. Typical potential energy curves calculated by these authors for the steric interaction between parallel plates in a good solvent for the polymer ($\alpha = 1.2$) are given in Figure 1. These

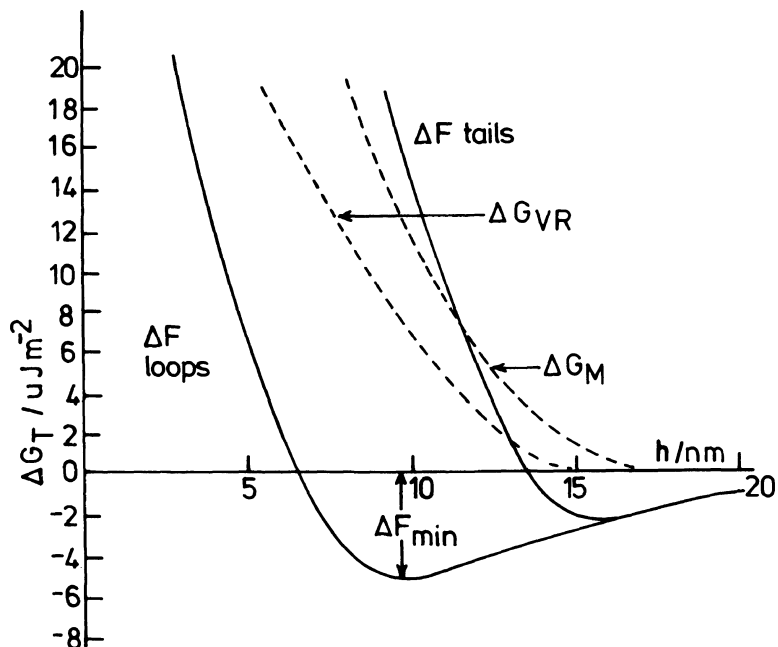


Figure 1. Potential energy-distance curves for two flat plates sterically stabilised by tail and loops according to Hesselink *et al.*

include the van der Waals attraction between the opposing plates.

The energy-distance curve shown in Figure 1 contains only one minimum G_{\min} whose depth depends on the extension of the polymer layer. With most sterically stabilised dispersions, the adsorbed layer extends sufficiently outwards (i.e. thick adsorbed layers are produced of the order of 10 nm or more) and hence G_{\min} is small compared to the thermal energy. It should be mentioned that steric repulsion at the larger distances of separation (compared to 2δ) arises from the mixing interaction, whereas the classic term becomes important on closer approach.

Hesselink *et al.*¹ concluded that the main parameter that determines the total free energy of steric interaction are: (i) the number or mass density of the stabilising chains; (ii) the molecular weight of the stabilising moieties; (iii) the modes of attachment of the polymer chains to the particle surface; (iv) the polymer solvent interaction, i.e. the Flory-Huggins interaction parameter χ ; (v) the particle geometry, and (vi) the van der Waals attraction between the particles.

Scheutijens and Fleer¹ considered the interaction of polymer layers between parallel plates using their theory of polymer adsorption^{11,12}. They restricted their analysis to the case of a homopolymer between two plates 1 and 2 which is in equilibrium with a constant solution concentration at any point during the approach of

the surfaces. A quasi-crystalline lattice model, with layers $i = 1, 2, 3, \dots, M$, was used to calculate the conformation of the polymer chains between the plates. The configurational probabilities and free energy of mixing were calculated with the assumption of random mixing within each layer, using the Bragg-Williams or mean field approximation. Any conformation is described as a step-weighted random walk in a lattice. Each step was considered to have three main contributions: an adsorption energy, entropy of mixing of solvent molecules displaced by the segments and the segment-solvent contact.

Control of dispersion stability

Four main criteria are required for effective steric stabilisation: (i) full coverage of the particles by adsorbed polymer layers. Any bare patches may result in flocculation as a result of van der Waals attraction or bridging, (ii) strong adsorption (anchoring) of the chains. This requires high affinity to the surface and low affinity to the medium. However, this does not provide an effect stabilisation which requires good solvency of the chains by the medium, i.e. $\chi < 0.5$. To provide this two opposing effects, i.e. strong anchoring and good solvency, block and graft copolymers must be used. These polymers consist of two main portions, namely A and B, where A provides the stabilisation, whereas B provides strong adsorption and anchoring. In this respect A is chosen to be strongly solvated by the medium with little affinity to the particle surface; B, on the other hand is chosen to have a strong affinity to the surface and very low affinity to the solvent (i.e. insoluble in the medium), (iii) the stabilising chains should provide sufficient extension from the surface, i.e. thick layers, in order to screen the van der Waals attraction. This, as discussed above, will give a G_{\min} that is small compared to the thermal energy (kT); (v) the stabilising chains should remain in good solvent conditions, i.e. $\chi < 0.5$ under all practical conditions, i.e. during temperature variations or addition of other ingredients to the dispersion.

EXPERIMENTAL METHODS FOR INVESTIGATION OF STERIC INTERACTIONS

For the investigation of steric interactions between adsorbed or grafted polymer layer one needs to measure the force as a function of separation between two surfaces containing these polymer layers. Two general procedures may be applied, namely those involving macroscopic bodies and these using dispersions of spherical particles. In the first case, the interaction of polymer chains attached to macroscopic objects that undergo highly controlled close-approach, may be measured. For this purpose cross cylinders, cross fibres, spherical caps and thin films may be used. In the second case, a dispersion of sterically stabilised particles may be compressed in two or three dimensions such that the polymer layers undergo some overlap and/or compression. A less commonly used procedure is to measure the rheological characteristics of a dispersion as a function of its volume fraction ϕ . When the latter reaches values corresponding to close-packing, strong interaction occurs and this is reflected in the flow characteristic (rheology) of the dispersion. This technique gives an indirect method of measuring steric interaction and still awaits a rigorous theory to convert some of the rheological parameters, such as the elastic modulus, to interparticle interaction. However, the rheological method is attractive in view of the simplicity by

which the measurements can be made. Below a brief account of the various methods, that may be applied for measuring steric interaction, is given.

Methods based on measurement of the force-distance between macroscopic bodies

Three main methods can be used for studying steric interaction between macroscopic bodies. The first and perhaps most developed is to use crossed mica cylinders to which polymer chains are adsorbed or grafted. The advantages of using mica is due to its molecularly smooth surface. This method was successfully applied by Israelachvili *et al*¹³ and by Klein^{14,15}. Israelachvili *et al* (13) measured the force of repulsion between crossed mica cylinders coated by poly(ethylene oxide) (PEO) in 0.04 mol dm⁻³ MgSO₄. At this electrolyte concentration, the PEO are still in good solvent condition (better than θ -solvent). Unfortunately, the results of these authors showed some unusual time-dependent irreversible phenomena which were attributed to some molecular association between the adsorbed PEO chains and those remaining in bulk solution. In addition, the poor anchoring of the PEO chains complicated the study since desorption and bridging could not be ruled out.

Klein^{14,15} measured the steric interaction between polystyrene adsorbed on mica in cyclohexane at 24°C, i.e. under θ -conditions (the θ -temperature for polystyrene in cyclohexane is 34°C). The results of the force-distance curve for this system are shown in Figure 2. The free-energy distance curve may be interpreted on the basis of the steric stabilisation theory. The attractive region in the profile could be attributed to the favourable interpenetration of the attached segments in a worse than θ -solvent ($X > 0.5$). This manifest itself in the potential energy curve by a decrease in potential energy in the domain $R_g \lesssim D < 3 R_g$, where D is the minimum distance between the mica plates. The dramatic increase in the measured force when $D < R_g$ arises from the elastic repulsion resulting from compression of the attached polystyrene chains. However, such elastic repulsion alone cannot account for the steep repulsion observed experimentally. Another repulsive interaction have to postulated to account for this affect¹⁶.

The second method to study interaction between polymer layers is to use cross quartz filaments, as discussed by Sonntag and Coworkers¹⁷. These authors measured the interaction between polyvinylalcohol (PVA) layers (partially hydrolysed polyvinylacetate, 88% hydrolysed) with various molecular weights. The results are shown in Figure 3. Sonntag *et al* interpreted that results in terms of Hesselink *et al* theory¹ and concluded that the average number of loops and tails was relatively small. These authors inferred that a small number of larger tails was responsible for the observed stabilisation.

The third method for measuring steric interaction was used by Ottewill and Coworkers¹⁸ who used two small hemi-spherical caps of silicone rubber coated with poly(methyl methacrylate) (PMMA) and contained adsorbed PVA layers. The upper cylinder was held fixed while the lower cylinder could be moved up and down. In this way, the soft elastic surface in the central region became distorted resulting in flat discs in the zone of interaction. The authors measured the equilibrium pressure developed as a function of distance of separation. The results are shown in Figure 4. Initial interaction occurred at a separation distance of 160 ± 20 nm, indicating that the

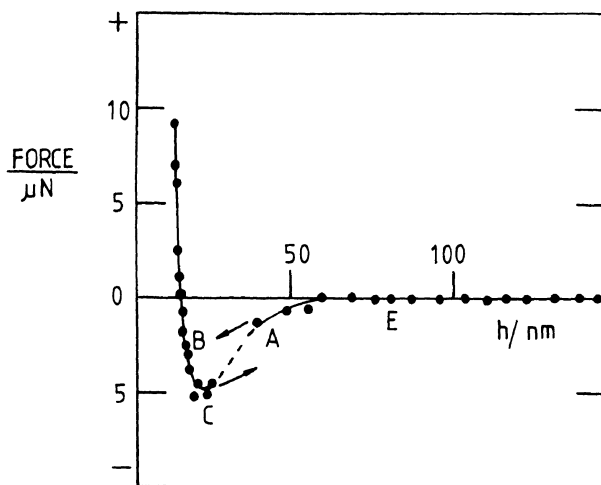


Figure 2 - Interaction of polystyrene layers ($M_w = 6 \times 10^5$) adsorbed on mica in cyclohexane at 24°C , according to Kelin (14, 15).

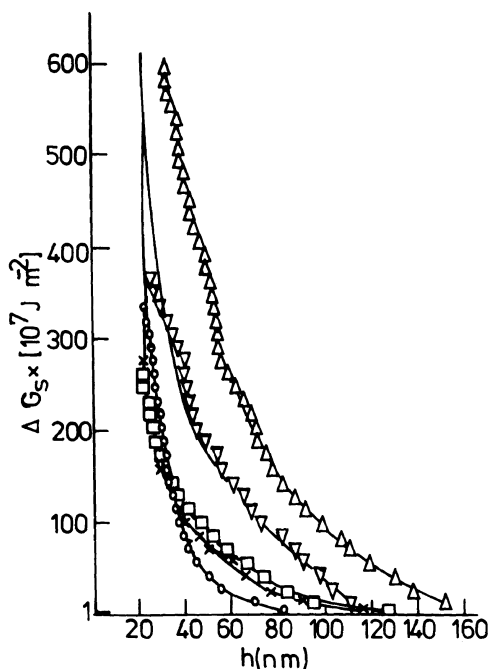


Figure 3 - Energy interaction-distance of separation between adsorbed PVA layer on quartz. $\circ M = 16,000$; $\times M = 55,000$; $\square M = 65,000$; $\nabla M = 110,000$; $\Delta M = 123,000$

thickness of the adsorbed layer may be ca 80 nm. This thickness is possible with the high molecular weight fractions of PVA in this sample¹⁹. At separation distances of < 50 nm, there was a sharp

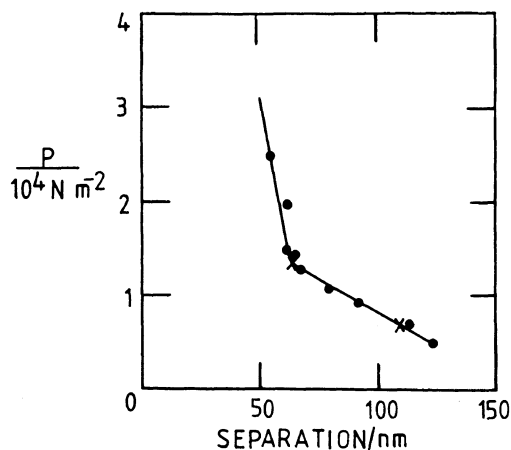


Figure 4 - Pressure-distance curve for PVA layers ($M_w = 45,000$) adsorbed on silicone rubber coated with PMMA.

rise in pressure which may be due to significant overlap and/or compression of the PVA layers.

Methods based on using particulate dispersions

As mentioned above steric interaction may be measured by compression of dispersions. Doroszkowski and Lambourne¹⁹ used a two dimensional array of sterically stabilised latex dispersions that were placed at the oil/water interface. For this purpose poly (acrylonitrile) particles stabilised by poly(methyl methacrylate-Co-methacrylic acid) g-styrene (that were grafted on the particle surface) were spread at the toluene-water interface. The particles were held at the o/w interface by their partial immersion in the aqueous phase. Electron microscopy showed that the particles were hexagonally close packed 2-D arrays with no holes. Using a specially designed surface balance, the surface pressure π versus particle area (A) was established. The free energy of interaction per contact for pairs of steric layers was calculated by integrating the area under the π versus A curves and dividing by the total number of contacts. Figure 5 shows the variation of $\Delta^S G$ with H_{01} and various theoretical calculations based on Hesselink *et al* theory¹. The latter predicts interactions that are too weak at large separation distance and too strong at short distances when compared with the experimental results.

Ottewill and Coworkers²¹ determined the distance dependence of steric repulsion between latex particles by measuring the osmotic pressure P as a function of volume fraction, using a specially designed cell. Poly (methyl methacrylate)/PMMA lattices sterically stabilised with poly(12-hydroxy stearic acid) (PHS) in n-dodecane were studied. The P - ϕ results obtained are shown in Figure 6. At low values, the resistance to compression was negligible. This resistance started to increase when ϕ increased above 0.54 and at $\phi > 0.566$, the resistance to compression increased considerably with even small changes in ϕ . At the onset of the almost-hard sphere repulsion ($\phi = 0.566$), the distance of separation for face-centered cubic (or hexagonal) arrays of such particles corresponds to 14.5 or a contribution of 7.25 nm for each shell. The fully extended length of PHS was calculated to be ca 9 nm, which indicates some inter-

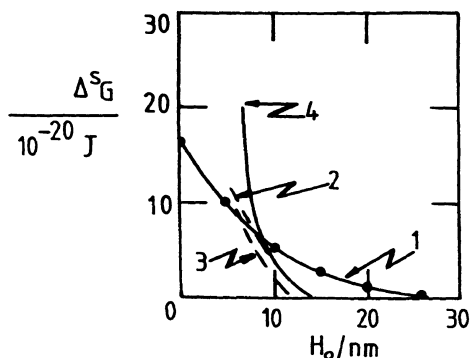


Figure 5 - Variation of steric interaction free energy with separation distance for polyacrylamide latex particles in toluene (1) experimental results, (2) theoretical mixing term, (3) theoretical elastic term, (4) total theoretical terms, after Doroszowski and Lambourne^{19,20}.

penetration and/or denting of the chains on close approach.

As mentioned above, rheology offers an indirect method for studying interparticle interaction. This was discussed in detail before^{22,23}. Basically, one measures the viscoelastic properties of a sterically stabilised dispersion as a function of volume fraction of the dispersion, e.g. using dynamic (oscillatory) measurements. In this way the viscoelastic parameters, namely the complex modulus G^* , storage modulus, G' and loss modulus G'' are measured as a function of frequency (in the linear viscoelastic region) at various ϕ values. Plots of G^* , G' and G'' (at a fixed frequency) versus ϕ are established and this allows one to investigate steric interaction. As an illustration, Figure 7 shows plots of G^* , G' and G'' (at $\nu = 1$ Hz) versus ϕ for a polystyrene latex dispersion (radius $a = 175$ nm) containing grafted PEO chains (with a molecular weight of 2000). These results show an interesting transition as the volume fraction of the dispersion is increased. At $\phi < 0.5$, $G'' > G'$, i.e. the dispersions show a predominantly viscous response (this is maintained in the frequency range $10^{-2} - 1$ Hz). This is not surprising since at $\phi < 0.5$, the surface-to-surface distance of separation between the particles h , is less than 2δ and hence the interactions between those terminally anchored PEO chains is weak. These chains are only slightly compressed showing a small decrease in δ from 20.5 to 15.0 as ϕ increases from 0.33 to 0.48²⁴. Such compression probably occurs with the larger PEO chains (note that grafted PEO chains are polydisperse) and such small effect does not lead to a predominantly elastic response within the frequency range studied. However, when $\phi > 0.5$, $G' > G''$ and the magnitude of the moduli starts to rise strongly with further increase in ϕ . For example, when ϕ is increased from 0.5 to 0.575, G' at $\nu = 1$ Hz increases by an order of magnitude and a further increase to 0.585, it increases by another two orders of magnitude. Moreover, at such high ϕ values, the moduli tend to show little dependency on frequency within the range studied. In other words, the dispersion behaves as a near elastic gel, as a result of the strong interaction between the PEO chains. The latter may undergo interpenetration of the peripheries of the larger PEO chains and compression of the whole grafted polymer layers. Indeed at

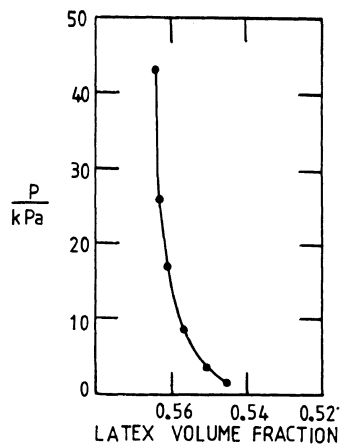


Figure 6 - Osmotic pressure of PMMA particles stabilised with PHS in n-dodecane.

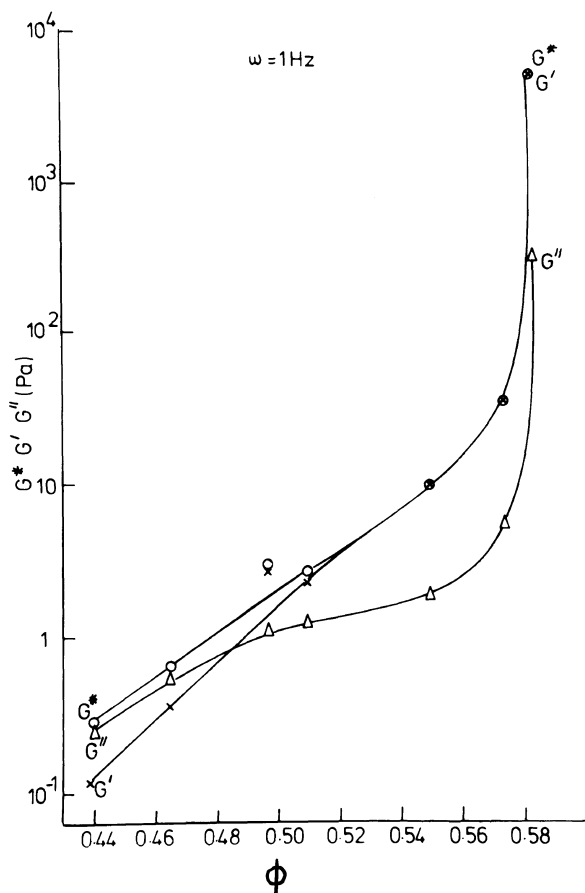


Figure 7 - Variation of G^* , G' and G'' ($\nu = 1$ Hz) with ϕ for polystyrene latex dispersions containing grafted PEO chains.

$\phi = 0.585$, $G^* \sim G' = 4.8 \times 10^3$ Pa and $\eta' = 8.32 \times 10^3$ Pas, whereas at $\phi = 0.65$, $G^* \sim G' = 1.12 \times 10^5$ Pa and $\eta' = 1.6 \times 10^5$ Pas, i.e. the latex behaves as a near elastic solid.

The above viscoelastic results clearly show that their value in studying steric interaction in concentrated dispersions. It is possible to convert the modulus versus ϕ curves to G' versus h curves using the following equation,

$$h = 2a [(\phi_m / \phi)^{1/3} - 1] \quad (3)$$

where ϕ_m is constant that is characteristic of the type of array e.g. 0.74 for hexagonal or face-centered cubic array, 0.68 for body centered cubic and 0.64 for random arrangement of particles. For the present calculation a value of $\phi_m = 0.68$ was used.

A plot G' versus h is shown in Figure 8. On the same figure, value of G° versus h are also shown. These were calculated from the force distance curves obtained using mica on which a polymer of PMMA with grafted PEO (with the same molecular weight as on polystyrene) was adsorbed. Calculation of $G' - h$ from $F - h$ curves was carried out by Castello²⁵ using the analysis proposed by Goodwin et al^{24,25}. Although the value of G' (exp) and G° (theor) very considerably, the general trend is the same, namely a rapid increase in the elastic modulus with decrease in h , when the latter is less than 30 nm. As discussed above, when $h < 30$ nm, interpenetration and/or compression of the PEO chains occurs. Thus, viscoelastic measurements can give a quantitative measurement of steric interaction between the particle in a concentrated dispersion.

EFFECT OF ADDITION OF FREE POLYMER-DEPLETION OF FLOCCULATION

For studying depletion flocculation of sterically stabilised polystyrene latex (with grafted PEO chains) two types of free polymers were investigated namely PEO and HEC (with various molecular weights). In these experiments, the volume fraction of the latex was kept constant ($\phi = 0.3$). Figure 9 shows the variation of G_{∞} (the shear modulus) and τ_{β} (extrapolated yield value) with volume fraction of free polymer, ϕ_p , for the PEO system ($M_w = 20000, 35000$ and 50000). Figure 10 shows the results for HEC with three different molecular weight (70000, 124000 and 223000). In all cases, the rheological parameter show a rapid increase above a critical ϕ_p value, which is denoted by ϕ_p^+ , i.e. the free polymer volume fraction above which depletion flocculation results in a structured system with measurable τ_{β} and G_{∞} . As discussed before²⁸⁻³⁰ τ_{β} may be related to E_{sep} the energy required to break each contact in a flocculated structure, i.e.

$$\tau_{\beta} = \frac{3 \phi n E_{sep}}{8 \pi a^3} \quad (4)$$

Assuming a value of n of 4, (where as a reasonable coordination number for an open floc structure) E_{sep} was calculated from τ_{β} . The results are given in Table 1 for the PEO and HEC systems. For comparison, the values of G_{dep} calculated using the Asakura and Oosawa's (A-O) theory³¹ as well as those using the Fleer, Scheutjens and Vincent (FSV)³² are given in the same table. G_{dep} is given by the following expression for A-O and FSV theories respectively

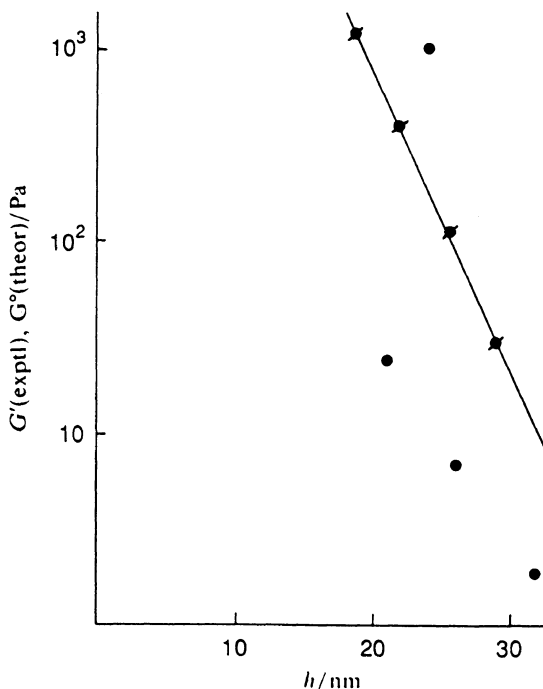


Figure 8 - Variation of G' with h for a sterically stabilised latex dispersions calculated from F/h relationship \circ experimental data for G' , M_w (PEO) = 2000).

$$G_{\text{dep}}/kT = - (3/2) \phi_2 \beta \chi^2 ; 0 < \chi < 1 \quad (5)$$

$$G_{\text{dep}}/kT = \frac{2 \pi a}{v_1} (\mu_1 - \mu_1^o) \Delta^2 \left(1 + \frac{2\Delta}{3a}\right) \quad (6)$$

where ϕ_2 is the volume concentration of the polymer; $\beta = a/\Delta$, where Δ is the depletion thickness (equal to R_g) and $\chi = [\Delta - (h/2)]/\Delta$ (note that if $h = 0$, $\chi = 1$). v_1 is the molar volume of the solvent and $(\mu_1 - \mu_1^o)$ is the difference in chemical potential of the solvent with the latex containing the free polymer (μ_1) and that in its absence (μ_1^o). This difference is given by the expression,

$$\frac{(\mu_1 - \mu_1^o)}{kT} = - \frac{\phi_p}{n_2} - (1/2 - \chi) \phi_p^2 \quad (7)$$

where n_2 the number of polymer segments and χ is the Flory-Huggins interaction parameter which for PEO is 0.473 and for HEC is 0.47.

For the PEO system, the calculated values based on Fleer *et al*²² model are significantly higher than the experimental E_{sep} value, whereas reasonable agreement is obtained using Asakura and Oosawa's model¹. In contrast with HEC, better agreement is obtained using the FSV model, particularly at high ϕ_p values. It should be mentioned, however, that several assumptions have to be made in calculating E_{sep} and, therefore, the agreement obtained is only qualitative. In addition, the theories for depletion flocculation are based on a hard-sphere model, which is not the case with the present latex dispersions containing grafted polymer chains. In this case, allowance should be made for the possible interaction between the free PEO and that on the particle surface. This will modify the value for

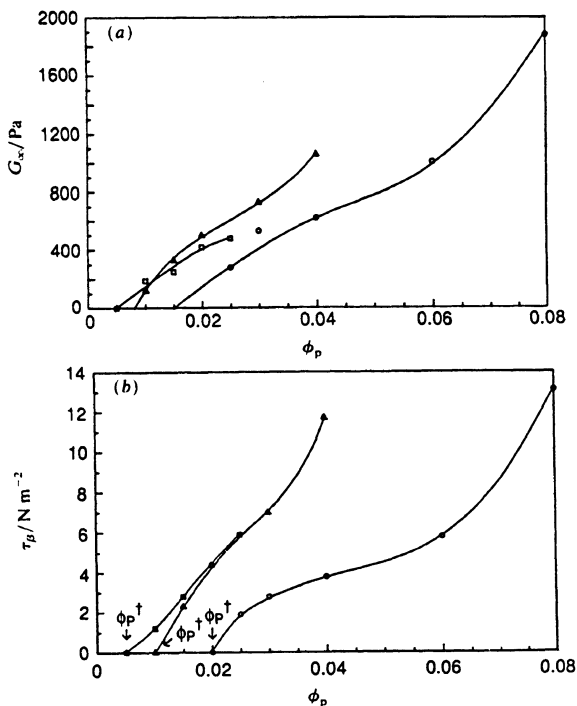


Figure 9 - G_{∞} and τ_{β} versus ϕ_p for PEO with various M_w using a latex dispersion with ($\phi = 0.3$) M_w (PEO): 0, 20,000, Δ 35,000; \square , 90,000.

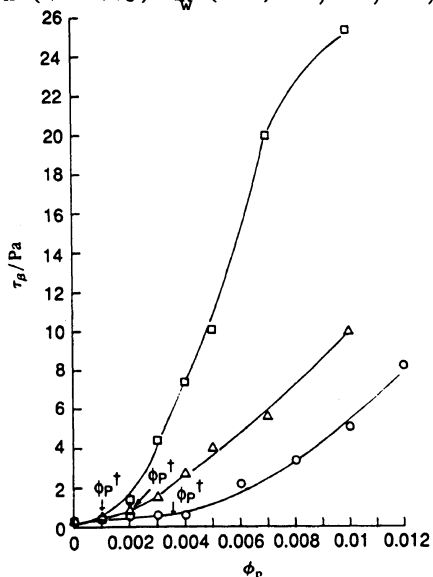


Figure 10 - τ_{β} versus ϕ_p for HEC with various M_w using a polystyrene latex dispersion with ($\phi = 0.3$). M_w : 0, 70,000; Δ , 124,000; \square , 223,000.

E_{sep}^{33} . In the case of HEC, this interaction is weaker since PEO and HEC are not compatible. For that reason, better agreement between E_{sep} and G_{dep} based on the FSV model is obtained particularly at the highest M_w HEC studied.

TABLE I

Summary of the results of E_{sep} calculated from the experimental values and G_{dep} calculated using Asakura and Oosawa's/Av) and Fleeer et al (FSV) models.

ϕ_p	$\tau_\beta / \text{Nm}^{-2}$	E_{sep} / kT ($n \approx 4$)	AO G_{dep} / kT	FSV
(a) PEO, $M_w = 20,000$				
0.025	2.0	18.2	25.3	81.9
0.03	2.8	25.4	30.3	102.9
0.04	2.8	24.6	40.5	149.5
0.06	5.8	52.8	60.7	261.1
0.08	13.1	111.2	80.9	397.4
(b) PEO, $M_w = 35,000$				
0.015	2.3	21.0	16.4	54.1
0.02	4.4	40.0	21.8	78.0
0.3	7.0	63.8	32.7	125.0
0.04	11.7	106.0	43.6	203.0
(c) PEO, $M_w = 90,000$				
0.01	1.2	11.0	12.3	48.4
0.025	2.8	24.5	18.4	85.6
0.02	4.4	40.0	24.5	131.3
0.025	5.9	53.8	30.6	185.7
(d) HEC, $M_w = 70,000$				
.002	0.05	4.6	2.7	28.6
.003	0.6	5.6	4.0	43.4
.004	0.7	6.4	5.4	58.5
0.006	2.2	20.0	8.0	89.7
0.008	3.4	3.09	10.7	122.2
0.110	5.1	46.4	13.4	156.0
0.012	8.3	75.4	16.0	191.0
(e) HEC, $M_w = 124,000$				
.001	0.5	4.6	1.6	17.0
.002	0.9	8.2	3.1	34.6
0.003	1.6	14.5	4.7	53.0
0.004	2.7	24.5	6.2	72.0
0.005	4.0	36.4	7.8	91.8
0.007	5.7	51.8	10.9	133.3
0.110	10.0	90.9	15.6	200.7
(f) HEC, $M_w = 223,000$				
0.001	0.4	3.6	1.8	20.7
0.002	1.9	17.3	3.7	42.9
0.003	4.9	44.5	5.5	66.7
0.004	7.9	71.9	7.3	91.8
0.005	10.7	97.3	9.2	118.5
0.007	20.0	181.8	12.8	176.3
0.010	25.4	231.0	18.3	274.2

REFERENCES

1. F.Th. Hesselink, A. Vrij, and J.Th.G. Overbeek, *J. Phys. Chem.* **75**, 2094 (1971).
2. D.J. Meier, *J. Phys. Chem.* **71**, 1861 (1967).
3. A.K. Dolan and S.F. Edwards, *Proc. Roy. Soc. London*, **A337**, 509 (1974).
4. A.K. Dolan and S.F. Edwards, *Proc. Roy. Soc. London*, **A343**, 627 (1975).
5. S.F. Edwards, *Proc. Roy. Soc.* **85**, 613 (1965).
6. P.R. Gerber and M.A. Moore, *Macromolecules* **10**, 476 (1977).
7. P.G. de Genner, *Rep. Progr. Phys.* **32**, 187 (1972).
8. J.M.H.M. Scheutjens and G.J. Fleer, *Adv. Colloid Interface Sci.* **16**, 341 (1982).
9. P.J. Flory and W.R. Krigbaum, *J. Chem. Phys.* **18**, 1086 (1950).
10. P.J. Flory, "Principle of Polymer Chemistry" Cornell University Press, Ithaca, N.Y. (1953).
11. J.M.H.M. Scheutjens and G.J. Fleer, *J. Phys. Chem.* **83**, 1619 (1979).
12. J.M.H.M. Scheutjens and G.J. Fleer, *J. Phys. Chem.* **84**, 178 (1980).
13. J.T. Israelachvili, R.K. Tandon and L.R. White, *J. Colloid Interface Sci.* **78**, 430 (1980).
14. J. Klein, *Nature* **288**, 248 (1980).
15. J. Klein, *J. Adv. Colloid Interface Sci.* **16**, 101 (1982).
16. D.H. Napper, "Polymeric Stabilisation of Colloidal Dispersions" Academic Press, London, N.Y. (1983) pp.301-304.
17. H. Sonntag, B. Ehmke, R. Miller and L. Knapschinsky, in "The Effects of Polymers in Dispersion Properties", Th.F. Tadros Editor, Academic Press, London (1982) p.207.
18. F.W. Cain, R.H. Ottewill and J.B. Smitham, *Disc Faraday Soc.* **65**, 33 (1978).
19. A. Doroszowski and R. Lambourne, *J. Polymer Soc.* **34**, 253 (1971).
20. A. Doroszowski and R. Lambourne, *J. Colloid Interface Sci.* **43**, 97 (1977).
21. R.J.R. Cairns, R.H. Ottewill, D.W.J. Osmond and I. Wagstaff, *J. Colloid Interface Sci.* **54**, 45 (1976).
22. Th.F. Tadros, *Langmuir*, **6**, 28 (1990).
23. Th.F. Tadros and A. Hopkinson, *Faraday Disc. Chem. Soc.*, in press (1990).
24. C. Prestidge and Th.F. Tadros, *J. Colloid Interface Sci.* **124**, 660 (1988).
25. B.A.De.L. Costello, Ph.D. Thesis, Imperial College London (1990).
26. J.W. Goodwin and A.M. Khider, *Colloid and Interface Sci.* Ed. M. Kerker, Academic Press, N.Y. (1976) Vol.IV, p.529.
27. R. Buscall, J.W. Goodwin, M.W. Hawkins and R.H. Ottewill, *J. Chem. Soc. Faraday Trans. I*, **718**, 2889 (1982).
28. D. Heath and Th. F. Tadros, *Faraday Disc. Chem. Soc.* **76**, 203 (1983).
29. C. Prestidge and Th.F. Tadros, *Colloids and Surfaces*, **31**, 325 (1988).
30. A. Hopkinson and Th.F. Tadros, *Faraday Disc. Chem. Soc.* (1990) in press.
31. S. Asakura and F. Oosawa, *J. Chem. Phys.* **22**, 1255 (1954); *J. Polym. Sci.* **33**, 245 (1958).
32. G.J. Fleer, J.M.H.M. Scheutjens and B. Vincent, *ACS Symp. Ser.* **240**, 245 (1984).
33. A. Jones and B. Vincent, *Colloids and Surfaces*, **42**, 113 (1989).