Weak, Reversible Flocculation Phenomena in Sterically-stabilised Dispersions*

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Received November 15, 1982

It is demonstrated, both theoretically and experimentally, that the two basic parameters controlling the onset and extent of flocculation in sterically-stabilised dispersions are the particle concentration and the depth of the pairwise interaction (free) energy minimum. It is also shown that the latter parameter is itself controlled, inter alia, by the thickness of the adsorbed polymer sheath, the solvency and the concentration of free polymer in solution.

INTRODUCTION

The physical properties of colloidal dispersion (e. g. their rheological, settling, optical and electrical properties) depend critically on the state of dispersion of the constituent particles. In certain applications a totally de-flocculated dispersion is desirable, in particular where settling or deposition need to be minimised (e. g. in detergency or the suspension of carbon deposits in engine oils). In other applications strong flocculation (or coagulation) is required (e. g. in water clarification or in bacterial harvesting in the single-cell protein manufacturing process).

In many processes or formulations, however, a state of controlled, weak, reversible flocculation is the objective. For example, in thixotropic paints, it is desirable that the pigment particles are weakly flocculated together, so that a continuous, weak gel structure forms. This leads both to non-settling in the can, and also the required rheological properties, i. e., low viscosity under high shear during application, but high viscosity under low or zero shear after application. Application of high shear leads to break-up of the gel network structure.

A second example where weak flocculation is required would be in the formulation of many concentrated, aqueous agricultural dispersions (e. g. of insoluble pesticides and herbicides). Here again »caking« (settling into a close-packed array, which can occur with large, dense particles which are stable to aggregation) needs to be avoided during storage. Also, spontaneous deflocculation on dilution by the farmer, prior to spraying, is necessary.

It is the achievement and control of this state of weak, reversible flocculation, rather than either total stability or total instability, which is the major challenge to the colloid chemist. It turns out that it is much easier to achieve this objective when polymeric additives are present in the dispersion, rather than in dispersions where the stability is controlled only by the electrostatic and van der Waals pairwise interactions between the particles.

PARTICLE INTERACTIONS IN THE PRESENCE OF POLYMER

We have to consider two regions of interaction between two approaching particles carrying adsorbed polymer layers (see Figure 1): (i) $h > 2\delta$, (ii) $h < 2\delta$.
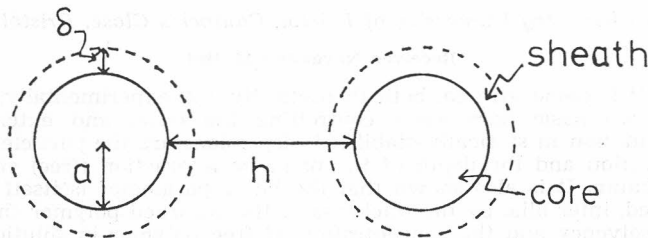

Figure 1. Interactions between two particles carrying adsorbed sheaths of polymer plus solvent.

$h > 2\delta$

In this region the interparticle interactions may be essentially described by the classical D.L.V.O. theory, i. e., the van der Waals term (G_A) plus any electrostatic contribution (G_E) arising from charges that my be present on the core particles. The presence of the polymer sheath around the particles modifies both G_A and G_E; this problem has been discussed elsewhere by this author.[1,2] Suffice to say that approximate values for G_A and G_E may be estimated if the following additional parameters are known: the thickness and effective Hamaker constant of the polymer sheath, and the electrostatic potential at the periphery of the sheath (usually assumed to be equivalent to the zeta potential of the particles).

$h < 2\delta$

Here G_A and G_E are more difficult to estimate.[1,2] However, it is usually assumed that the total interaction is now dominated by other forces which come into play as a direct result of the interactions between the two polymer sheaths and the polymer sheaths with the opposing core particles. It is convenient to divide these »direct« interactions into three contributions:

i) the *elastic* term (G_{el}): this arises from the loss in conformational entropy of the chains. Depending on the coverage (Θ) and the configuration of the adsorbed polymer molecules, this may or may not be a significant contribution for $\delta < h < 2\delta$, but clearly becomes very important for $h < \delta$. Napper[3] has given the following expression for G_{el} for two parallel flat plates,

$$G_{el} = 2\,kT\,\Gamma_2 \ln \frac{\Omega\,(h)}{\Omega\,(\infty)} = 2\,kT\,\Gamma_2\,R_{el}\,(h) \tag{1}$$

where Γ_2 is the number of adsorbed chains per unit area, and $\Omega(h)$ and $\Omega(\infty)$ are the number of conformation available to the adsorbed polymer chains at $h = h$ and $h = \infty$, respectively; R_{el} is a geometric function whose form depends on the form of the segment density distribution $\varrho(z)$ for the adsorbed chains. G_{el} is always a *repulsive* contribution.

ii) the mixing term (G_{mix}): this arises from the local segment/solvent interactions and the change in segment concentration in the interaction region between the particles. It comes into play for all values of $h < 2\delta$. Napper[3] derived the following expression for two parallel flat plates,

$$G_{mix} = \frac{2\,kT\,V_2^2\,\Gamma_2^2}{V_1}\,(1/2 - \chi)\,R_{mix}(h) \tag{2}$$

where V_2 and V_1 are the molar volumes of the polymer and solvent, respectively. R_{mix} is again a geometric function which depends on the form of $\varrho(z)$; χ is the Flory segment/solvent interaction parameter. Clearly, G_{mix} can be positive or negative (i. e. *repulsive* or *attractive*) depending on the magnitude of χ. For a theta-solvent $\chi = (1/2)$, $G_{mix} = 0$.

iii) the *bridging* or *adsorption* term (G_{ad}): this results from the change in the net number of surface/segment contact (i. e. $<p>$) as h decreases. G_{ad} (like G_{el}) may or may not be significant for $\delta < h < 2$, depending on the configurational changes that occur in this region, but becomes very important when $h < \delta$, since segments may now become adsorbed on the surface of the *opposing* core particle or plate, in addition to any changes in $<p>$ arising from the formation of larger trains (at the expense of smaller loops or tails) on the original surface. One may write the following expression for G_{ad}, for parallel flat plates,

$$G_{ad} = 2\,kT\,\Gamma_2\,x\,\Delta\,p\,\Delta\,\varepsilon^\sigma \tag{3}$$

where x is the number of segments per chain; Δp is the net change in $<p>$ and $\Delta \varepsilon^\sigma$ is the net adsorption energy change when a segment replaces solvent molecule(s) at the surface. Since, as h dereases, Δp is generally positive and $\Delta \varepsilon^\sigma$ generally negative, G_{ad} will be in most cases negative, i. e. an *attractive* contribution.

Similar expressions to eqns. (1)—(3) may be derived for spherical particles.[2,3] The overall form of the net interaction free energy (G_i) particle separation (h) curve is clearly complex, since $G_i = G_{el} + G_A + G_{el} + G_{mix} + G_{ad}$. We shall just consider two special cases here (Figure 2): (i) at low coverages, (ii) at high coverages. In both cases we shall assume, for simplicity, that $G_E = 0$ (i. e. uncarged particles), and that $\chi < 1/2$ (good solvent).

The form of $G_i(h)$ for low Θ (Figure 2a) shows a significant minimum (G_{min}), resulting from the dominance of (i) G_{ad} for $h \lesssim \delta$, and (ii) G_s ($= G_{el} +$

$+ G_{mix}$) for $h \ll \delta$. This may lead to so-called »bridging« flocculation of the particles. At high Θ, on the other hand (Figure 2b), $G_i(h)$ the net minimum is very small and is due to the long range van der Waals term (G_A). Clearly, provided G_{min} is small enough, the system will be stable to flocculation; this corresponds to so-called »steric stabilisation«. The question of just how deep
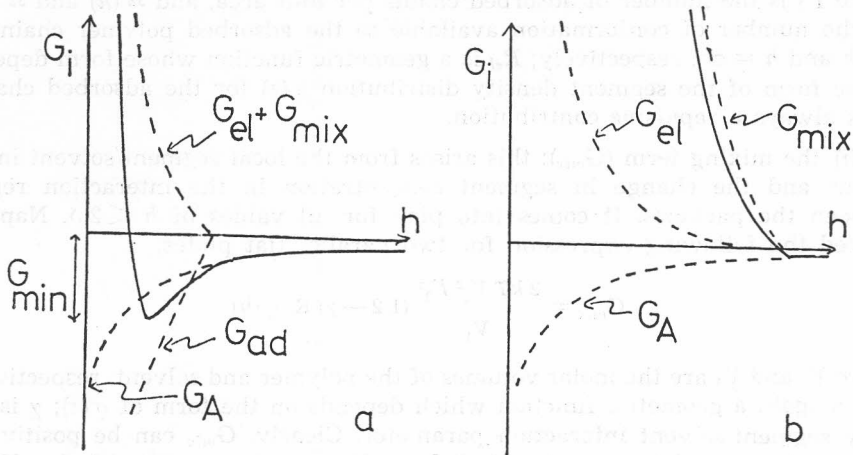
Figure 2. $G_i(h)$ curves for: (a) low coverage; (b) high coverage ($\Theta \to 1$).

$|G_{min}|$ has to be for flocculation to be observed will be discussed later in the paper.

So far it has been implicitly assumed that the concentration (c_2) of free polymer in solution has been zero or negligible. If, however, c_2 is sufficiently great then the analysis of $G_i(h)$ becomes even more complex. This situation has been dealt with recently by several authors[2,4-7] and will not be discussed in detail here. Suffice to say that Vincent et al[6] have shown that if $c_2 > c_2^*$, where c_2^* is the polymer concentration at which free polymer coils in solution begin to overlap with each other, then there will also be overlap between free polymer coils and the adsorbed polymer sheaths around the particles. This leads to an increase in $|G_{min}|$, which may result in flocculation. At high enough c_2 values (in general, beyond c_2^{**}, i. e. in the so-called »concentrated« polymer solution region) there is no net effect of free polymer on G_{min} since there is uniform segment concentration everywhere in the system. G_{min} thus passes through a maximum in the (semi-dilute) region: $c_2^* < c_2 < c_2^{**}$.

STABILITY/FLOCCULATION BEHAVIOUR: THEORETICAL PREDICTIONS

For neutral[†] particles, as we have seen, the form of the $G_i(h)$ curve is characterised by a minimum, G_{min}. Vincent et al.[6,8,9] have shown that, for a given value of G_{min}, flocculation will only be observed if the particle volume fraction, Φ, exceeds a critical value, c.f. Φ. For $\Phi <$ c.f. Φ the dispersion is thermodynamically stable. One may map-out a stability/flocculation diagram as a function of Φ and G_{min}; this is shown in Figure 3.

The boundary between »reversible« and »irreversible« flocculation (dotted line) has been somewhat arbitrarily selected here to be at $G_{min} = 5 kT$. This is not well defined, and is only put in to indicate a transition region in observed

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† With charged particles, contributions from G_E (at $h > 2\delta$) have to be considered. This may lead to a maximum in $G_i(h)$ and corresponding metastability (or kinetic stability) of the dispersion, as in conventional DLVO theory.
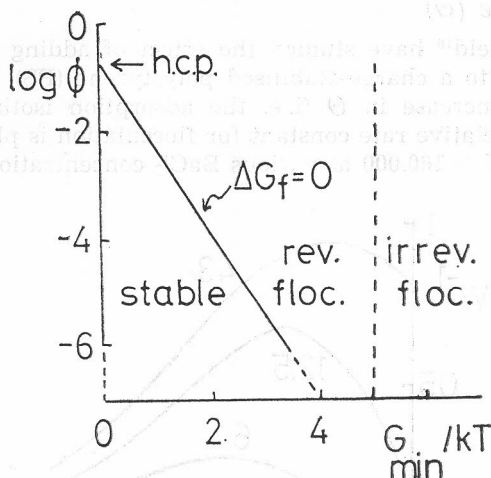
Figure 3. Theoretical stability/flocculation diagram relating G_{min} and log Φ. The $\Delta G_f = 0$ line represents the boundary condition that the free energy of flocculation is zero.

behaviour. Irreversible flocculation may be taken to correspond to the situation where, at equilibrium, there would be effectively zero concentration of singlet particles. At a fixed value of Φ (in the normal experimental range) as $|G_{min}|$ increases, so one observes transitions from stability $\rightarrow$ weak, reversible flocculation $\rightarrow$ irreversible flocculation. For a given system the main variables which control the value of $|G_{min}|$ are: a, δ, χ, c_2 and Θ. To summarize the behaviour at high Θ ($\Theta \rightarrow 1$):

i) in a good solvent ($\chi < 1/2$) and for $c_2 \rightarrow 0$: $|G_{min}| \uparrow$ as $a \uparrow$ (fixed δ) or as $\delta \downarrow$ (fixed a).

ii) for fixed a and δ, and for $c_2 \rightarrow 0$: $|G_{min}| \uparrow$ as $\chi \uparrow$. There is a dramatic $\uparrow$ in $|G_{min}|$ in the region of $\chi = 1/2$ (theta-solvent) for cases where G_{el} is small with respect to G_{min} (Figure 2b) (e. g. high M.W. terminally-anchored tails); in other cases the $\uparrow$ in $|G_{min}|$ is more gradual.

iii) for fixed a, δ, χ ($< 1/2$): $|G_{min}|$ goes through a maximum over the range $c_2^* < c_2 < c_2^{**}$.

The effect of varying Θ itself has not been analysed in such detail, but as Figure 2 illustrates the magnitude of $|G_{min}|$ presumably gradually decreases as Θ increases. Unfortunately, it is only possible, experimentally to study the variation of Θ with charge-stabilised systems; otherwise, in the limit $\Theta \rightarrow 0$, irreversible coagulation occurs. Thus, contributions from G_E have to be taken into consideration.

STABILITY FLOCCULATION BEHAVIOUR: SOME EXPERIMENTAL OBSERVATIONS

In this section some experimental results obtained with several types of system will be presented and discussed in the light of the theoretical predictions of the previous section.

Effect of Coverage (Θ)

Ash and Clayfield[10] have studied the effect of adding low concentrations of high M.W. PEO to a charge-stabilised polystyrene (PS) latex. The increase in c_2 reflects the increase in Θ (i. e. the adsorption isotherm). In Figure 4 the change in the relative rate constant for flocculation is plotted as a function of c_2 (Θ) for PEO M = 160,000 at various BaCl$_2$ concentrations.
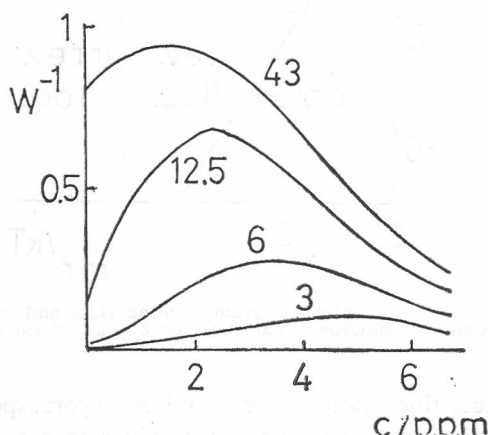

Figure 4. Effect of electrolyte(BaCl$_2$) concentration on the relative rate constant (1/w = k/k_o; k_o = Smoluchowski fast rate constant) versus polymer (PEO, M = 160,000) concentration. Number indicates BaCl$_2$ in mmol dm^{-3}.

For c_2 and $\Theta = 0$, the increase in k/k_o with increasing ionic strength merely reflects the increase in the coagulation rate constant: at a high enough BaCl$_2$ concentration $k/k_o \to 1$, i. e. the Smoluchowski fast coagulation rate is achieved. At a given BaCl$_2$ concentration, k/k_o passes through a maximum with increasing c_2 (Θ); this reflects the onset of bridging flocculation, followed by steric stabilisation as $\Theta \to 1$. The decrease in k/k_o beyond the maximum is associated with the decrease in $|G_{min}|$ referred to in the previous section.

Effect of Adsorbed Layer Thickness (δ)

Cowell and Vincent[11] have shown that for PS latex in the presence of adsorbed low M.W. PEO ($\Theta = 1$) and sufficient added electrolyte to remove G_E contributions, a c. f. Φ exists (Figure 5). The value of the c. f. Φ decreases as the M.W. of PEO (and therefore δ) decreases, i. e. as $|G_{min}|$ increases, in line with Figure 2.

Effect of Solvency (χ)

Figure 6 illustrates the sudden onset of flocculation at a critical value of T (i. e. of χ) for a (neutral) PS-g-PEO latex (PEO M.W. = 750) in 0.26 mol dm^{-3} MgSO$_4$; this critical value of T is referred to as the c. f. T. Φ for this experiment was fixed at a low value,[9] i. e. 10^{-4}.

The dependence of the c. f. T. on the particle volume fraction (Φ) is illustrated in Figure 7 for a similar PS-g-PEO latex system (PEO M. W. = 1600)
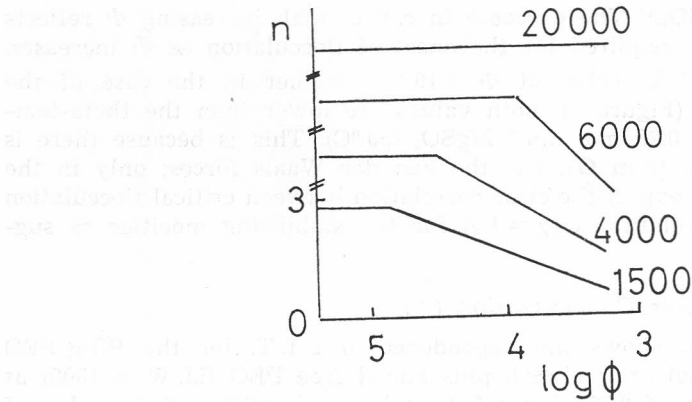
Figure 5. n (= $dlog\ \tau/dlog\ \lambda$) versus log Φ plots for polystyrene latex with pre-adsorbed PEO in 10^{-2} mol dm^{-3} $Ba(NO_3)_2$ solution, (after 3 min).[11] Numbers indicate M.W. of PEO.

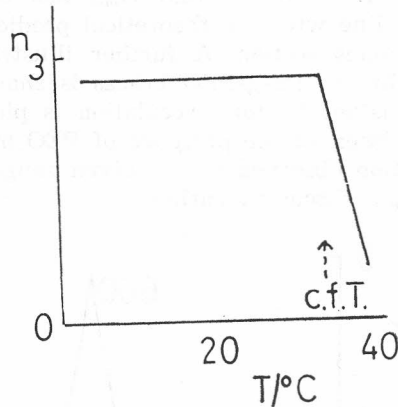Figure 6. n (=$dlog\ \tau/dlog\ \lambda$) versus temperature (T) for a PS-g-PEO latex (PEO M.W. = 750) in 0.26 mol dm^{-3} $MgSO_4$ solution.[9]
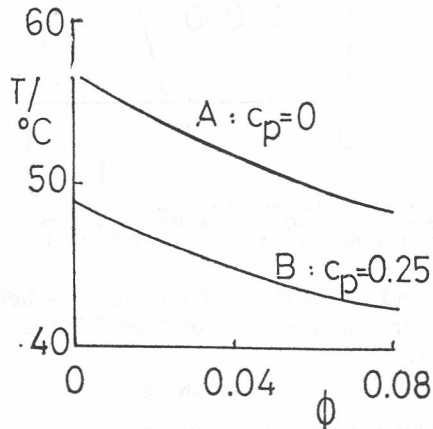

Figure 7. c.f.T. as a function of polystyrene latex particle volume fraction (Φ) in 0.26 mol dm^{-3} $MgSO_4$. A, no added polymer; B, plus PEO (M.W. 1500) at a polymer volume fraction, c_p = = 0.25.[12]

in 0.26 mol dm^{-3} $MgSO_4$.[12] The decrease in c. f. T. with increasing Φ reflects the decrease in $|G_{min}|$ required for the onset of flocculation as Φ increases.

Note that the c. f. T. value of $\Phi = 10^{-4}$ is higher in the case of the PS-g-PEO (750) latex (Figure 7); both values are lower than the theta-temperatures for PEO in 0.26 mol dm^{-3} $MgSO_4$ (59 °C). This is because there is a contribution to G_{min} from G_A, i. e. the van der Waals forces; only in the limit of high δ can we expect the close correlation between critical flocculation conditions and theta-conditions ($\chi = 1/2$) for the stabilising moeities as suggested by Napper.[3]

Effect of Free Polymer Concentration (c_2)

Line B, Figure 7, shows the dependence of c. f. T. for the PS-g-PEO (1600) latex in 0.26 mol dm^{-3} $MgSO_4$ plus added free PEO (M. W. = 1500) at a volume fraction (Φ_2) of 0.25. The c. f. T. is lowered, at any given value of the particle volume fraction, Φ, compared to that in the absence of added free polymer (line A). This implies that G_{min} has been increased by the addition of the PEO in line with the theoretical prediction of Vincent et al.[6] referred to in the previous section. A further illustration of the effect of c_2 (or Φ_2) on the stability of PS-g-PEO latices is shown in Figure 8.[9] Here the normalised rate constant (s) for flocculation is plotted as a function of Φ_2 for PS-g-PEO (750) latex in the presence of PEO 600 and 10,000 at fixed Φ. The (weak) flocculation observed over a given range of Φ_2 corresponds to predicted effect on $|G_{min}|$ discussed earlier.
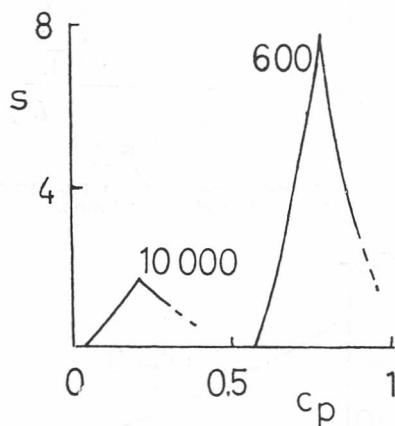

Figure 8. Flocculation rate constant (s) normalized for bulk viscosity changes, plotted against bulk polymer (PEO) volume fraction (C_p), for a PS-g-PEO latex (PEO M.W. = 750) in water, for two different PEO M.W.'s (600 and 10,000).[6]

A general survey and comparison of the stability behaviour of PS-ad-PEO and PS-g-PEO latices in the presence of free PEO has been given recently by Cowell and Vincent.[11]

CONCLUSIONS

It is clear from the discussion of the last section that the stability/flocculation behaviour of the various types of latex plus non-ionic polymer systems referred to is varied and complex. The basic configuration of the

adsorbed layer is paramount in determining the observed behaviour. Therefore further, even qualitative, progress in the interpretation of the experimental observations awaits more detailed determination of the conformational properties of the polymer sheaths in each case, and how these vary with coverage, temperature, electrolyte concentration, etc. Quantitative interpretation awaits further developments in the theory of interparticle interactions; this too depends on detailled knowledge of the specific conformational behaviour of the various types of adsorbed polymer and how this changes with particle separation.

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SAŽETAK

Fenomeni slabe interakcije i reverzibilne flokulacije u sterički stabiliziranim disperzijama

B. Vincent

Teorijski i eksperimentalno je pokazano da su dva osnovna parametra, koji kontroliraju početak i doseg flokulacije u sterički stabiliziranim disperzijama, koncentracija čestica te dubina minimuma slobodne energije za interakciju čestice sa česticom. Pokazano je također da je taj posljednji parametar kontroliran, osim nizom drugih faktora, i debljinom sloja adsorbiranog polimera, te topljivošću i koncentracijom slobodnog polimera u otopini.