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Steric stabilization I

Comparison of theories with experiment

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With 2 figures and 1 table

Introduction

Steric stabilization refers to the stabilization of colloidal particles (e.g., polymer latex particles) against flocculation that is imparted by nonionic macromolecules (1, 2). Several statistical thermodynamic theories of steric stabilization have been proposed since the early experiments by *Zsigmondy* (3) on the "protective action" of natural macromolecules. More recent experimental studies (4–8) on model latices now permit the qualitative validity of the various theories to be assessed. These model latices, which are designed to ensure that the stabilizing macromolecules are attached irreversibly to the surfaces of the particles, appear to undergo reversible, thermodynamic flocculation (4–8).

In what follows we will show that with the notable exception of *Fischer*'s solvency theory (9), all of the theories of steric stabilization advanced heretofore are apparently in conflict with experiment. Possible reasons for these discrepancies are then explored.

Comparison of theories with experiment

We begin by comparing the predictions of the various theories of steric stabilization with the results of experiments.

(i) Entropy theories

Mackor (10, 11) was the first to attempt to calculate the repulsive potential energy in steric stabilization. He argued that the close approach of the two colloidal particles resulted in a decrease in the volume accessible to the stabilizing moieties and thus to a decrease in the configurational entropy of the stabilizing chains. The loss of configurational entropy was calculated for short rods, freely jointed at the particle surface, by using the *Planck-Boltzmann* relationship ($S_{conf} = k \ln W$) (10). The free energy of repulsion (ΔG_R) was then calculated from $\Delta G_R = -T \Delta S_{conf}$. Using essentially this approach *Clayfield* and *Lumb* (12–15) have performed elaborate *Monte Carlo* calculations for stabilizing polymer chains to find ΔS_{conf} and hence ΔG_R.

It is clear that calculations of this type seemingly ignore the presence of any molecules of the dispersion medium (hereafter also termed the solvent) that are associated with the chains. The macromolecules alone are assumed to contribute to ΔS_{conf}. This approach implies that a stable dispersion once formed, cannot be flocculated merely by changing the solvency of the dispersion medium. Yet there is compelling experimental evidence (4–8) to show that the solvency of the dispersion medium critically determines the stability of sterically stabilized dispersions. Moreover there exist thermodynamic arguments (7) which imply that those dispersions that flocculate on heating (e.g., many aqueous latices) are enthalpically stabilized, not entropically stabilized. *Mackor*'s approach ignores all enthalpy changes.

We infer that theories of steric stabilization that are couched solely in terms of the configurational entropy of the polymer and that ignore the presence of the solvent are, in general, incompletely formulated. Possibly they may be applicable to some dispersions

for which the dispersion medium is an athermal solvent for the stabilizing chains.

We also conclude that the synonymous use (16–18) of the terms "steric" and "entropic" stabilization is both incorrect and misleading. Sterically stabilized dispersions may be stabilized either entropically or enthalpically, or by a combination of enthalpic and entropic mechanisms (5, 7, 19).

(ii) Fischer's solvency theory

In an article published in this journal, *Fischer* (10) was the first to point out the critical importance in steric stabilization of the quality of the solvency that the dispersion medium displays towards the stabilizing chains. According to *Fischer*'s theory, if the dissolved polymer sheaths surrounding two sterically stabilized particles were to interpenetrate, the chemical potential of the solvent in the interaction zone would decrease. A gradient in chemical potential would thus be established between the solvent molecules in the interaction zone and those in the external dispersion medium. As a result, solvent external to the interaction zone would diffuse into the zone and so force the stabilizing moieties, and the particles, apart. This corresponds to the generation of an excess osmotic pressure. *Fischer* related the repulsive potential energy to the second virial coefficient (B) of the polymer in *free* solution using the *Flory-Huggins* theory:

$$\Delta G_R \sim 2 B R T \langle c_g \rangle (\Delta V) \qquad [1]$$

where $\langle c_g \rangle$ is the mean segment concentration and (ΔV) is the overlap volume.

It must be admitted that several important criticisms of *Fischer*'s theory may be raised: first, the use of a mean segment concentration is obviously an approximation because the segment density is a function of the distance from the particle surface; second, *Fischer*'s theory by concentrating on interpenetration tends to ignore the compression of the polymer chains that must occur when the minimum distance between the particle surfaces is less than the contour length of the polymer chains. We note also that *Fischer*'s theory disregards all virial coefficients higher than the second.

Despite these obvious quantitative shortcomings, *Fischer*'s theory predicts all the qualitative features of incipient flocculation that have been observed thus far (4–8). These features are discussed in detail below but briefly *Fischer*'s theory predicts (i) that

instability should be evident in solvents worse than θ-solvents, (ii) that the transition from stability to instability should occur near to the θ-point and (iii) that no marked dependence of the incipient instability point upon the molecular weight of the stabilizing moieties or the particle radius should be observed. Although all of these qualitative predictions have been verified experimentally (4–8), this does not imply that *Fischer*'s theory is necessarily correct quantitatively.

(iii) Entropy plus solvency theories

The assumption by *Fischer* that the mean segment concentration may be used to calculate the distance dependence of the repulsive potential energy is obviously an approximation. It corresponds to approximating the segment density by a step function. *Meier* (20) therefore evaluated the segment density distribution function at planar interfaces for linear chains terminally attached at one end ("tails"). His calculations are incorrect due to the inclusion of certain conformations that actually penetrate the impenetrable particle surfaces (21). *Hesselink* (21, 22), has corrected this mistake and extended the theory to "loops" (i.e., linear chains which are attached at both ends). The distribution functions of both *Meier* and *Hesselink* fail to go to zero at distances greater than the contour lengths of the attached chains; however, this shortcoming may be neglected for many purposes.

Meier (20) also combined the entropy approach of *Mackor* (10) and *Clayfield* and *Lumb* (12–15) with *Fischer*'s solvency theory (9) to produce a generalized hybrid theory of steric stabilization. His quantitative predictions are in error because of the use of an incorrect segment density function as mentioned previously. Again, *Hesselink, Vrij* and *Overbeek* (23) (HVO) have corrected this error and extended the theory to stabilization by loops.

The major predictions of the HVO theory for dispersions of flat plates stabilized by tails are succinctly presented in fig. 1. This displays the predicted lines of demarcation between stable and unstable dispersions for varying molecular weight of the stabilizing polymer, different surface coverages and different edge lengths. The abscissa, the intramolecular expansion factor α, is a measure of the quality of the solvency of the dispersion medium for the stabilizing macro-

molecules. Although these results apply to tails, HVO theory for loops undoubtedly predicts qualitatively similar conclusions. Moreover, HVO admit that qualitatively similar findings will hold for spheres, although quantitative differences will be evident; this is substantiated in Part II by the use of the *Deryagin* (24) method for calculating the repulsion for spheres from the repulsion potential for flat plates.

The following comparisons of the predictions of the HVO theory (23) with experiment may be made:

(a) It is clear from fig. 1 that the points corresponding to $\alpha = 1.00$ (i.e., to θ-solvents) have no special significance *vis-à-vis* flocculation. Theta points are just like other
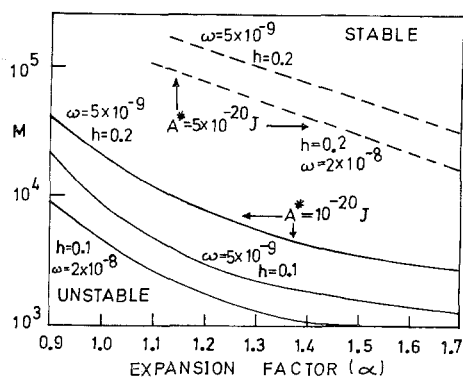

Fig. 1. The lines of demarcation between stable and unstable dispersions of flat plates according to HVO theory. The stabilizing moieties are tails: ω is the weight of stabilizer per unit surface area (g/cm²), h is the plate length (μm)

points on the curves. Yet there is abundant experimental evidence (4–8), which will not be fully retabulated here because it is too extensive, that the θ-point corresponds closely to the limit of stability of sterically stabilized dispersions. (Some typical results are, however, included below in table 1.) The θ-point and the critical flocculation point (c.f.p.) correlate strongly for both aqueous and non-aqueous latices whether flocculation is induced by addition of non-solvent, or by heating or cooling the latices. Over 40 different c.f.p.s. have been shown to correlate with their corresponding θ-points (4–8, 19).

Apparently HVO theory fails to predict this correlation between the c.f.p. and the θ-point.

(b) The HVO theory implies that the boundary between stability and instability is strongly dependent upon the molecular

weight (M) of the stabilizing moieties (fig. 1). For a decade increase in M, α is predicted to decrease from e.g., 1.7 to 1.1. This is a large change in α. These two α values may be substituted into, e.g., the *Flory* relationship (25):

$$\alpha^5 - \alpha^3 = 2C_M\psi_1(1 - \theta/T)M^{1/2} \qquad [2]$$

where $\psi_1 = $ entropy of dilution parameter and $\theta = (\varkappa_1/\psi_1)T$, where $\varkappa_1 = $ enthalpy of dilution parameter. The parameter C_M in eqn. [2] is a constant for a given polymer in a given solvent such that

$$C_M = (27/2^{5/2}\pi^3)(\bar{v}_2^2/N_A \bar{V}_1)(M^{3/2}/\langle r^2 \rangle_0^{3/2})$$

where $\bar{v}_2 = $ partial specific volume of the polymer, $\bar{V}_1 = $ molar volume of the solvent and $\langle r^2 \rangle_0^{1/2} = $ unperturbed r.m.s. end-to-end length of the polymer chains in *free* solution. It is found from eq. [2] that the large change in α from 1.7 to 1.1 corresponds to a change in the c.f.p. of at least 100–200°K, for a θ-temperature within 50 °K of room temperature. The flocculation temperature of two latices stabilized by polymer chains which differ in molecular weight by a factor of ten should thus differ by 100–200 °K according to the HVO theory.

Table 1. Molecular weight dependence of the critical flocculation temperature (C.f.t.)

Stabilizing moieties	$\langle M \rangle$	C.f.t. (°K)	θ (°K)
PEO	1.0×10^6	317 ± 2	315 ± 3
PEO	8.0×10^5	316	316
PEO	3.2×10^5	315	314
PEO	9.6×10^4	316	315
PEO	4.9×10^4	316	314
PEO	2.3×10^4	314	315
PEO	1.0×10^4	318	319
PAA	9.8×10^3	287 ± 2	287 ± 5
PAA	1.9×10^4	289	287
PAA	5.2×10^4	283	287
PAA	9.0×10^4	281	287

Table 1 summarizes the incipient instability results obtained with latices stabilized by poly(ethylene oxide) (PEO) (5) and by poly(acrylic acid) (PAA) (8). The critical flocculation temperature (c.f.t.) is the temperature at which a sharp transition from stability to instability is observed. This was achieved by heating the latices stabilized by PEO but by cooling the latices stabilized by PAA. The former are enthalpically stabilized whereas the latter are entropically stabilized (4, 7, 8). The molecular weight of the PEO was varied over three decades

and that of PAA over one decade. Although small changes (< 10 °K) were evident, the c.f.t. was quite insensitive to M. Certainly any changes in c.f.t. are at least an order of magnitude less than those predicted by the HVO theory.

These experimental results, moreover, are consistent with those discussed in paragraph (a) above where it was mentioned that the c.f.p. correlates strongly with the θ-point. Because the θ-point is in principle independent of M, so must the c.f.p. (in this case the c.f.t.) be independent of M if the results are to be internally consistent.

Clearly the predictions of the HVO theory with respect to M are not substantiated by experiments with model dispersions.

HVO (23) cited the early data of *Heller* (2) as evidence for the validity of their theory. *Heller* did in fact observe a molecular weight dependence of the flocculation point (at least for lower values of M) of electrostatically stabilized latices that were additionally stabilized by *unanchored* PEO. These latices flocculated, e.g., in 0.5 M KCl at 20 °C. We have repeated *Heller*'s experiments and confirm the essential correctness of his observations. However latices stabilized by *anchored* PEO chains are quite stable in 0.5 M KCl. Indeed they are quite stable in 3 M KCl, which is a substantially worse solvent for PEO than is 0.5 M KCl. Apparently dispersions stabilized by unanchored PEO chains flocculate in 0.5 M KCl because the chains are not sufficiently well-anchored to the particle surface. This may be due to either lateral movement of the PEO away from the interaction zone or even desorption, both of which are expressly forbidden by the assumptions of the HVO theory. The molecular weight dependence observed with unanchored chains appears to be an artifact of displacement flocculation (7). *Molau*'s emulsion studies (25–28) suffer from the same artifact: our emulsion studies suggest that it is very difficult to eliminate displacement flocculation with emulsions (29).

Of course the values of M cited in table 1 refer to the overall molecular weight of the chains. The possibility must be considered that adsorption onto the surface at various points along the chains may drastically reduce these nominal values. There exists, however, convincing experimental evidence against this possibility: first, ultracentrifuge studies of the conformation of the chains attached to the particles (30) suggest that the stabilizing chains are quite extended

normal to the surface, as indeed *Ottewill* (31) has also found in similar systems; second, for fully covered particles the surface area needed to convert extended polymers of nominal $M = 1 \times 10^6$ into polymers of actual $M = 1 \times 10^3$ by adsorption (either on close approach of the particles or on changing the solvency) is greater than the available area by a factor of ca. 10^3; third, when suitable surface groups are provided to generate additional adsorption of the stabilizing chains onto the surface in this way, experiments show that no longer is it possible to apply the thermodynamic parameters for the polymers in free solutions because the chains are too constrained (32). The θ-temperatures in table 1 all refer to the chains in free solution. We conclude that adsorption at points along the chains cannot explain the large discrepancy between HVO theory and experiment.

(c) HVO theory predicts that stability may be observed in solvents considerably worse than θ-solvents. It follows from what has been summarized in paragraphs (a) and (b) that such stability has not been observed for either tails or loops. We have in fact observed stability in solvents somewhat worse than θ-solvents but only when the polymer chains have been anchored at so many points (multipoint anchoring) that the free solution properties of the polymer are no longer relevant (32). This phenomenon may be termed "enhanced" steric stabilization.

(d) The HVO theory predicts that the stability of latices should be inversely dependent upon the particle radius in *Deryagin*'s approximation. We have shown that the c.f.p. of both aqueous and non-aqueous sterically stabilized latices are quite insensitive to the particle radius (4, 5, 7, 8). Again the HVO theory appears to lead to erroneous predictions.

We conclude that the major predictions of the HVO theory appear to be at odds with the results of experiments on model latices. The validity of the HVO theory must therefore be called into question. In particular, the experimental results suggest that the HVO theory appears to contain a significant term that improperly fails to become small near the θ-point

Formulation of entropy plus solvency theories

We now offer one possible origin for the disagreement between HVO theory and

experiment. It is proposed that the discrepancy arises from an insidious difficulty that intrudes when the entropy and solvency theories are combined. The HVO theory (23), following that of *Meier* (9), calculates the repulsive free energy by considering two processes:

(i) The loss of configurational free energy of the polymer molecules *alone* on the approach of the second particle. This is termed the volume restriction (VR) effect and is the effect postulated by *Mackor* (10).

(ii) An osmotic pressure (OP) effect that results from the interpenetration and compression of the polymer chains on close approach of the particles. This is, at least in part, the contribution first discussed by *Fischer*.

Contribution (i) was calculated from the loss of configurational entropy of random flight "lines-in-space" chains, composed of non-interacting segments. Contribution (ii) was calculated using the *Flory-Krigbaum* theory (33).

Fig. 2 provides a diagrammatic representation of what happens when two sterically stabilized flat plates are brought from infinite separation to a finite separation (d). The concomitant free energy change (ΔG_R) is the repulsive potential energy. When
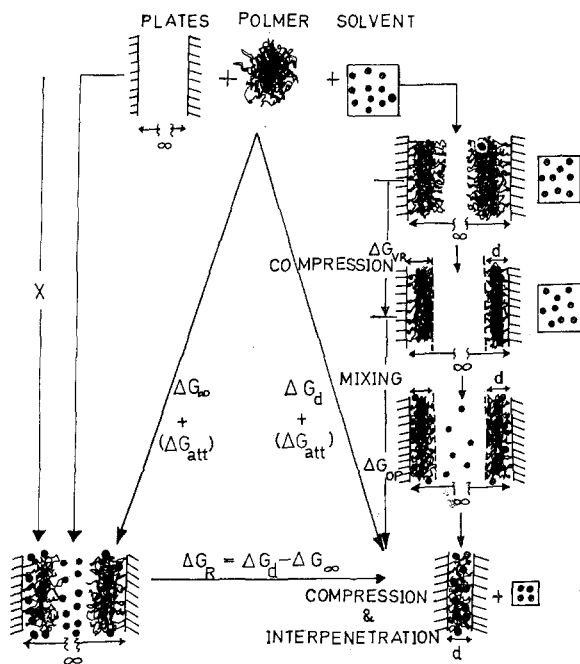

Fig. 2. Diagrammatic representation of the close approach of two flat plates and the calculation of the Gibbs free energy change using the *Flory-Krigbaum* theory

$L \leqslant d < 2L$, where L is the contour length of the polymer chains (assumed to be monodisperse), only interpenetration can be operative. But when $d < L$, both interpenetration and compression may occur (4, 5).

To illustrate precisely what HVO have calculated, we have split up the process in fig. 2 into various steps. The standard state for the polymer in *Flory-Krigbaum* theory is pure, randomly oriented polymer chains whose centres of gravity are fixed in space. No problems arise in step X where the plates are coated with stabilizing chains at infinite separation. Note that we need not include the free energy of attachment (ΔG_{att}) of the chains to the plates in the following discussion; the centres of gravity are fixed in the standard state and ΔG_{att} may reasonably be assumed to be independent of the distance of separation. *Flory-Krigbaum* theory is directly applicable to find ΔG_∞, but step Y, which produces compressed polymer, is not straightforward in the HVO formulation. The prior calculation of the free energy of volume restriction (ΔG_{VR}) results in the solvent being mixed with *compressed* polymer chains in this step. Note, however, that compressed chains are not the standard state for the polymer in *Flory-Krigbaum* theory, yet the HVO theory is forced to treat them as such if the results of the *Flory-Krigbaum* theory are to be applicable to this step and the volume restriction term is calculated separately. It is this difficulty with the standard state that appears to render the predictions of the HVO theory inapplicable to real chains.

Assuming that the free energy of attachment of the polymer chains is independent of the distance of separation of the plates, thermodynamic considerations of fig. 2 yield

$$\Delta G_R = \Delta G_d - \Delta G_\infty. \qquad [3]$$

This shows that the volume restriction term is allowed for implicitly in this type of application of *Flory-Krigbaum* theory. (This is explicitly proven in the development of the basic dissolution equation in Part II). The origin of the improperly vanishing term in HVO theory thus becomes apparent. It is the volume restriction term, which clearly is non-zero in a θ-solvent or any solvent for that matter.

There is a sense in which this non-zero term is inevitable if a polymer chain in a θ-solvent is considered to be thermodynamically (as distinct from conformationally) equivalent to a random flight chain, com-

posed of non-interacting lines-in-space, as assumed by HVO. The latter model chain loses configurational entropy on compression and no enthalpy changes need be considered because the non-interacting system is essentially athermal. Real polymer chains in θ-solvents also lose configurational entropy on compression; however, because θ-solvents, are not athermal [except at the experimentally inaccessible absolute zero of temperature (34)] but rather slightly poor solvents there is an additional (usually counteracting) enthalpy change that is involved in compression. It is this enthalpy term associated with compression that is apparently unaccounted for in the HVO theory. In Part II we show that an extension of *Fischer*'s solvency theory permits this term to be included.

Finally we note in agreement with the foregoing discussion that *Doroszkowski* and *Lambourne* (35), as a result of their measurements on steric barriers, have concluded that models which ignore the volume restriction term best describe their experimental results.

Summary

A comparison is presented between the qualitative predictions of the various theories of steric stabilization with the results of experiments. It is shown that with the notable exception of *Fischer*'s solvency theory, all of the theories advanced to-date are at odds with results of experiments.

Possible reasons for these discrepancies are discussed.

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