Enhanced Steric Stabilization

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An extensive series of experiments has previously demonstrated that for model sterically stabilized dispersions, θ-solvents for the stabilizing chains in free solution represent the limit of colloid stability. It has now been shown that by anchoring the stabilizing chains to the particle surfaces at many points along the chains, the pattern of flocculation behavior may be profoundly altered. Polystyrene latices stabilized by poly(ethylene oxide) have been prepared that are stable in dispersion media with solvency for the stabilizing moieties markedly worse than θ-solvents for the chains in free solution. Multipoint anchoring in these systems results from the hydrogen bonding between the ether oxygens of the stabilizer and surface carboxylic acid groups. The enhancement of steric stabilization is a function of the pH and the molecular weight of the stabilizing chains. It originates in the perturbation of the conformation of the stabilizing macromolecules that renders the free solution properties of the chains no longer relevant.

INTRODUCTION

An extensive series of experiments (1–5) has shown that for model sterically stabilized dispersions, a strong correlation exists between the point of incipient instability and the corresponding theta (θ)-point for the stabilizing moieties in free solution. This correlation has been demonstrated for both aqueous and nonaqueous dispersion media, irrespective of whether flocculation is induced by heating or cooling, or by the addition of nonsolvent. At least sixty critical flocculation points (cfp's) have now been correlated with their corresponding θ-points. A quantitative theoretical description of steric stabilization has also been developed recently (6, 7).

Whether or not stable sterically stabilized dispersions can be prepared in θ-solvents themselves remains a moot point. Certainly by definition the second, and therefore the third (8), virial coefficients of the stabilizing moieties in free solution must vanish in θ-solvents. As the major component of the repulsion in steric stabilization originates in these two nonideal components, any repulsion in θ-solvents must necessarily be relatively small. The fourth and higher virial coefficients are, however, nonzero in θ-solvents; presumably these nonideal components may be sufficiently large at high segment densities to impart stability in θ-solvents. In addition Born repulsion between polymer segments, which is disregarded in all theories advanced to date, may also contribute to stabilization. Unfortunately the experimental results to date lack sufficient precision to establish whether or not stable dispersions may be prepared in θ-solvents.

Nonetheless it can be stated quite categorically that there are no previously reported examples of sterically stabilized dispersions that exhibit stability in dispersion media which are markedly worse solvents than θ-solvents for the chains in free solution. By markedly worse solvency we mean that

The case of coagulation by shear viscous flow is interesting in that respect in that we deal with the situation $\lambda = 1$ which was not considered above. The dependence $K(g, n) = (g^{\frac{1}{3}} + n^{\frac{1}{3}})^3$ possesses a number of features which simplify the solution of Eq. [1]. The details of the solution will be published elsewhere. Here we only note that the results in this case are very similar to those obtained for the model $K(g, n) = g + n - 1$. An interesting circumstance is that the asymptotic form of the size distribution differs from the self-preservation form. In this case $c_g = N^4\psi(gN^2)$ rather than $c_g = N^2 f(gN)$ as assumed by Swift and Friedlander (10). It is a consequence of the divergency of integrals on the left-hand side of Eq. [2] at a low limit ($n = 0$).

3. The result [28] is seen to be very close to the Friedlander self-preservation hypothesis (see Eq. [5]). Substituting Eq. [30] into Eq. [28] we obtain:

$$c_g = N^2\psi(gN).$$

It should be emphasized however that the scaling theory has a different sense. The regime [28] arises as a consequence of the scaling invariance of Eq. [2], and the dependence of ψ on the argument $gt^{-1/(1-\lambda)}$ appears independently of the fact that

$$N(t) \sim t^{-1/(1-\lambda)}.$$

APPENDIX

Here we derive the recurrence relations [20] and [21]. Let us substitute

$$\nu_g(\tau) = \tau^{g-1} \sum_{k=0}^{\infty} b_g{}^k \tau^k \qquad [A1]$$

into Eq. [12] and gather the coefficients of equal powers of τ. The coefficients of τ^k on the left-hand side of Eq. [12] is of the form:

$$(k + g - 1)b_g{}^k. \qquad [A2]$$

The substitution of Eq. [A1] into the first term on the left-hand side of Eq. [12] yields

$$\sum_{n=1}^{g-1} \sum_{l,l'=0}^{\infty} K(g-n, n) b_n{}^l b_{g-n}{}^{l'} \tau^{l+l'}.$$

Introducing $l' = k - l$ we find the coefficient at τ^k

$$\sum_{n=1}^{g-1} \sum_{l=0}^{k} K(g-n, n) b_{g-n}{}^l b_n{}^{k-l'}. \qquad [A3]$$

After the substitution of Eq. [A1] into the second term it takes the form:

$$\sum_{n=1}^{\infty} \sum_{l,l'=0}^{\infty} L(g, n) b_g{}^l b_n{}^{l'} \tau^{n+l+l'}.$$

Again, replacing $n + l + l' = k$, $l' = k - p$, $l = p - n$, we obtain the coefficient of τ^k:

$$\sum_{p=1}^{k} \sum_{n=1}^{p} L(g, n) b_g{}^{p-n} b_{k-p}{}^n. \qquad [A4]$$

Grouping Eqs. [A2]–[A4] we obtain to the relations [20] and [21].

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incipient flocculation would only be evident in excess of 10 K beyond the free solution θ-temperature. Flory (9) and others (7, 10) have stated clearly the reason for this: in solvents worse than θ-solvents the stabilizing sheaths are self-attracting, i.e., collisions are "sticky," and so the particles flocculate. Recent calculations have verified the essential correctness of this view (7).

We have now found that by using the phenomenon of multipoint anchoring of the stabilizing moieties to the particle surface, it is possible to prepare latices that display stability in dispersion media of considerably worse solvency than θ-solvents for the chains in free solution. This is possible because the anchoring of the macromolecules at many points along the chains so changes their conformation that the free solution properties of the chains are no longer relevant. An experimental investigation of this phenomenon, which we have termed "enhanced steric stabilization" (6), is now presented.

THEORY

We begin by establishing via a new theoretical route that, to a first approximation, θ-solvents for the stabilizing chains in free solution are the limit of colloid stability for dispersions sterically stabilized by tails or loops. By tails and loops we imply linear high polymers that are attached to the particle surface at one and both ends, respectively. We will assume that the configurational entropy of the core particles in the dispersion medium may be neglected; this is, of course, a standard assumption in colloid stability theory (e.g., in DLVO theory) but it could perhaps introduce some inaccuracy in certain circumstances. We shall, of course, take into account the configurational entropy of the stabilizing chains.

We want now the free energy of mixing ($\Delta\tilde{G}_M$) of randomly oriented tails or loops, whose centers of gravity are fixed in space, with solvent molecules. This is readily obtained from the theory developed by Flory and Krigbaum (11):

$$\Delta G_M{}^{FK} = \Delta G^{ATT} + \Delta\tilde{G}_M. \qquad [1]$$

Here $\Delta G_M{}^{FK}$ is the free energy of mixing of pure randomly oriented polymer chains, whose centers of gravity are fixed in space, with pure solvent, and ΔG^{ATT} is the free energy of attachment of randomly oriented chains to form tails or loops in the absence of solvent molecules. Thus

$$\Delta\tilde{G}_M = -\Delta G^{ATT} + kT[\tilde{n}_1 \ln (1 - \tilde{v}_2) + \tilde{n}_1 \chi_1 \tilde{v}_2]. \qquad [2]$$

where n_1 is the number of solvent molecules, v_2 is the volume fraction of the polymer segments, and χ_1 the polymer–solvent interaction parameter for chains in free solution. Note that the tilde is used to denote that the quantity refers not to the total system but only to that part of the system which is accessible to the stabilizing chains if the particles were all fixed in space. This differentiation is necessary because the Flory–Krigbaum theory (11) cannot be applied to the system as a whole: those regions of the dispersion medium between the coated particles contain a negligibly small polymer concentration which violates one of the basic requirements for the application of the Flory–Krigbaum theory. Only in the spatial regions occupied by the stabilizing chains is the segment density function sufficiently large and continuous to justify the Flory–Krigbaum approach.

To calculate the excess chemical potential of the solvent in the volume accessible to the polymer we need $[\partial(\Delta\tilde{G}_M)/\partial\tilde{n}_1]_{T,P}$. This differential is easily evaluated if we recall that $\tilde{v}_2 = (\tilde{n}_2 x)/(\tilde{n}_1 + \tilde{n}_2 x)$, where $\tilde{n}_2$ is the number of tails or loops and x is the number of lattice sites occupied by each chain, assumed to be monodisperse. Consequently, on differentiation we have

$$\tilde{\mu}_1 - \mu_1{}^0 = RT[\ln (1 - \tilde{v}_2) + \tilde{v}_2 + \chi_1 \tilde{v}_2{}^2], \qquad [3]$$

where $\mu_1{}^0$ is the standard chemical potential of the solvent (i.e., the chemical potential of pure solvent). Note that we have here ignored the configurational entropy of the core particles and so for equilibrium we may set $\tilde{\mu}_1 = \mu_1$, where the absence of the tilde denotes the system as a whole.

Flory (12) has shown that the requirements for incipient noncrystalline phase separation of the polymer solutions are

$$[\partial\mu_1/\partial v_2]_{T,P} = 0, \qquad [4]$$

$$[\partial^2\mu_1/\partial v_2^2]_{T,P} = 0. \qquad [5]$$

Phenomenologically we may relate incipient phase separation to incipient flocculation of sterically stabilized particles. Equations [4] and [5] can then be used to identify the critical flocculation point. The equivalent relationships in this case are

$$[V_T/\tilde{V}_T][\partial\tilde{\mu}_1/\partial\tilde{v}_2] = 0, \qquad [6]$$

$$[V_T/\tilde{V}_T][\partial^2\tilde{\mu}_1/\partial\tilde{v}_2^2] = 0, \qquad [7]$$

where V_T is the total available volume and $\tilde{V}_T$ is the volume accessible to the chains.

Combining Eqs. [3] and [6] yields

$$1/(1 - \tilde{v}_2) - 1 = 2\chi_1\tilde{v}_2, \qquad [8]$$

whereas Eqs. [3] and [7] yield

$$1/(1 - \tilde{v}_2)^2 = 2\chi_1. \qquad [9]$$

The solution of Eqs. [8] and [9] that is relevant is $\chi_1 = \frac{1}{2}$. This shows that to a first approximation θ-solvents, which are characterized by $\chi_1 = \frac{1}{2}$, are the limit of stability of particles stabilized by loops and tails (8). A very considerable body of experimental evidence (1-5) supports this theoretical conclusion. The conclusion is, however, at odds with that of Hesselink, Vrij, and Overbeek (13) who predict stability in dispersion media considerably worse than θ-solvents for dispersions stabilized by either tails or loops. The reason for their erroneous prediction has been pointed out elsewhere (6) but briefly it resides in assuming in the calculation of polymer compression that all θ-solvents are athermal. Flory (14) has asserted that θ-solvents are only athermal at the experimentally inaccessible temperature of absolute zero.

The foregoing discussion implies that if stability is observed in solvents markedly worse than θ-solvents, specific interactions may be operative between the stabilizing chains and the particles so that the chains are no longer tails or loops.

EXPERIMENTAL

Two types of polystyrene latices were prepared by emulsion polymerization. The first, termed "high carboxyl" latices, were prepared according to the method of Ottewill and Shaw (15) at elevated temperatures ($\geqslant 50$°C), using potassium persulphate or hydrogen peroxide as the initiator and sodium dodecyl sulphate as the surfactant. Potentiometric titrations and electron microscopy established that the latex particles so prepared contained surface carboxylic acids (ca. one carboxyl group per 150-500 Å^2). The "low carboxyl" latices were prepared in a similar fashion but initiation by potassium persulphate was effected at 20-30°C and oxygen was rigorously excluded from the system. The complete absence of surface carboxyl groups could not be established unequivocally for these latices but the surface concentration of carboxyl groups was sufficiently small for them not to be detectable by potentiometric titration. Poly(vinyl acetate) latices were prepared by the solution polymerization of vinyl acetate in the absence of surfactant (16); no surface carboxyl groups could be detected with these latices.

The preparation of the amphipathic block copolymers of poly(ethylene oxide) with polystyrene and poly(vinyl acetate) has been described previously (2), as have the measurements of the critical flocculation temperatures and the poly(ethylene oxide) viscosity average molecular weights.

RESULTS

The critical flocculation temperature (cft) of various aqueous latices coated with well-anchored poly(ethylene oxide) (PEO) chains was determined in 0.39 *M* $MgSO_4$. All latices

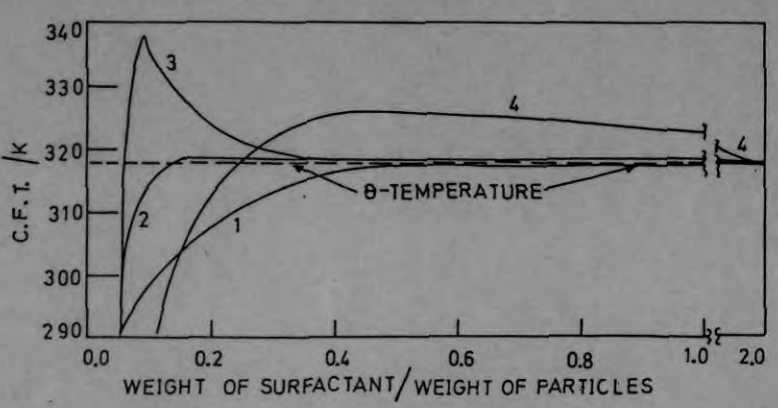

FIG. 1. Plots of the cft versus the ratio of the nominal weight of stabilizer in the bulk phase to the weight of latex particles. PEO molecular weight is 10,000 and pH = 4.65. Curve 1—poly(vinyl acetate) latices; curve 2—"low carboxyl" polystyrene latices; curve 3—"high carboxyl" polystyrene latices; curve 4—poly(styrene-*co*-acrylic acid) latex particles.

flocculated on heating, demonstrating that the latices were enthalpically stabilized (4). The cft of these latices is defined as the minimum temperature at which flocculation was evident (2, 3).

Shown in Fig. 1 are plots of the cft versus the nominal concentration of the amphipathic PEO stabilizer, the PEO chains having a viscosity average molecular weight ($\langle M_V \rangle$) of 10,000. Although these plots are not strictly adsorption isotherms, the adsorption of the stabilizer presumably increases monotonically to a constant value as the abscissa increases. Smooth curves have been drawn through the large number of points that were determined for each curve.

For poly(vinyl acetate) latices, the cft increased monotonically with increasing concentration of stabilizer (curve 1) to the limiting value corresponding to the θ-temperature (318 K) for free PEO chains in 0.39 *M* $MgSO_4$ (2, 17). Similar results were obtained for "low carboxyl" polystyrene latices (curve 2). The "high carboxyl" latices, however, exhibited a definite maximum (curve 3) in their cft. The maximum (in this case 338 K) was significantly higher than the θ-temperature, showing that in the vicinity of the cft it is possible to prepare latices that are stable in dispersion media considerably worse than θ-solvents. This is the phenomenon of enhanced steric stabilization. Note that the position of the maximum along the abscissa axis depends upon the efficiency of the anchor group in attaching the PEO to the particle surface. Beyond the maximum the cft decreased to the θ-temperature. Clearly it was only at the lower concentrations of stabilizer that enhanced steric stabilization was observed and then only with the "high carboxyl" latices.

Dispersions that exhibited enhanced steric stabilization flocculated irreversibly. Only at higher stabilizer concentrations, when the cft was close to the θ-temperature, was reversible flocculation observed.

It was suspected that the existence of enhanced steric stabilization was associated with the hydrogen (H) bonding between the –OH groups in the surface carboxyl groups and the ether oxygen of the PEO chains. To test this hypothesis the cft's were determined for a PEO of $\langle M_V \rangle = 10{,}000$ at three pH values (2.06, 4.65, and 10.6). Some results are shown in Fig. 2. At the lowest pH the cft maximum was significantly higher than that for pH = 4.65. No curve is shown for the alkaline pH because at the concentrations of stabilizer corresponding to the maximum in the cft curves, the "high carboxyl" polystyrene latices flocculated at temperatures well below room temperature.

The influence of the molecular weight of the

bilizing PEO on enhanced steric stabiliza-
n is displayed in Fig. 3. The same "high
rboxyl" latex was used in all experiments.
ry high molecular weight PEO ($(\langle M_V \rangle$
800,000) did not seemingly exhibit a maxi-
m in the cft and no enhanced steric stabiliza-
n was observed with this polymer at this
I. However, as the molecular weight was de-
eased the maximum in the cft plots ap-
ared. The maximum was small for a PEO
$\langle M_V \rangle = 96{,}000$ but it increased significantly
the molecular weight decreased. For a
EO of $\langle M_V \rangle = 1540$ the enhancement of
eric stabilization was so large that the cft
the range of the dotted line of Fig. 3 ex-
eded the boiling point of the aqueous dis-
rsion medium and so could not be measured.
he data are, however, strongly suggestive of
maximum in the curve. The cft in this case
creased only very slowly at higher stabilizer
ncentrations.

Particles of polystyrene into which 10%
rylic acid had been copolymerized were also
ed as the adsorbent for anchored PEO.
hese particles were prepared under conditions
at normally gave "low carboxyl" latices.
he latices, which also possessed surface
rboxyl groups, exhibited enhanced steric
abilization (curve 4 in Fig. 1). The cft peak
as, however, quite broad.

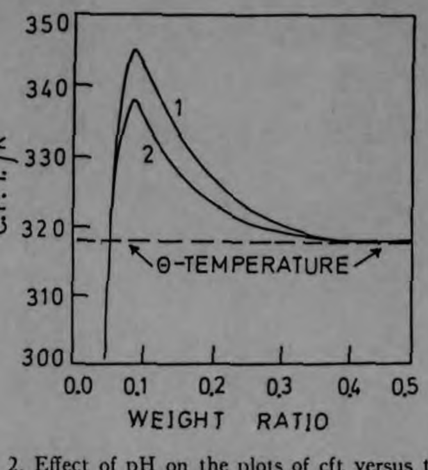

FIG. 2. Effect of pH on the plots of cft versus the ratio of the weight of stabilizer to the weight of latex particles. PEO molecular weight is 10,000. Curve 1—pH = 2.06; 2—pH = 4.65.

DISCUSSION

The foregoing results are consistent with the hypothesis that enhanced steric stabilization results from H bonding between the -OH group of the surface carboxyl species and the PEO ether oxygens (Fig. 4). In the absence of surface carboxyl groups, e.g., with poly(vinyl acetate) latices, no definite maximum was observed in the cft plots. As the bulk stabilizer concentration was increased more PEO chains were presumably adsorbed; in the plateau region the particles were fully coated. Reversible flocculation was then observed close

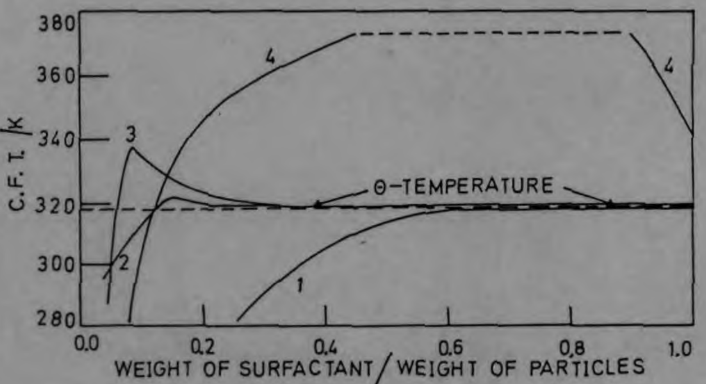

FIG. 3. Effect of PEO molecular weight on the plots of cft versus the ratio of the weight of stabilizer to the weight of latex particles at pH = 4.65. $\langle M_V \rangle$: curve 1—800,000; curve 2—96,000; curve 3—10,000; curve 4—1540.

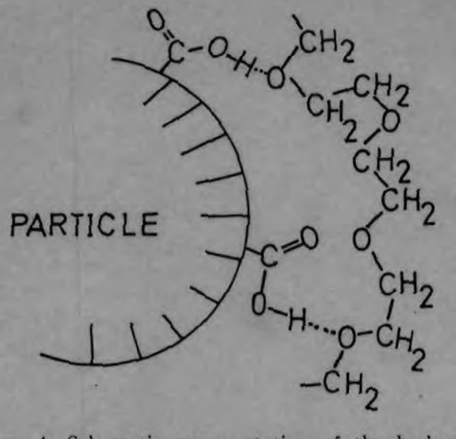

FIG. 4. Schematic representation of the hydrogen bonding interaction between the ether oxygens in PEO and the surface carboxylic acids.

to the θ-temperature for the stabilizing chains in free solution. This is the normal behavior of sterically stabilized latices (1, 15), as predicted by the above theoretical discussion. Note that the electrostatic contribution to stability is negligible at the high ionic strengths studied, as was shown previously (4).

Enhanced steric stabilization was only observed when, in the absence of surface carboxyl groups, the surface would be incompletely covered. This suggests that under these conditions the conformation of the stabilizing moieties is changed because of the many H-bonding interactions between the PEO and the surface carboxyl groups. Presumably the chains interact with the surface so as to adopt a less extended conformation [the transformation (a) to (b) shown in Fig. 5]. As a result of this flat conformation, the thermodynamic parameters that govern segment–solvent and segment–segment interactions are no longer those relevant to the chains in free solutions or to chains attached to interfaces with which they do not interact strongly.

That the change in conformation due to multipoint anchoring can be significant is illustrated by the following approximate calculation. Potentiometric titration studies suggested that there was one carboxyl group per, say, 200 Å^2. For a PEO of molecular weight 10,000, the area occupied by the macromolecule on the surface is approximately 5000 Å^2. Hence, each chain could interact with 25 carboxyl groups. This would on the average lower the molecular weight of the PEO between anchor points to only 200, i.e., pentamer ($-CH_2CH_2O-$) groups. Clearly even interaction with only half of the surface carboxyl groups (as occurs at pH = 4.65) would significantly change the conformation of the PEO chains to one with only a small number of segments between anchor points.

The foregoing discussion suggests that if the surface carboxyl groups were deprotonated, the H bonding could not occur. Thus latices exhibiting enhanced steric stabilization would be converted into latices exhibiting incomplete surface coverage [transformation (b) to

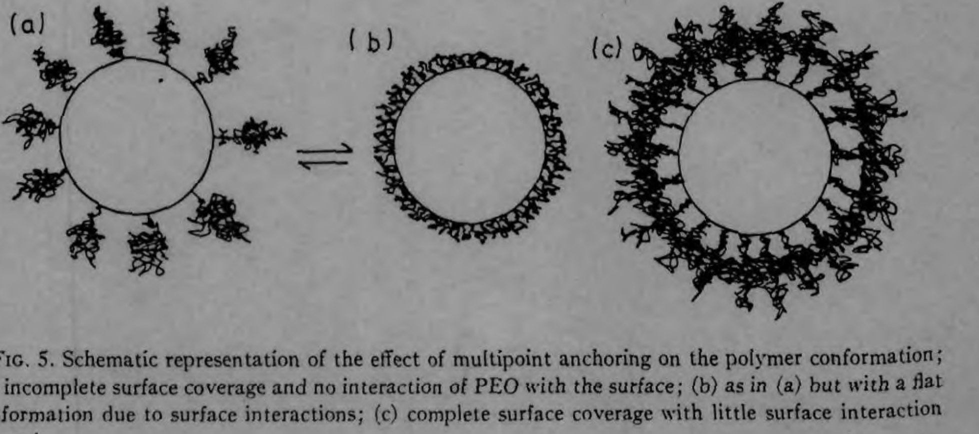

FIG. 5. Schematic representation of the effect of multipoint anchoring on the polymer conformation; (a) incomplete surface coverage and no interaction of PEO with the surface; (b) as in (a) but with a flat conformation due to surface interactions; (c) complete surface coverage with little surface interaction allowed.

(a) in Fig. 5]. Latices with incomplete PEO surface coverage were shown previously (2) to flocculate at lower temperatures. This explains why latices exhibiting enhanced steric stabilization flocculated when the pH of the dispersion medium was made alkaline. Moreover, it explains the increase in the cft maximum when the pH was lowered from 4.65 to 2.06. The surface carboxyl groups have a pK_a corresponding to a bulk pH of 4.6 (15, 18). Thus at pH = 4.65 only about half the surface groups would be protonated. Lowering the pH to 2.06 results in increased protonation of the surface carboxyl groups. The increased interaction of these groups with the PEO chains perturbs the conformation of the stabilizing chains even more than at pH = 4.65. An even greater cft maximum is thus observed.

The decrease in the cft values beyond the maximum is presumably associated with the increased adsorption of the anchored PEO chains on the particle surface. The upshot of this is that to accommodate further stabilizer adsorption, the adsorbed chains must adopt a more vertically oriented conformation [see (c) in Fig. 5] rather than a flat one. Moreover the anchor polymers may well cover many of the surface carboxyl groups. It is scarcely surprising that under these conditions high carboxyl latices flocculate reversibly near to the θ-point for chains in free solution.

The influence of the PEO molecular weight on the enhancement of steric stabilization was marked. Very high molecular weight chains were not significantly influenced by interactions with the surface, presumably because most of the segments are distant from the surface and are not affected by surface interactions. Conversely for very low molecular weight chains almost all the segments are perturbed as the calculation presented above shows. This accentuates the enhancement of steric stabilization.

The experiment on the poly(styrene-*co*-acrylic acid) particles confirms the importance of surface carboxyl groups. The very broad cft observed for this latex probably arises from the projection of the polyacid chains into solution.

The preceding discussion provides a qualitative picture of the likely origin of enhanced steric stabilization. It is necessary to consider more closely why the cft at the maximum is greater than the θ-temperature for the chains in free solution. It is not known as yet whether the cft's observed near the maximum correlate strongly with the θ-temperatures of the perturbed chains. However, in view of the strong correlations reported previously (1–5), this seems likely and we will adopt this assumption in the following discussion.

The critical flocculation temperature (T_C) is obtained by setting ΔG_R ($=\Delta H_R - T\Delta S_R$) $=0$, where ΔG_R is the free energy of close approach of two sterically stabilized particles. Thus for model sterically stabilized PEO lattices (2–5)

$$T_C = \theta = \Delta H_R / \Delta S_R.$$

Experimentally it was found that dispersions that exhibited enhanced steric stabilization flocculated irreversibly. This suggests that in order to induce flocculation it is necessary to break some H-bonding interactions. Bond breakage converts the particles into a system with incomplete surface coverage, which has been shown previously to result in irreversible flocculation (2). Therefore, we may write

$$T_C = \frac{\Delta H_R + (n/N_A)\Delta \bar{H}_{HYD}}{\Delta S_R + (n/N_A)\Delta \bar{S}_{HYD}}, \quad [10]$$

where N_A is Avogadro's constant, n the number of H bonds formed in the interaction zone, and $\Delta \bar{H}_{HYD}$ and $\Delta \bar{S}_{HYD}$ are the molar enthalpy and entropy changes associated with H-bonding. If we consider the H-bonding terms as perturbations of ΔH_R and ΔS_R, we can use the binomial theorem to transform Eq. [10] into

$$T_C = \theta + \theta\left(\frac{n}{N_A}\right)\left(\frac{\Delta \bar{H}_{HYD}}{\Delta H_R}\right) - \theta\left(\frac{n}{N_A}\right)\left(\frac{\Delta \bar{S}_{HYD}}{\Delta S_R}\right), \quad [11]$$

where terms higher than the first are neglected and θ refers to chains in free solution.

We have shown previously (4) that ΔH_R and ΔS_R are both positive. Intuitively both $\Delta\bar{H}_{HYD}$ and $\Delta\bar{S}_{HYD}$ should be negative. Provided that $|\Delta\bar{S}_{HYD}/\Delta S_R| > |\Delta\bar{H}_{HYD}/\Delta H_R|$, Eq. [11] predicts cft values larger than θ. In agreement with the preceding discussion enhanced steric stabilization should therefore result from the significant decrease in configurational entropy that H-bonding interactions impose on the stabilizing chains. Moreover, Eq. [11] predicts a maximum in the cft as n increases to a maximum and then decreases to near zero. It also suggests that as

$$\Delta S_R \gg (n/N_A)\Delta\bar{S}_{HYD}$$

for high molecular weight chains, surface interactions should not perturb the cft greatly in this case; conversely a large increase in cft should be evident for low-molecular-weight chains, as observed experimentally.

The foregoing discussion hinges on the assumption that surface carboxylic acids can H bond with ether oxygens. Pimentel and McClellan (19) in their classic book on H-bonding list carboxylic acids and ethers as well recognized H-bonding acids and bases, respectively. They also assert that the properties of any combination of these compounds will be affected by H–bond formation. The occurrence of strong H-bonding between the ether oxygens of PEO and the carboxyl groups of poly(acrylic acid) is evident from the mutual precipitation of the two polymers from aqueous solutions at suitably acid pH (20–22). There seems little doubt that the H-bonding postulated to explain enhanced steric stabilization can occur.

CONCLUSIONS

These experiments show that by anchoring the stabilizing moieties at a large number of points along the chain, the pattern of flocculation behavior of sterically stabilized dispersions may be profoundly altered. No longer are θ-solvents for the chains in free solution the limit of colloid stability. Instead stabili may be observed in solvents of considerab worse solvency for the stabilizing chains th θ-solvents. This is because the multipoi anchoring so perturbs the polymer conform tion that the thermodynamic parameters th govern the chains in free solution are no long relevant. For PEO chains multipoint anchori may be achieved through H-bonding int actions between the ether oxygen of t stabilizing chains and surface carboxyl grou However, it ought to prove possible to anch polyfunctional macromolecules, e.g., poly(vin alcohol), at many points along their chain thus they should also impart enhanced ste stabilization.

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