The Effect of Temperature, Particle Volume Fraction, and Polymer Concentration on the Stability of Aqueous Polystyrene Latex Dispersions in the Presence of Poly(vinyl alcohol)

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A study has been made of the critical flocculation temperature (c.f.T.) of polystyrene latex particles in aqueous solution (2 M $NaNO_3$), in the presence of various molecular weight fractions of poly(vinyl alcohol)(PVA). There is a strong dependence of the c.f.T. on particle volume fraction and an even stronger dependence on polymer concentration. At very low polymer concentrations bridging flocculation is thought to occur. At monolayer coverage of the polymer, the c.f.T. greatly exceeds the θ-temperature of the polymer molecules in solution. With further increase in polymer concentration, the c.f.T. appears to follow the cloud point behavior of the polymer in the continuous phase.

INTRODUCTION

The temperature at which a sterically stabilized dispersion flocculates has been defined by Napper (1) as the critical flocculation temperature (c.f.T.), and he has demonstrated a close relationship between the c.f.T. and the theta (θ)-temperature of the stabilizing polymer chains in free solution (1, 2). In most of Napper's studies the molecular weight (M) of the stabilizing chains has been high (generally $>10^4$), and the chains have been attached terminally to the surface (i.e., single point anchoring). Recent studies have indicated, however, that the correlation between the c.f.T. and the θ-temperature is weakened if the stabilizing chains are of low M (3, 4), or there is multipoint anchoring (5). Studies on aqueous polystyrene latex particles stabilized by anchored poly(ethylene oxide) chains of M = 750 and 2000 (3), and also on poly(methyl methacrylate) latex particles stabilized by anchored polydimethylsiloxane chains of M = 7000 and dispersed in n-alkanes (4), have shown that flocculation under much better than θ-conditions occurs and, moreover, the c.f.T. was found to be dependent on the volume fraction, ϕ, of the particles. This latter finding has not been reported in any of Napper's studies.

latex [illegible] particle polymer unstabl(.) polym

A thermodynamic interpretation of the results for these pseudo, "two-component" systems has been presented by one of us (3). This is justified since the flocculation was found to be reversible and reached an equilibrium state; indeed, a temperature–particle concentration phase diagram could be established (3). Thus, not only could a critical flocculation temperature be detected for a given ϕ, but also a given critical flocculation volume fraction (c.f.ϕ) could be determined for a given T. An explanation for the different behavior between low and high molecular weight stabilisers was given (3) in terms of the interparticle interaction (free) energy minimum, $G_{\min}$. In the case of high molecular weight chains, where the segmental mixing term in the steric interaction

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comes into play in advance of the elastic term (2), there is a sudden, rapid change in $G_{\min}$ on passing through the θ-condition. With low molecular weight chains, on the other hand, because of the much higher average segment density in the adsorbed layer, there will be relatively little interpenetration of two interacting layers, and so the elastic term is the dominant term and any changes in the segmental mixing term are considerably masked. Thus, $G_{\min}$ changes smoothly with temperature, and these changes are controlled more by subtle variations in adsorbed layer thickness with temperature than by changes in the χ-parameter. Of course, these two types of behavior are limiting cases and one can expect a steady transition from "low M" to "high M" behavior as the nature and size of the stabilizing moieties are varied. The point is, the lower M, the less one can expect to find any correlation between the c.f.T. and the θ-temperature.

Dobbie *et al.* (5) have shown that one can observe c.f.T.s well in *excess* of the θ-temperature (i.e., stability in worse-than-θ-solvents) if multiple-point anchoring of the polymer to the surface is occurring. The system studied was an aqueous polystyrene latex, stabilized by an *adsorbed* polystyrene/poly(ethylene oxide) block copolymer (PEO molecular weight ~ 50,000). At *high* coverages the c.f.T. was close to the θ-temperature, and the flocculation was reversible. At *lower* coverages, however, a region was observed where the c.f.T. greatly exceeded the θ-temperature; this effect was particularly marked when the polystyrene surface contained a high concentration of undissociated carboxylic acid groups. It was suggested that at low coverages the PEO chains fold back onto the surface, resulting in a loop and train configuration, rather than a single extended tail. It was also suggested that the polymer–surface interaction is largely controlled by hydrogen bonding between the surface carboxylic acid groups and the ether oxygens of the PEO chains. This adsorption mechanism has recently been confirmed in this laboratory (Bristol) (6). At low surface coverage, therefore, the adsorbed layer thickness is relatively small and again there will be little interpenetration of adsorbed layers during particle interactions, so here too one can expect the interaction to be controlled primarily by the elastic term, with a subsequent weakening of the correlation between the c.f.T. and the θ-temperature.[2]

In this paper we extend these studies in order to determine the effect of particle volume fraction and polymer concentration on the c.f.T. for a dispersion stabilized by adsorbed polymer over a wide molecular weight range. The system chosen was an aqueous polystyrene latex plus poly(vinyl alcohol) (PVA) adsorbate, in 2 M $NaNO_3$. PVA was selected since the adsorption of this polymer onto polystyrene particles at 25°C has been extensively studied by us in earlier papers (9, 10), and, in the preceding paper (11), the temperature dependence of the adsorption and adsorbed layer thickness are reported. In preference to pure water, 2 M $NaNO_3$ was used, in order, first, to eliminate electrical double layer effects and, second, to reduce the solubility of PVA in water, such that the c.f.T. values fell within a convenient range for study (in water alone, the c.f.T. values would exceed the normal boiling point of water).

EXPERIMENTAL

Materials

All the water used was doubly-distilled from an all-Pyrex apparatus; $NaNO_3$ and $Ba(NO_3)_2$ were BDH AnalaR grade and used

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[2] An alternative explanation in terms of the significantly lower segment density in loops, as opposed to tails, has recently been offered by Smitham and Napper (7). The lower segment density means that one has to go to temperatures in excess of θ to achieve a critical value of the energy minimum, $G_{\min}$. Bagchi (8) has also given an interpretation of stability in worse-than-θ-solvents in terms of his so-called "denting model."

as supplied. The polystyrene latex was prepared by dispersion polymerization of styrene (ex BDH; redistilled under vacuum) at 70°C using potassium persulfate as initiator (12–14). Electron microscopy gave a mean particle radius of 105 ± 3 nm. The latex was extensively dialyzed against water before use.

The poly(vinyl alcohol) narrow molecular weight fractions used were those described in an earlier publication (9). They were prepared using a G.P.C. separation technique (9) from a sample of PVA 88-10 ($\bar{M}_v$ 45,000). The fractions used in this work were PVA 4000 (Q), PVA 8000 (O), PVA 17,000 (M), and PVA 52,000 (G).

Cloud Points

The cloud points of aqueous solutions of PVA 52,000 were determined in 2 *M* $NaNO_3$, over the concentration range 0–0.5% (w/w), by turbidiometry using an SP 600 Pye-Unicam spectrophotometer with a specially constructed thermostatted cell-housing. The cloud point was taken as the temperature at which the optical density first increased, on raising the temperature in 0.5°C increments, at intervals of 30 min.

Flocculation Experiments

The technique has been described in detail elsewhere (3). Samples of varying particle volume fraction (i.e., $\phi = 10^{-5}$ to 10^{-3}) and chosen PVA concentration were allowed to equilibrate in 2-, 10-, or 40-mm optical cells as appropriate. The electrolyte concentration was then adjusted to 2 *M* $NaNO_3$.[3] No flocculation of any of the dispersions was observed at this stage. The optical cells were then placed in the thermostatted cell-housing of a Pye Unicam SP 600 spectrophotometer. The temperature was raised in selected increments (1°C close to the c.f.T.). After each temperature increase the samples were allowed to stand at the new temperature for 30 min and then a turbidity (τ)-wavelength (λ) scan was carried out over the range $\lambda = 400–600$ nm. As shown in previous publications (3, 15), this is a sensitive technique for detecting low levels of flocculation, since the slope, n, of a log τ-log λ plot is very sensitive to small changes in the average particle size in the dispersion. A typical n vertus T plot for locating the c.f.T. is shown in Fig. 1: it can be seen that there is a sharp break in the plot at the c.f.T.

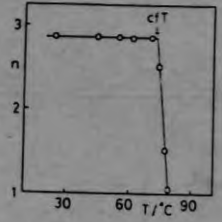

FIG. 1. A typical $n(= d \log \tau / d \log \lambda)$ versus T plot to establish the c.f.T. $\phi = 9 \times 10^{-4}$; $M = 17{,}000$: [PVA] 400 ppm.

In order to check that one is indeed observing flocculation of the particles and not some artifact associated with the polymer solution in the continuous phase, some direct observations were made using a light microscope equipped with a hot-stage. There appeared to be a direct correlation between the c.f.T. observed turbidiometrically and that observed visually.

A few measurements of the c.f.ϕ, at 25°C, were made by adjusting the electrolyte concentration for a series of different ϕ values and plotting n, measured at some chosen time interval, against log ϕ (15).

RESULTS AND DISCUSSION

Cloud Points and θ-Temperature in 2 M $NaNO_3$

The cloud point data for PVA 52,000 in 2 *M* $NaNO_3$ are shown in Fig. 2. According

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[3] Since the adsorption of PVA onto polystyrene is irreversible (9), one can assume, to a first approximation, that the amount of PVA adsorbed is unchanged by addition of electrolyte at this point, although there may well be subtle changes in the adsorbed layer thickness.

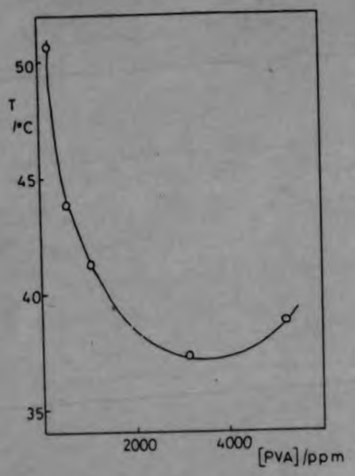

FIG. 2. The cloud point temperature versus the polymer concentration, for PVA 52,000 in 2 *M* $NaNO_3$.

to Cornet and van Ballegooijen (16), a plot of the reciprocal of the cloud point versus the logarithm of the polymer concentration, extrapolated to pure polymer, gives the reciprocal of the θ-temperature. Such a plot for the data in Fig. 2 does not lead to a good straight line, but the θ-temperature is estimated to be 25 ± 5°C, in reasonable agreement with that quoted by Napper (17) for PVA in 2 *M* NaCl (i.e., 25 ± 3°C).

Flocculation Studies

Long *et al.* (15) have demonstrated the existence of a c.f.ϕ for the system: aqueous polystyrene latex plus an adsorbed alkyl ethylene oxide condensate ($C_{12}E_6$) in 100 m*M* $Ba(Cl)_2$. Indeed they showed that the c.f.ϕ moves to lower ϕ values the larger the particle size and, hence, the deeper the minimum, G_{min}, in the interparticle interaction energy curve (15). One would expect similar trends, if one keeps the particle size fixed and changes the adsorbed layer thickness, i.e., varies the polymer molecular weight. One objective of these studies was to test this hypothesis.

In Fig. 3 the results are shown for the latex plus PVA 4000 (at 400 ppm); Fig. 3a demonstrates the time dependence of *n* at two values of $\phi(>$ c.f.$\phi)$. It can be seen that a steady value of *n* is reached within 1 day; this indicates that flocculation has reached an equilibrium state. Due to the close density match between the particles and the continuous phase, the eventual settling into two separate "phases," i.e., singlet phase plus a floc phase (3), takes much longer (~weeks), and careful thermostatting is required.

Figure 3b shows the *n* versus log ϕ plot for the same system at t = 17 hr (i.e., at equilibrium). The c.f.ϕ is at $8.0 \pm 0.2 \times 10^{-5}$. Attempts to locate the c.f.ϕs for the higher molecular weight fractions were unsuccessful. Initially, it was thought that this was due solely to the fact that as a result of the increase in adsorbed layer thickness, the energy minimum, G_{min}, was reduced to such an extent that the c.f.ϕs would be above $\phi = 10^{-3}$, i.e., outside the range that can be conveniently covered by light scattering or turbidimetric techniques. However, the situation is not as simple as this, since it seems that the conditions under which flocculation occurs depend critically on the polymer concentration used, as well as on the volume fraction of the latex particles.

This point is illustrated in Fig. 4. This shows the c.f.T. data as a function of log

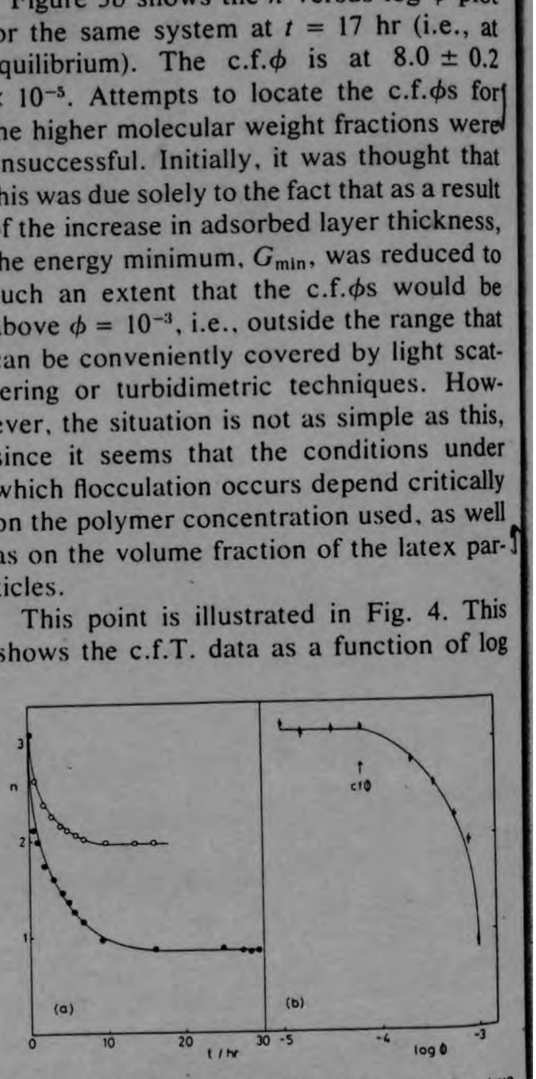

FIG. 3. (a) *n* as a function of time (t) for two different particle volume fractions, ϕ: ●, 8.0×10^{-4}; ○, 9.2×10^{-4}. (b) *n* versus log ϕ at t = 17 hr. $\bar{M}$ = 4000; [PVA] = 400 ppm. 30 m*M* $Ba(NO_3)_2$ in both cases.

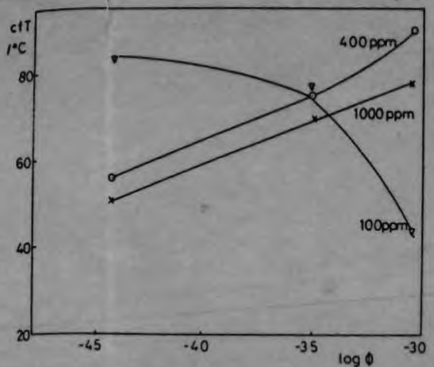

FIG. 4. c.f.T. versus log ϕ for different concentrations of PVA 8000: ∇, 100 ppm; ○, 400 ppm; ×, 1000 ppm; 2 M NaNO$_3$ in each case.

ϕ for the latex plus PVA 8000 at various initial PVA concentrations. The expected decrease in the c.f.T. with increasing log ϕ, as observed, for example, in the experiments of Cowell *et al.* (3), referred to above, occurs only at low PVA concentrations (~100 ppm). Moreover, if one were to extrapolate the 100 ppm curve to $T \sim 20°C$, then one would obtain a c.f.ϕ value for PVA 8000 at this concentration at $\phi > 10^{-3}$, in line with the remarks made in an earlier paragraph. However, at PVA concentrations around 400 ppm and above, the c.f.T. appears to *increase* with log ϕ. Clearly one can no longer interpret this behavior in terms of the phase separation of a pseudo, "two"-component system, i.e., polymer-covered particles + solvent (aqueous electrolyte). At these higher concentrations of PVA, a significant amount of the polymer remains in the continuous phase after adsorption equilibrium has been achieved. We thus have, effectively, a pseudo, "three"-component system. Cowell *et al.* (3) have also considered similar systems.

Similar results to those given in Fig. 4 for PVA 8000 were obtained for PVA 17,000 and PVA 52,000, i.e., above a certain initial polymer concentration the c.f.T. increases with log ϕ, rather than decreases (Fig. 5). At a given ϕ, the c.f.T. decreases with increases in M.

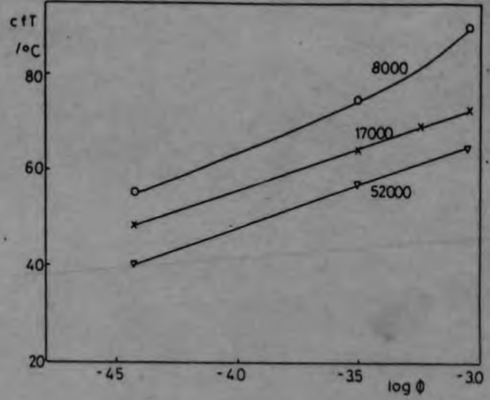

FIG. 5. c.f.T. versus log ϕ for different PVA fractions in the "plateau regions" of the isotherms (8), i.e., 400 ppm PVA concentration: ○, PVA 8000; ×, PVA 17,000; ∇, PVA 52,000; 2 M NaNO$_3$ in each case.

In Figs. 6 and 7 results are given for the c.f.T. as a function of PVA concentration (up to ca. 4000 ppm), at fixed ϕ values, for the latex plus PVA 8000 and plus PVA 52,000, respectively. Both figures show similar features:

(a) An initially steep rise in the c.f.T., with total initial PVA concentration to a maximum value. In some cases this approaches 100°C, i.e., more than 70°C above the θ-temperature of PVA in 2 M NaNO$_3$. (b) A

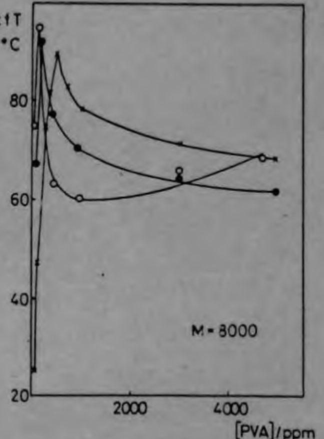

FIG. 6. c.f.T. versus total PVA concentration for PVA 8000, at different particle volume fractions (ϕ): ○, 3.83×10^{-5}; ●, 3.19×10^{-4}; ×, 9.18×10^{-4}; 2 M NaNO$_3$ in each case.

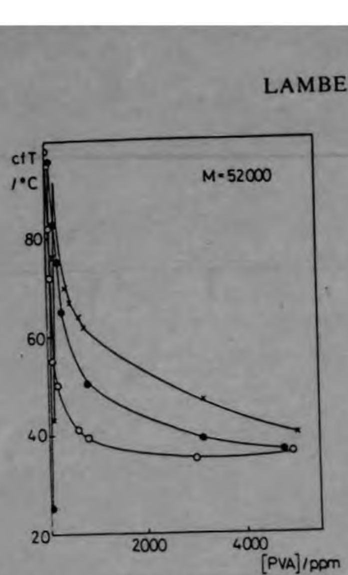

FIG. 7. c.f.T. versus total PVA concentration for PVA 52,000 at different particle volume fractions (ϕ): ○, 3.83×10^{-5}; ●, 3.19×10^{-4}; ×, 9.18×10^{-4}; 2 *M* $NaNO_3$ in each case.

fall in the c.f.T. beyond the maximum toward a limiting value, i.e., ~65 ± 5°C for PVA 8000 and ~40 ± 3°C for PVA 52,000.

Region (a) is presumably associated with the build-up of the adsorbed layer toward monolayer coverage. The mode of aggregation here is most probably bridging flocculation (2). It is significant in this respect that the maximum in the c.f.T. occurs at a higher PVA concentration for PVA 8000 than for PVA 52,000.

The maximum in the c.f.T. probably corresponds to monolayer coverage of the particle surface, with the polymer adsorbed in a loop and train type of conformation. This situation would be similar to the "multipoint anchoring" situation discussed by Dobbie *et al.* (5). Thus, again in this case one would not expect any correlation between the c.f.T. and the θ-temperature, since the elastic term in the steric interaction dominates the mixing term, as discussed in the Introduction.

Beyond the PVA concentration corresponding to the maximum in the c.f.T. multilayer adsorption of PVA at the surface is probable. There is evidence for multilayer adsorption of PVA onto polystyrene latex particles from the work discussed in the preceding paper (11);[4] this would hold both for PVA 8000 (c.f.T. maximum 200–500 ppm) and PVA 52,000 (c.f.T. maximum 50–200 ppm). It is not clear what the conformation of the polymer molecules in a multilayer would be, but, intuitively, one might expect the outer layer to be somewhat similar to the random coil, solution conformation. This being the case one might have expected the c.f.T. to fall to the θ-temperature as was found by Dobbie *et al.* (5) in their studies. This is not the case here, however. The c.f.T. can be seen to level off with increasing PVA concentration (Figs. 6 and 7) at temperatures greatly in excess of the θ-temperature (ca. 25°C). Furthermore, there is some indication that the c.f.T. may go through a minimum with increasing PVA concentration in this region. With increasing ϕ, at a given *initial* PVA concentration, the c.f.T. increases. This is presumably because the *equilibrium* PVA concentration is decreasing. All this strongly suggests that the flocculation behavior observed is indeed connected with the presence of polymer in the continuous phase. If one, in fact, compares the c.f.T. data for the latex plus PVA 52,000 (Fig. 7) with the cloud point data for the same polymer (Fig. 2), then one can see that the c.f.T. of the latex (at the lowest ϕ studied[5]) corresponds fairly closely to the cloud point of the polymer solution *in the continuous phase*. (As was pointed out in the Experimental section, experiments were carried out to ensure that with the turbidiometric method, used for assessing the c.f.T., one is actually observing flocculation, an not just the phase separation of the poly

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[4] Unfortunately, adsorption data at PVA concentr tions beyond about 600 ppm were difficult to esta lish (11), because one is then measuring the sma difference between two increasingly larger numbe (i.e., the initial and equilibrium bulk concentr tions).

[5] i.e., where the *initial* calculation of PVA w not be too different from the *equilibrium* conce tration in the continuous phase.

mer.) As far as the authors are aware, such a correlation has not been reported before.

Just as the phase-separation of the polymer solution is reversible to temperature changes, so the flocculation behavior appears to be reversible also. Thus, if a dispersion is flocculated by heating to above the c.f.T., then it was found that redispersion occurred on cooling below the c.f.T. Moreover, the stability/flocculation boundary lines shown in Figs. 6 and 7 may be crossed "horizontally" as well as "vertically." To confirm this point a latex dispersion at $\phi = 3.19 \times 10^{-4}$, containing PVA 800 at 200 ppm in 2 *M* $NaNO_3$, was heated at 85°C; it remained stable. However, when the PVA concentration was increased to 1600 ppm at this temperature (85°C), the dispersion flocculated, i.e., the flocculation boundary line was crossed.

Flocculation of sterically stabilized particles by the addition of free polymer to the continuous phase has been previously reported by us (3, 18, 19). However, the systems used in those studies were polystyrene particles having terminally anchored, short poly(ethylene oxide) (PEO) chains. Such systems seem to behave differently from those in which PVA is physically adsorbed to the polystyrene particles. For example, as pointed out in the Introduction, the c.f.T. of the systems with terminally anchored PEO (in the absence of free polymer) lies *below* the θ-temperature of the stabilizing polymer, rather than above it, as in the present studies. If free polymer is added to systems where the θ-temperature exceeds the c.f.T. then, obviously, the c.f.T. must always be reached before the cloud point of the polymer solution in the continuous phase, since the θ-temperature corresponds to the *minimum* experimental cloud point (in the limit of infinite *M*).[6]

The flocculation observed with the anchored-PEO systems when free polymer is added to the continuous phase occurs at much higher concentrations of polymer than those reported in this work, and it would seem (3) that the critical polymer concentration in that case corresponds approximately to that concentration at which overlap of the polymer coils in the solution phase begins to occur. Thus, for example, the minimum concentration of PVA ($M = 45{,}000$) required to achieve flocculation of the latex particles carrying terminally anchored PEO-750 chains at 25°C was found to be 7% (70,000 ppm), i.e., much greater than the concentration range studied in the present work. Clearly, the mechanism for the flocculation is different in the two sets of experiments, although in both cases the systems can be regarded as pseudo, "three"-component ones, and the flocculation behavior observed is reversible.

In conclusion, it is clear that the stability/flocculation behavior of dispersions stabilized by polymer *adsorbed* from solution, and in which free polymer remains in the continuous phase, is more complex than for those systems in which the stabilizing polymer chains are terminally anchored to the surface and there is no free polymer in the continuous phase. For the former class of systems the conditions (e.g., temperature) under which flocculation is achieved may depend critically not only on the particle volume fraction, but also on the polymer concentration (for a given molecular weight). There would seem to be a particularly strong dependence of the c.f.T. on polymer concentration, when the c.f.T. of the particles, in the absence of polymer in the continuous phase, greatly exceeds the corresponding θ-temperature of the polymer. Here the c.f.T. behavior closely parallels the cloud point curve for

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[6] It is interesting, in this connection, that in some preliminary experiments (20) in which physically adsorbed, homopolymer *PEO* ($M = 300{,}000$ at 500 ppm) has been used instead of PVA, the c.f.T. occurs at temperatures much less than the corresponding cloud point of the polymer in $NaNO_3$ solution.

the corresponding polymer solution, as the concentration of free polymer is increased beyond that corresponding to completion of the initial monolayer coverage of the particle surfaces.

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• – indicate present in RHI (phtd. for NCW)

✓ – indicate very impt.

Clark *et al.* (24) found from electron paramagnetic resonance studies that as the thermodynamic quality of the solvent decreased, the fraction of segments of one adsorbed polymer in trains increased, provided the nonsolvent did not compete with the polymer for surface sites. This implies that the loop size and, hence, the adsorbed layer thickness, becomes smaller as the solvent become poorer. As pointed out in the introduction, the theoretical position with regard to this point is not unambiguous. Our results seem to suggest that there is a definite decrease in adsorbed layer thickness for PVA on polystyrene as water becomes a poorer solvent on raising the temperature. However, we would suggest from the results of this work that it is more meaningful to test the effect of solvency on ϕ (or better still the segment density distribution) than on δ itself. This is particularly the case where multilayer adsorption is suspected. For PVA on polystyrene, ϕ does appear to increase significantly with increasing temperature; this is, intuitively, what one would expect as the solvent becomes poorer.

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The Surface Areas of Amorphous Mixed Oxides and Their Relation to Potentiometric Titration

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The surface areas of amorphous mixed oxides of silica with alumina, ferric oxide, and titania have been measured by adsorption of ethylene glycol, water, and nitrogen. Surface areas from ethylene glycol adsorption give improbably high values. Isotherms of water adsorption indicate microporosity and estimates of the external surface area from water adsorption are similar to areas from nitrogen adsorption. An estimate of surface areas from potentiometric titration curves is made and compared to the areas from the other measurements. The area determined by titration falls between the areas from water and nitrogen adsorption. It is concluded that the most meaningful estimation of surface areas of hydrous amorphous oxides is obtained by considering an external surface area measured by nitrogen adsorption and an internal pore volume obtained from analysis of the water adsorption isotherm.

INTRODUCTION

Amorphous materials generally have rge surface areas in the range 50–1000 m^2/ , have a considerable pore structure which frequently microporous (1–3), and conin appreciable quantities of water which re both adsorbed onto the surface and inorporated into the structure. These charcteristics make the meaning of the term surface area" difficult to specify except nder well-defined conditions. Assignment f a specific surface area to amorphous marials should be related to the purpose for hich the surface area is to be used and ill depend on the method used for the area etermination to a greater extent than for ystalline minerals. There is a considerable terature on the surface properties of amorhous oxides, but much of it considers the rface area to be well defined, rather than major source of uncertainty (4–6). The rface areas of synthetic amorphous oxides ave been measured by a variety of methds, including adsorption of water (7), nitroen (4, 8), and polystyrene (9), and examination by electron microscopy (10) and low-angle X-ray diffraction (11, 12). Surface areas estimated from electron microscopy have generally provided little information, both because of the lack of any identifiable primary particles and the porous nature of the material. These methods have also been used on natural amorphous silico-aluminas (13) that occur in soils, often termed "allophane"; in addition, the adsorption of glycerol, ethylene glycol, ethylene glycol monoethyl ether (1, 14), and long chain organic molecules (15) have been used. Often there is little agreement between the different methods.

A distinction can be drawn between samples that have been prepared entirely at low temperature and those that have been subjected to calcination. The former samples, which usually include allophane, tend to be microporous (1–3) and to show areas from water adsorption that are greater than those by nitrogen adsorption (3, 16). Calcined samples on, the other hand, are rarely considered to be microporous (17), generally

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