Reversible Swelling of Poly(vinyl acetate) Latex Particles in Sodium Dodecyl Sulfate Solution

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ABSTRACT: Dynamic light scattering and ultracentrifugation studies have shown that, in aqueous solutions of some anionic surfactants such as sodium dodecyl sulfate (SDS), poly(vinyl acetate) (PVAc) latex particles swell up to 60 times their original volume. The process is reversible on dilution. This unexpectedly large swelling always commences at a surfactant concentration below the critical micelle concentration, *e.g.*, at 4.5 mM for SDS. The swelling rate is best expressed by a Kohlrausch−Williams−Watts dispersive kinetics expression—initially very fast and then becoming progressively and continuously slower. Swelling is inferred to be due to the formation throughout the particle of polymer−micelle complexes, the structure of which is similar to those reported in systems containing certain water-soluble synthetic polymers and surfactants. The swelling is reversible and on dilution the particles contract rapidly to slightly less than their original size. The difference is due to the escape of some lower molecular weight material from the particles. The reversibility shows that a degree of morphological integrity of the particle is preserved on swelling. This is attributed to the existence of microdomains of intrinsic entanglements probably formed during the original emulsion polymerization process.

Introduction

The dissolution of the latex particles of water-insoluble poly(vinyl acetate) (PVAc),[1] poly(vinyl formal), and poly(vinyl butyral)[2,3] in anionic surfactants such as sodium dodecyl sulfate (SDS) has been reported in some detail. It had been found that there was a significant increase in such properties as the viscosity and the transparency of the latices at SDS concentrations above the critical micelle concentration (cmc). In mixtures or copolymers of PVAc and poly(vinyl alcohol) (PVAl), the PVAc interacted more strongly than did the PVAl.[4] It was considered that, below the cmc, surfactant was bound to the polymer as a monolayer and this then acted as a nucleus for attachment of the ordinary micelles above the cmc.[5] Another suggestion was that surfactant penetrated slowly into the interior of the PVAc particles, taking water molecules with it and causing swelling and dissolution of the polymer chains.[6] The separated solubilized polymer chains behaved like polyelectrolytes with negative charges.[3] Similar interactions have not been reported between water-insoluble polymers and cationic or nonionic surfactants. On the other hand, certain intrinsically water-soluble synthetic polymers and some proteins have been reported to form complexes with anionic, cationic, and nonionic surfactants,[7] and these complexes are capable of solubilizing water-insoluble dyestuffs[8] and smaller molecules.[9] Breuer and Robb,[7] Robb,[10] and Goddard[11] have reviewed these studies and have also made comparisons with the work on PVAc/anionic surfactant systems. Recently, dodecyltrimethylammonium chloride and SDS have been shown to affect the swelling and volume phase transition temperature of poly(*N*-isopropylacrylamide) gel.[12]

In the present investigation we have established that particles of a PVAc latex, containing polymer of M_w = 784 000 prepared by a standard recipe, swell in SDS solution both below and above the cmc and that this swelling is reversible. We have made a time-resolved study of the dramatic volume increase, which is initially very fast and then proceeds more slowly over hours and days before reaching a quasi steady state with a 3−4-fold increase in hydrodynamic diameter, corresponding to a 30−60-fold change in volume of the original particle size. During swelling some low molecular weight polymeric material is released into the aqueous phase and remains there during any subsequent shrinkage. The results obtained by dynamic light scattering (DLS) have been confirmed by studying the two phases after separation by ultracentrifugation. On dilution the particles contracted to slightly less than their original volume—the difference being equivalent to the solubilized low molecular weight portion. This reversible swelling and concomitant shrinkage may have some industrial consequences when SDS or similar surfactants are used in the manufacture of latices and also where controlled swelling of a water-insoluble polymer can be utilized. For example, being able to measure and understand the degree of swelling should assist in polymerization studies in such systems. It has been reported that polymerization of vinyl acetate in 60 mM SDS yields[13] a "solubilized aqueous polymer". In addition, the swelling of PVAc and similar polymers by anionic surfactants may affect film formation in such important industrial applications as surface coatings. A critical factor in film formation and in such properties as the degree of gloss is the interpenetration of polymer chains between different particles, and this is drastically affected by the extent of swelling of the polymer by solvents (*i.e.*, more open polymer structures yield faster and more complete polymer interpenetration). In typical emulsion latex paints there is anionic surfactant present from both the initial charge of surfactant and that created *in situ* by the action of initiator and monomer. As films dry, the concentration of these surfactants increases and this may aid the formation of swollen polymer networks. The system could also serve as a model for certain protein and lipoprotein systems.

Additional abbreviations which we shall use are PMMA (poly(methyl methacrylate)), PS (polystyrene), PEO (poly(ethylene oxide)), PMA (poly(methyl acry-

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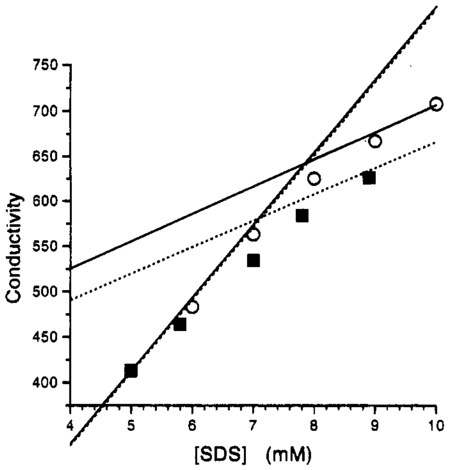

Figure 1. Conductivity (arbitrary units) *vs* SDS concentration (mM) at 25 °C: (–○–) no PVAc; (--■--) 1000 ppm PVAc. Lines are extrapolations of measurements at SDS concentrations lower and higher, respectively, than shown in the figure.

late)), PPO (poly(propylene oxide)), and VAc (vinyl acetate).

Experimental Section

Chemicals. VAc (ICI Australia) was fractionated by vacuum distillation. SDS (BioRad, electrophoresis purity) showed a "knee" at 7.9 mM in the conductivity *vs* concentration plot for aqueous solutions at 25 °C, in fair agreement with the accepted value of 8.3 mM[14,15] for the critical micelle concentration (cmc). SDS, sodium octyl sulfate (SOS) (Sigma), partially hydrolyzed PVAl/PVAc (Aldrich), and other reagents (AR or equivalent grade) were used without further purification.

PVAc Latices. Except where otherwise noted, experiments were carried out on a PVAc latex prepared as follows: purified vinyl acetate (104 g), 10% SDS solution (6 g), 2% $NaHCO_3$ solution (10 g), 5% $K_2S_2O_8$ (6 g), and water (450 g) were stirred at 40 °C under a N_2 atmosphere for 18 h. The temperature was then raised to 90 °C for a further hour. The latex was dialyzed for 5 days, leaving residual SDS found by chemical analysis (see below) to be about 0.03% of the PVAc. Viscosity measurements in acetone indicated a molecular weight of the order of 0.5×10^6. Measurement by GPC showed M_w = 784 000 ± 14 000. The latex particle diameter (measured by DLS; see below) was 142 ± 2 nm, and the DLS "polydispersity" factor was 0.05.

Some experiments were carried out using two other PVAc latices (C8, C9) which had been prepared 8 years earlier using the same methodology. The particle diameters were 165 and 450 nm, respectively. The swollen particles of preparation C9 were large enough to be visible in an optical microscope at 1000× magnification under crossed polarizers. They appeared as spheres floating freely as individuals of diameter about 1.5 μm. The diameter according to DLS was 1.4 μm. Another PVAc latex, GR4 (diameter 136 nm), was prepared at 40 °C using Aerosol MA80 (sodium dihexyl sulfosuccinate) as surfactant.

All samples containing <40 mM SDS and >500 ppm PVAc remained cloudy. Samples containing >40 mM SDS and 500–1500 ppm PVAc gradually cleared after several days.

Viscosity. Viscosities were measured using an Ostwald viscometer calibrated with distilled water. Aldrich poly(vinyl acetate) secondary standard, M_w = 195 000, M_n = 63 600, was used as a standard for both viscosity and GPC measurements.

Conductivity. The conductivity of SDS solution with and without 1000 ppm PVAc is plotted against [SDS] in Figure 1. The "knee" at 6.9 mM SDS as compared with the cmc literature value 8.3 mM[14,15] shows a small amount of impurity in the SDS used. The presence of PVAc had no effect on the conductivity up to 5 mM SDS.

Surface Tension. Surface tension measurements were made using an Analite surface tension meter fitted with a Wilhemy glass plate.

Chromatography. Gel permeation chromatography (GPC) measurements were made on a Waters Associates Model 510 using an Ultrastyragel column and a dual R401 refractive index/UV-50 detector system.

For hydrodynamic chromatography measurements of the latex particles, a column of monodispersed 15 μm styrene/divinylbenzene polymer particles and ultraviolet detection at 214 nm were used. The instrument was calibrated with Dow Chemical Co. PS 88 and PS 109 (the numbers are nominal diameters in nanometers) in 20 mM SDS. A sample containing 120 ppm PVAc/20 mM SDS gave values of 580 and 640 nm, in fair agreement with the DLS values of 500 and 560, respectively.

Chemical Analysis. Poly(vinyl acetate) was analyzed for by the reddish plum coloration developed with iodine. SDS did not interfere. In 1 cm cells at wavelength 513 nm an absorbance of 1 corresponded to ~260 μg of PVAc. Sodium dodecyl sulfate was analyzed for by an adaptation of the Standard Method[16] using the methylene blue complex extracted into chloroform.

The sediments from centrifuged samples containing >8 mM SDS redispersed readily in water. Those from samples containing <6 mM SDS were hard disks and were left to stand for 2 h in acetone (1 g), after which time an aliquot was taken and diluted with water for SDS analysis. Total solids were determined by evaporating a weighed sample to dryness at 50 °C to constant weight. In general, the solids content was in good agreement with the chemical analysis.

Ultracentrifugation. Typically, samples were centrifuged for 2 h at 28 000 rpm (equivalent to 55 600*g*) and the clear supernatant was poured off from the sediment. The two fractions were analyzed gravimetrically for total weight and weight of solids and chemically for PVAc and SDS. The results of several experiments are given in Table 1. There was good agreement with DLS measurements. The readily soluble material in the supernatant was found by GPC to have peak M_w = 180 000 with a considerable amount of lower molecular weight material. Since it developed the expected strong color with iodine, this material was not degraded or hydrolyzed polymer, *i.e.*, poly(vinyl alcohol), which we have shown does not give a color with iodine at wavelength 513 nm.

Particle Size Measurements: DLS. Particle size measurements were made by DLS using a Malvern Model 4700C photon correlation spectrometer with a 488 nm, 150 mW argon laser (Omnichrome 543-AP). The *z*-average hydrodynamic diameter calculated by cumulants analysis was corrected for the viscosity of the SDS solution, for particle interactions, and for the loss of readily soluble material. Measurements could be made within 40 s of mixing the reagents and later were made at 2 min intervals or as appropriate. Except for times of rapid change during the kinetic runs, several measurements each of 2 min were made on a sample and the results averaged for greater accuracy. Except where otherwise noted, all measurements were at 25 °C. The sample compositions will be designated as follows: ppm PVAc/mM SDS and the time after mixing and/or temperature added when appropriate. In general, our results will be expressed in terms of the increase in volume of the particles relative to the original volume—the volume swelling ratio.

Results

Surfactant Concentration. The SDS concentration at which swelling was observed to commence was found to be independent of latex concentration over the range 63–2000 ppm PVAc.

Long-time values, v_{LT}, at 3 days are plotted in Figure 2. For 1000 ppm PVAc latex at 25 °C, no increase was observed for SDS concentrations below 4.5 mM (cmc[15] is 8.3 mM), increasing swelling was found over the range 5–8 mM, and swelling was not very dependent on surfactant concentration above 12 mM.

Kinetic Measurements. The DLS results are plotted against the time for samples 500/19/20 °C, 500/8/25 °C, and 1000/8/25 °C in Figure 3. There was an initial

Table 1. Analyses from Ultracentrifuge Experiments (998 ppm PVAc)

	[SDS] (mM)				
	4	6	8	12	20
readily soluble PVAc in supernatant					
% of original	trace	9	19	24.5	23.7
cf. dilution experiment (Figure 9)					25
composition of particles in sediment					
% PVAc	100	21	4.7	2.5	2.3
% SDS	trace	0.34	0.54	1.9	2.1
% water	trace	79	95	96	96
VA units/SDS molecule		200	30	4.5	3.6
volume swelling ratio					
centrifuge	1	6	26	57	55
cf. DLS (Figure 2)	1	5.5	31	51	57

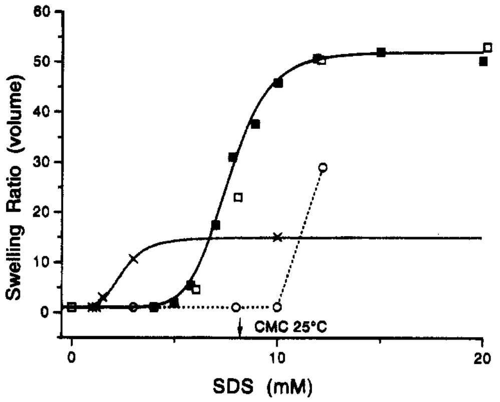

Figure 2. Effect of SDS concentration: swelling ratio (volume) *vs* SDS concentration (mM). DLS measurements, (■) 1000 ppm PVAc/25 °C, (×) 1100 ppm PVAc/25 °C/135 mM NaCl, (○) 1100 ppm PVAc/60 °C; ultracentrifuge measurements, (□) 1000 ppm PVAc/25 °C. Lines are Hill–Langmuir fits.

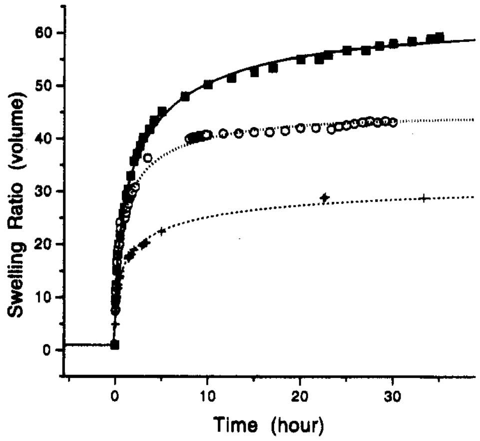

Figure 3. Kinetic runs: swelling ratio (volume) *vs* time (h). (■) 500 ppm PVAc/19 mM SDS/20 °C, (○) 500 ppm/8 mM SDS/25 °C, (+) 1000 ppm PVAc/8 mM SDS/25 °C. Lines are three-exponential fits.

very rapid swelling continuously decreasing in rate to a very slow value at 30 h. The initial rate is much the same for the three different experimental conditions.

The kinetic measurements were fitted using the software package Origin 2.8 (Microcal, Inc., 1992). The values of the statistical quantity, χ^2, were used as a measure of the goodness of fit for different functions. Very good fits were obtained by using the sum of three exponentials ($\chi^2 = 0.26$), but we feel this has no physical significance.

Alternatively, the data could be fitted ($\chi^2 = 0.64$) by the Kohlrausch–Williams–Watts (KWW) dispersive kinetics relationship described by Plonka and others[17–24] whereby the rate constant decreases continuously with time to give what is essentially a stretched exponential:

$$v_t = v_{\mathrm{LT}} - (v_{\mathrm{LT}} - 1)\exp(-pt^{\alpha}) \qquad (1)$$

where p is an adjustable parameter and the exponent α has a value between 0 and 1. Table 2 lists the values found for v_{LT}, p, α, and χ^2 for different mixtures using these procedures, and some plots are given in Figure 4. The physical significance of this expression will be discussed later.

The increase in viscosity with time as the particles swelled is plotted in Figure 5. By adjustment of the two vertical scales, the early relative viscosity increase and swelling ratio determined by DLS can be made to lie on the same curve but diverge later because the increasing interaction of the swelling particles has been corrected for in evaluating the DLS measurement. The contribution of this interaction has not been removed from the values plotted for the measured viscosity.

Rate of Swelling. Two runs were carried out on latex GR4 to see if very slow swelling made any difference to the hydrodynamic diameter at long time. SDS solution was added from a microsyringe at a slow constant rate over 11 days or solution was allowed to evaporate over 34 days to give ppm PVAc/mM SDS 1410/17.7 and 1230/21.6, respectively. The resulting uncorrected hydrodynamic diameters for these two experiments were 645 and 664 nm and, on dilution to 3 mM, 135 and 136 nm, which were similar to the values found when the components were mixed rapidly (658 nm) and on dilution (136 nm). The particle count for slowly swelled samples was similar to that found for rapidly swelled samples.

Temperature. Most runs were carried out at 25 °C and others at 20, 45, 50, and 60 °C (Table 2 and Figures 3 and 4). KWW dispersive kinetic fit lines are given in Figure 4 together with comparable data at 25 °C. The higher the temperature, the higher is the SDS concentration at which swelling starts and the greater is the swollen size (Figure 6).

Reversibility. Samples which had reached equilibrium swelling at 64 mM were diluted to 1000 ppm PVAc but different SDS concentrations. The resulting contraction occurred more rapidly than could be observed by DLS—in less than 30 s. Values found after 24 h for the uncorrected hydrodynamic diameters are compared with values for corresponding samples swollen by the same concentrations of SDS in Figure 7. In every case the values are slightly less than the corresponding values for freshly swollen samples due to the release of some readily soluble material from the particles at the higher SDS concentration. However, the return of all

Table 2. Kinetic Runs

experimental conditions and results					dispersive kinetics fit parameters[a]			
run no.	temp (°C)	SDS (mM)	PVAc (ppm)	diam[b] (nm)	v_{LT}	p	α	χ^2
7	25	6	100	399				
3	25	6	500	284	3.9	0.116	0.28	0.012
4	25	6	500	296	5.1	0.093	0.39	0.061
5	25	6 → 7	500	420	21.5	0.012	0.46	0.24
6	25	7 → 8	500	491	30.8	0.013	0.45	0.89
2	25	8	500	523	46.5	0.025	0.43	0.66
15	25	8	1000	441	30.1	0.041	0.35	0.26
65	25	12	330		57.5	0.019	0.47	1.01
16	25	12	1000	607	62.2	0.032	0.36	1.47
8	25	18	100	564				
1	20	19	500	523	60.9	0.014	0.46	0.64
21	50	20	1000		66.8	0.032	0.36	1.68
11	45	8.4	500	333				
10	45	18	500	571				

[a] See text eqs 1. [b] DLS diameter at 24 h.

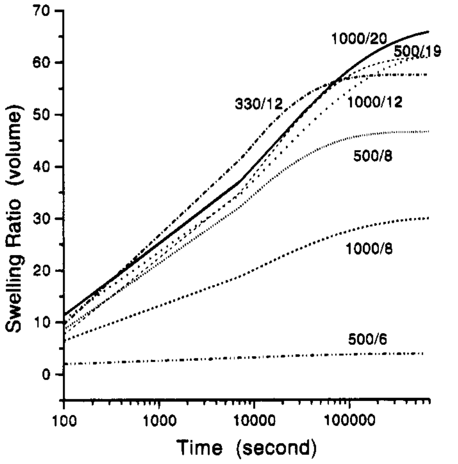

Figure 4. Kinetic effect of PVAc and SDS concentration: semilogarithmic plot of swelling ratio (volume) *vs* time (s). Dispersive kinetic fitted curves (ppm PVAc/mM SDS) at 20 °C [(··) 500/19] and 25 °C [(—) 1000/20, (···) 1000/12, (-··-) 330/12, (...) 500/8, (— — —) 1000/8, (- - -) 500/6].

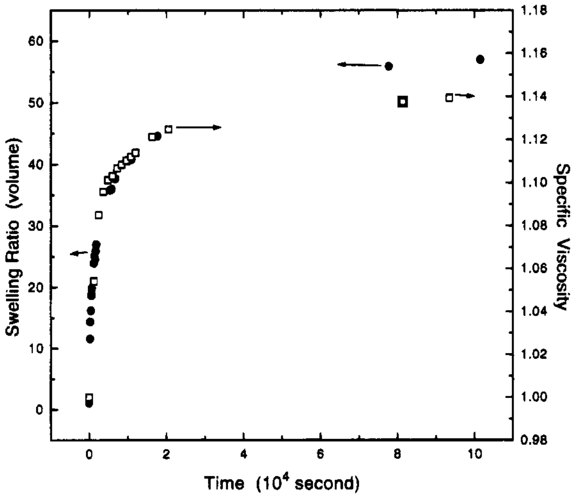

Figure 5. (□) Specific viscosity and (●) swelling ratio (volume) *vs* time (s): 1000 ppm PVAc/12 mM SDS/25 °C.

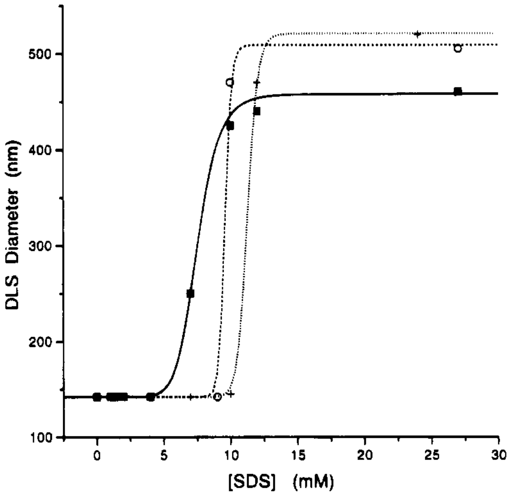

Figure 6. Effect of temperature: uncorrected hydrodynamic diameter (nm) *vs* SDS concentration (mM) for 1000 ppm PVAc. (■) 25 °C; (○) 50 °C; (+) 60 °C. Lines are Hill–Langmuir fits.

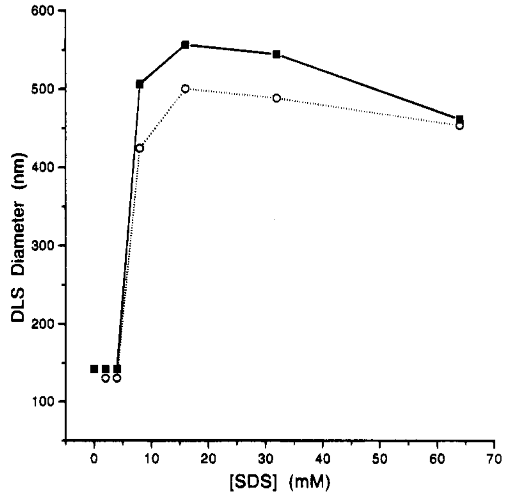

Figure 7. Dilution of swollen particles. Particles were previously swollen in 64 mM SDS and diluted, and the size was then measured. (○) Uncorrected hydrodynamic diameter (nm) *vs* SDS concentration (mM) for dilution of 1000 ppm PVAc/64 mM SDS to indicated SDS concentration. For comparison: (■) diameter of 500 ppm PVAc/indicated SDS concentration.

samples at low SDS concentration to slightly less than the original size showed that the swelling is reversible and that a "memory" of the original size, and presumably structure, remained.

A sample which had been swollen and then diluted to 2.5 mM [SDS] was again exposed to 12 mM [SDS]. Swelling as a function of time was similar to that for a fresh sample of the same composition (Figure 8). If the temperature of a 1000 ppm PVAc/8 mM SDS mixture was raised from 25 to 45 °C, a size contraction occurred reflecting the slightly higher cmc (9 mM)[15] at 45 °C. When SDS concentration was reduced to ~1 mM by precipitation with a slight excess of calcium nitrate in

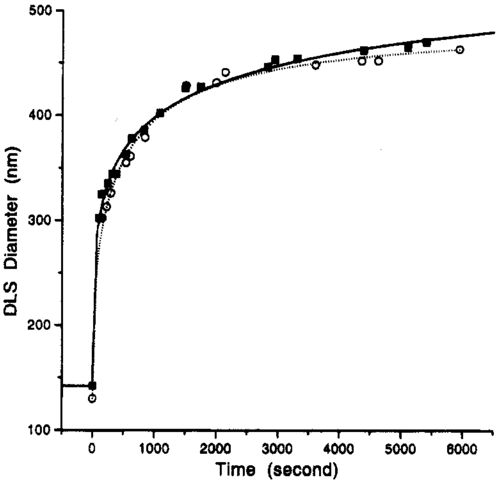

Figure 8. Reswelling. Particles were previously swollen, then diluted, and again swollen. Uncorrected hydrodynamic diameter (nm) *vs* time (second). 330 ppm PVAc/25 °C. (■) Fresh sample/12 mM SDS; (○) swollen, diluted to 2.5 mM SDS, and reswollen in 12 mM SDS.

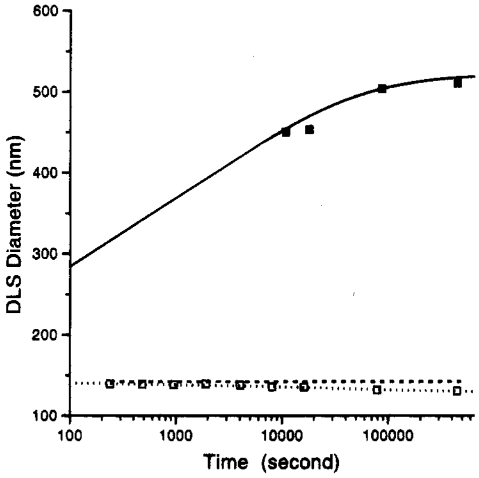

Figure 9. Dilution of swollen particles: time profile. Samples were taken during a swelling run and immediately diluted, and the size were then measured. Uncorrected hydrodynamic diameter (nm) *vs* log(time) (s). (- - -) Original unswollen; (–■–) swelling of 1000 ppm PVAc/20 mM SDS; (··□··) eightfold dilution to 125 ppm PVAc/2.5 mM SDS. Lines are dispersive kinetics fits.

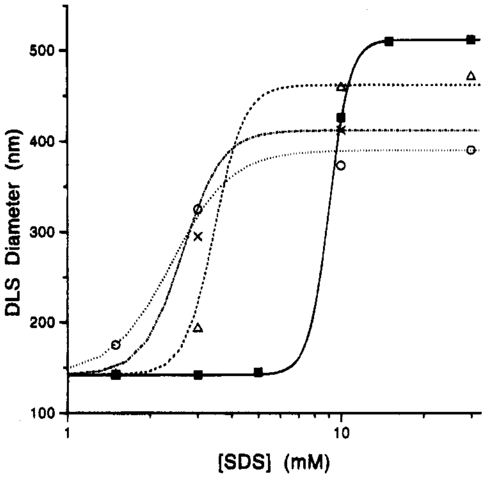

Figure 10. Effect of salt on swelling. Semilogarithmic plot of uncorrected hydrodynamic diameter (nm) *vs* SDS concentration (mM) for 1000 ppm PVAc. (■) 0 mM NaCl; (△) 15 mM NaCl; (×) 45 mM NaCl; (○) 135 mM NaCl. Lines are Hill–Langmuir fits.

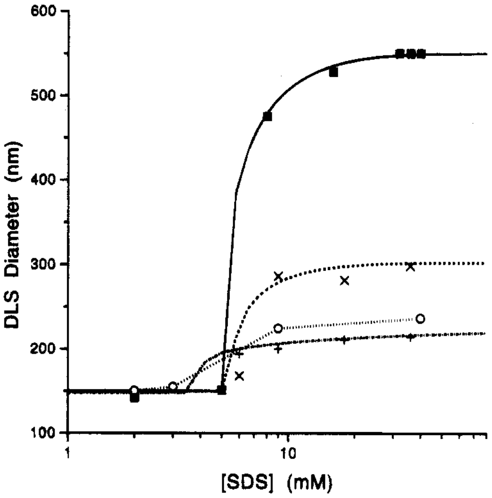

Figure 11. Effect of cross-linking and of iodine. Semilogarithmic plot of uncorrected hydrodynamic diameter (nm) *vs* SDS concentration (mM) for 1000 ppm PVAc: (■) Control; (×) γ cross-linked; (○) iodine; (+) divinylbenzene cross-linked.

aqueous solution followed by filtering with a Millipore 0.45 μm membrane, the PVAc particle size contracted again to somewhat below the original unswollen value. In another experiment, 1000 ppm PVAc/20 mM SDS was allowed to swell. Samples were taken at intervals of time during the swelling, immediately diluted eightfold to 125 ppm PVAc/2.5 mM SDS, and allowed to stand for 24 h to attain equilibrium of labile SDS and water between the interior of the particle and the surrounding aqueous fluid. The DLS diameters were measured and are plotted in Figure 9. The values decreased steadily with increasing time of swelling.

Effect of Monomer. In the absence of SDS, vinyl acetate monomer (2.5% relative to the total weight) was found to swell the particles to ~1.7 times their original volume after 3.5 h at 25 °C. The threshold for swelling by SDS was much higher, *viz.*, ~40 mM, and the equilibrium swelling was much less than in the absence of VAc. If a latex swollen for 1 day in 16 mM SDS was made up to contain an aqueous concentration of 1.25% vinyl acetate, it contracted to 1.11 times the unswollen volume—the size expected in the absence of SDS. It follows that PVAc has a greater affinity for VAc than for SDS but VAc attracts little or no water into the particle.

Additives. The addition of sodium chloride is known to lower the cmc of SDS. In 135 mM NaCl (cmc = 1.3 mM)[15] swelling was observed at 1 mM SDS (compare 4.5 mM in the absence of salt). After 2 days in 15 mM SDS, the uncorrected hydrodynamic diameter was 390 nm whereas in the absence of salt it was 512 nm (Figure 10).

Since unswollen and swollen particles took up the same amount of iodine, iodine is capable of penetrating PVAc latex particles to form the colored complex. Figure 11 shows the uncorrected diameter in 0.013% I_2/0.033% KI solutions (expressed in terms of the total volume) after 1 day as a function of [SDS]. Beyond 5 mM [SDS] the iodine suppressed the swelling, showing that iodine competed for the same sites as were occupied by SDS along the polymer chain but more strongly. Iodine was added to another sample of 1000 ppm PVAc latex to make the solution 0.013% iodine/0.033% KI and then SDS was added to make the solution 20 mM in SDS. After centrifuging, none of the readily soluble PVAc material was detected in the supernatant.

Cross-Linking. Two samples of the original latex (both 9.5% PVAc)—of which one had no additive and the other had added 1 day previously the cross-linking agent divinylbenzene (0.38% by weight of the PVAc)—were irradiated in a ^{60}Co γ source for 105 h at 0.77 kGy h^{-1}. The samples were diluted to 1000 ppm PVAc at SDS concentrations over the range 0–64 mM and left 1 day before being measured. Figure 11 shows the effect of radiation and chemical cross-linking. The sample irradiated with γ rays without cross-linking agent showed a lower swelling—298 nm (uncorrected diameter) compared with 550 nm for the control. The sample to which cross-linking agent had been added had a swollen diameter of 214 nm. Both samples showed a small increase in hydrodynamic diameter in the absence of SDS.

Other Preparations. The quantitative results reported herein are characteristic for the particular polymer samples described here. They include different particle sizes (120, 142, 150, 165, and 450 nm diameter), different ages (1–8 years), and different conditions for polymerization (temperature 40–65 °C, preparation surfactant SDS or Aerosol MA80). Other preparations of PVAc latices may differ in degree. Preliminary experiments on poly(methyl acrylate) showed similar behavior. The monomers of PMA and PVAc are isomers, the positions of the –CO– and –O– in the ester side chain being reversed. The PVAc latex GR4, which was prepared in the presence of the surfactant Aerosol MA80, contracted on deswelling to very nearly its original size, suggesting that little, if any, readily soluble material had been leached out.

No swelling was found for PMMA or PS latices although Brown and Zhao[25] recently reported a twofold increase in the volume of PS latex particles in 6.5 mM SDS and thought that at least some of this must have been caused by penetration of the particles by the surfactant.

Other Surfactants. The following surfactants showed swelling (the threshold concentration and the cmc[15] are given in mM in parentheses): sodium octyl sulfate (110, 130 mM), sodium tetradecyl sulfate (1.3, 2 mM), and SDS at 60 °C (9.5, 10 mM). Lithium and cesium dodecyl sulfate behaved similarly to SDS. Sodium hexadecyl sulfate and sodium dodecylbenzenesulfonate also showed reversible swelling. Surfactants which gave no swelling of PVAc were Aerosol MA80, CTAB (cetyltrimethylammonium bromide), and potassium oleate. Also no swelling was found with the long-chain alcohols dodecanol and hexadecanol.

Discussion

Validity of the Measurements. The agreement between the DLS measurements (Figure 2), the ultracentrifugation results (Table 1), and the hydrodynamic chromatography measurements (see under Results) showed that the particles do in fact increase dramatically in size over the range 5–15 mM [SDS]. The smaller increase observed (see Figure 11) for cross-linked particles showed that this was not due simply to aggregation or flocculation of the particles. The observation in the optical microscope study showed that the particles were free and separate. Simple aggregation of particles would not increase the total volume of sediment as found in the ultracentrifuge studies (Table 1). The fact that 24–25% of the original material (the low molecular weight material) was extracted into the aqueous phase in 12 and 20 mM SDS and that the sediment from ultracentrifugation contained ~96% water and 2% SDS both indicate access by the SDS solution to the interior of the particles.

Readily Soluble Material. The supernatant solutions from the ultracentrifugation experiments at [SDS] = 12 and 18 mM were found to contain ~25% of the original PVAc (Table 1). If the sediment was redispersed in 18 mM [SDS] and again centrifuged, very little (<5%) of the PVAc was found in the supernatant. The readily soluble material was short-chain material, which would be expected to be not greatly entangled within the swelling particle and had been readily released from the particle. GPC measurement showed $M_w = 180\,000$. There are reports[26] indicating that molecular weight is an important factor in governing the solubilization of PVAc by SDS. The present study has been confined in the main part to a single PVAc latex, and we have found that the molecular weight of the chain appeared to be important in determining that the shorter chains escape into the surrounding fluid. A latex particle comprised of such low molecular weight material would be expected to become soluble rather than retain its particulate integrity.

If the swollen PVAc/15–20 mM SDS was diluted or the SDS removed by dialysis, the diameter returned to a value of 131 nm (compared with the original 142 nm), close to that expected (129 nm) after removal of the 25% readily soluble material. In Figure 9 the volumes of the deswelled particles decreased progressively with time of swelling, and this has been taken as a measure of the rate of escape of readily soluble material during the swelling. After 48 h ~25% of the original PVAc had escaped and thereafter the changes were quite slow.

Patsiga *et al.*[27] detected (by its coloration with iodine) solubilized material amounting to 4% of the total PVAc in a seed preparation in the presence of SDS. A further 8% could be removed from the coagulum by washing with water. With regard to the different conditions, this is in general agreement with our finding.

Residual SDS Concentration. Analysis of the dialyzed PVAc preparation showed a residual SDS content of 0.03% of the weight of the PVAc. Assuming spherical particles and each SDS molecule occupying[28] 0.3 nm^2 (see next paragraph), this would correspond to a surface coverage of ~2%. The stock latex contained 9.5% (w/w) PVAc and was still quite stable after 3 years. A contributing factor could be the presence in the surfaces of the particles of negatively charged initiator sulfate groups as end groups on PVAc chains anchored within the particles. These would act in the same way as adsorbed surfactants and confer additional stability on the latex against coagulation. However, the ionic effect on the DLS diameter being small compared with that for PS suggests a small degree of ionic stabilization for this preparation. The treatment at 90 °C may have hydrolyzed some of the surface sulfate groups to hydroxyl groups.

0–4 mM SDS Concentration Range. Over the range 0–4 mM [SDS], Ahmed *et al.*[28] measured the adsorption of SDS by PVAc particles and found an S-shaped adsorption. This they attributed to partial absorption of the surfactant by the polymer acting as a porous solid. It should be noted that we found no swelling over this range of SDS concentrations. Although this S-shape can also indicate the presence of traces of impurities[29] or of detached low molecular weight material outside the particle, reconsideration of their data shows that an alternative interpretation would be that SDS is adsorbed as pairs of associated molecules (two-mers) on the surface of the particles and this appears to be confirmed by their having found an area of 0.3 nm^2 was occupied by each molecule of SDS—half the area they found to be occupied by SDS on PMMA particles. However, our results show that the leveling out of the amount adsorbed, which corresponds to the molecular area 0.3 nm^2 at 5−7 mM [SDS], is beyond the concentration at which swelling commences in our experiments, and this suggests a reinterpretation of their values obtained over this range of [SDS] is necessary. Nevertheless at ~4 mM [SDS], where we have found no swelling, the amount of SDS which Ahmed *et al.* found adsorbed on or absorbed by PVAc latex particles was almost twice that which they found on PMMA latex particles. This may simply reflect a difference in "required areas" between the two polymer surfaces (a spread of values has been reported in the literature[30]) but is in agreement with the interpretation that SDS adsorbs on PVAc particles over the range 0−4 mM [SDS] as two-mers so that each SDS molecule occupies half the area (0.57 nm^2) occupied on PMMA. As expected, they found that on the surface of PMMA particles, SDS adsorbed according to the Langmuir isotherm as single molecules. Gilanyi and Wolfram[31] and Hall[32] discuss the possibility of SDS adsorption on water-soluble polymers as single molecules or as two-mers over this range of [SDS]. In the absence of definitive data, we will assume that a layer of SDS molecules builds up on the surface of our unswollen PVAc particles over the range 0−4 mM [SDS] either as two-mers or as single molecules. Simple calculation shows that for 1000 ppm PVAc this accounts for the equivalent of 0.2 mM SDS. However, it is not known what surface microstructure of PVAc latex particles is needed for this adsorption.

Mechanism of Swelling. Figure 2, Figure 10, and other examples in the Results section show that the threshold surfactant concentration was below the cmc in all cases, yet paralleled the cmc. This suggests that induced micelle formation or some similar process was responsible for the swelling. Furthermore, it is apparent from Figures 3 and 4 that there were no great differences in the initial rates of swelling under a variety of conditions. At 6 mM the concentration of ordinary micelles is very low whereas at an initial concentration of 20 mM SDS the equivalent of 60% of the total SDS concentration is in the form of ordinary micelles. Hence ordinary micelles are not the predominant species involved in swelling.

Swelling and the presence of up to 96% water indicate a high osmotic gradient between the interior of the particles and the surrounding fluid. Some mechanism has to be present to concentrate a high content of strongly hydrophilic species in the interior of the particle, *i.e.*, a much higher SDS concentration than in the surrounding fluid in order to overcome the attractive forces between PVAc chains in the poor solvent water; these attractive forces provide the stresses resisting the expansion. (The stresses, principally elastic and surface forces, restore the size when the SDS is removed.) At the same time there are still equilibria existing between all species that are present both inside the particle and in the surrounding fluid. The sigmoidal behavior (Figure 2)—a range of concentrations over which there was no effect followed by a steep increase and a leveling out—indicates that the swelling involved the formation of species consisting of clusters or aggregates of SDS molecules in dynamic equilibrium with the molecular SDS in the aqueous phase. These results imply that bound surfactant molecules over this SDS concentration range were in the form of clusters along the PVAc chain and that these "polymer−micelle complexes" each involved a smaller number of SDS molecules than are found in ordinary SDS micelles above the cmc in pure water.[33] Polymer−micelle complexes (PMCs) are a form of cooperative binding with the polymer chains. Their existence has been established over many years in studies on several water-soluble polymer/surfactant systems.[11,34−37] Furthermore, in relation to their degree of interaction with SDS,[7] these water-soluble polymers together with PVAc have been considered as being members of a series. However, there appears to be no earlier report of PMCs having been found in the system PVAc/SDS or PMA/SDS or in any other water-insoluble polymer/surfactant system. Other terms that have been used to describe these and similar PMC species are mixed micelles, minimicelles, protomicelles, and hemimicelles. The probable structure of the PMCs will be discussed later.

Cabane[37] could find no NMR evidence for single attached SDS molecular species in the case of the soluble polymer PEO in SDS solution. There is strong evidence that PEO and PPO[34] form PMCs and there are many similarities in the behavior of PPO and PVAc toward SDS.[7] However, it is possible that PVAc differs fundamentally from these more polar water-soluble polymers in having single molecules or two-mers attached along the chain and in not going on to form PMCs but this seems unlikely.

The curlover in the sigmoidal plot of swelling *vs* [SDS] started at about 9−10 mM [SDS] total, and at this point we believe that the molecular [SDS] as single ionic pairs in aqueous solution had risen to no more than 5 mM so that its concentration was still below the cmc—the concentration needed for conventional micelle formation. The curlover could indicate an approach to a saturation of available sites suitable for formation of PMCs or a balance had been achieved between the osmotic forces swelling the particles and the constraints limiting the swelling. The later stages of the curlover corresponded to the molecular SDS concentration for the onset of ordinary micelle formation as indicated by the conductivity and by the surface tension measurements.

The plateau was reached at ~15 mM [SDS] total. At this stage the concentration of molecular SDS would have risen to the cmc for ordinary micelle formation and from then on the formation of ordinary micelles would be favored thermodynamically and additional SDS went into this. We estimate (see later) that the PMCs and the polymer chains linking them were far enough apart to enable the ordinary micelles to enter the particles or to form inside the particles. In this case there would be an equilibrium between the interior of the particles and the surrounding fluid, and thus ordinary micelles would not contribute to the osmotic gradient and hence the swelling. In circumstances such as salt solutions where the cmc is lower and ordinary micelle formation is favored, it is possible that they could be forming before the particles have swollen enough to allow them to enter.

Equilibrium Relationships. It can be assumed that the volume swelling ratio is a measure of the extent of interaction, *i.e.*, of the number of sites occupied by PMCs. The plot of extent of swelling against [SDS] total

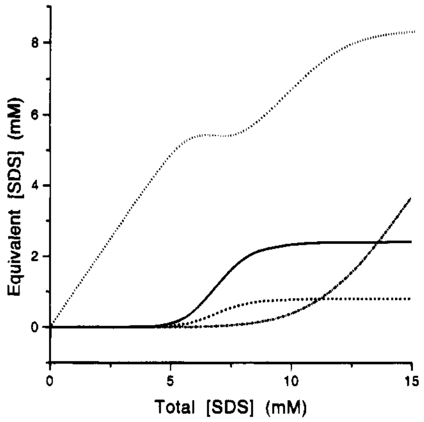

Figure 12. SDS locations *vs* SDS total concentration. 1000 ppm PVAc at 25 °C. (•••) Molecular (single ionic species); (—) in particles; (- - -) associated with readily soluble material; (—•—) as ordinary micelles.

(Figure 2) can be fitted by the Hill–Langmuir isotherm,[38] $v_{LT} = K[S]^n/(1 + K[S]^n)$, where K is an equilibrium constant, [S] is the concentration of molecular SDS, and n is the aggregation number of the PMC, *i.e.*, the number of SDS molecules in each PMC. Zhu and co-workers[39] have developed equations describing hemimicelles building on a monolayer of adsorbed surfactant on various materials. However, these treatments are not applicable to this system since their derivation depends on the number of sites for adsorption of PMCs being constant over the total SDS concentration range. Furthermore, the amount adsorbed should be plotted against the molecular SDS concentration rather than against the total SDS concentration. In any case, from these relationships alone it is not possible to separate K and n and determine values for them. The adsorption processes open up further sites for occupation, and in that sense the swelling is autocatalytic. However, the simple relationships for catalytic systems cannot be applied in this case because the number of new sites made available by each increment of swelling is not constant over the [SDS] range or over the time of a kinetic experiment and is not quantifiable in terms of the degree of swelling. There is some formal resemblance to the swelling of cross-linked gels but the high ionic content of the swelling PVAc particles means there is a greater osmotic pressure to give a higher degree of swelling than is usually encountered in cross-linked systems.

In Figure 12 the quantities of SDS according to their location in the system have been plotted against total [SDS]. The molecular SDS has been estimated from conductivity measurements and from the surface tension measurements assuming there is no contribution from either the unswollen or swollen particles or from the readily soluble material. Another independent estimate can be made from the analyses of the ultracentrifuge supernatants (Table 1), allowing 0.9 g of SDS as associated with each gram of readily soluble PVAc.

Kinetic Relationships. For purposes of comparison, the observed wide and orderly increase in rates is accommodated better by the Kohlrausch–Williams–Watts (KWW) dispersive expression. This kinetic treatment involves having a rate constant decreasing with time as expressed by eq 1, which is an approximate representation of the more meaningful "as the reaction proceeds". Originally an empirical relationship, this equation now has a sound theoretical basis[23,24] and has been used extensively in characterizing experimental data in many fields.[19–22] It expresses a range of rate constants for the reactants so that the effective overall rate constant appears to decrease with time during reaction as the more active species are used up rapidly at earlier times.[22] Dissado[24] derived a similar expression by considering a reactant exploring a discrete lattice or matrix to find suitable reaction conditions. It is apparent that there is a parallel with the phenomena in the PVAc/SDS system; the SDS molecules are continuously exploring the particle surface—and later the interior of the particles—by forming PMCs which can then break up to re-form elsewhere, seeking segments of chains which can be prized away from their immediate neighbors while still retaining an attachment via the rest of the chain to the bulk of the particle. This allows ingress of solution, resulting in the formation of more PMCs and completing that process at the molecular level. This manifests itself as swelling as more solution enters and exposes fresh surfaces and the hitherto buried sites for reaction. The segments which are the easiest to be released interact first and then progressively the more difficult. Some short chains disentangle altogether and become solubilized in the surrounding solution. The value of the coefficient α ($0 < \alpha \leq 1$) in eq 1 is a measure of the distribution of rate coefficients. When $\alpha = 1$ the rate coefficient is constant and eq 1 reduces to the normal first-order relationship. The smaller the value of α, the wider the range of rate coefficients encountered. In the present study α was found to have values between 0.35 and 0.50 (Table 2).

Mechanism of Loosening the Surface Chains. The initial attack must take place at the interface between the aqueous phase and the surface of the PVAc particle and thence continue into the interior of the particle. This means that the chains must first be partially loosened. Initially, the SDS molecules probably interact with the surface microstructure of the unswollen PVAc particle, forming an almost complete layer of adsorbed single molecules or two-mers at 4.5 mM [SDS].[28] It is necessary to consider how the SDS is able to penetrate into the interior of the particles at higher SDS concentrations. In this regard the penetration process at the surface is quite fast and does not seem to depend on PVAc concentration, *i.e.*, PVAc/SDS ratio, or to involve ordinary micelles (see earlier). Although the surface of the PVAc would be expected to contain relatively close-packed polymer chains, the VAc units neighboring a sulfate group from the initiator or hydroxyl group from hydrolysis of a sulfate or acetate group could intrude into the aqueous phase. During the final stages of polymerization when the material is a viscous fluid, there could be some disturbance of the microscopic smoothness of the spherical particle. These factors could provide segments on which PMCs might form and then partially expose the under layers.

It has been suggested[6,40] that single molecules of surfactant might enter into the interior of the particle and then attract water, resulting in swelling. The polymer possesses both hydrophobic and hydrophilic character—each to a small degree. Because of the strongly polar ionic SO_4^- group together with its positive counterion, the salts SDS and SOS or other ionic surfactant would not be expected to be sufficiently soluble in bulk PVAc to leave the aqueous phase and to partition between the aqueous phase and the interior of the polymer particle. Nor would other SDS species, such as the uncharged acid form, be present in high enough concentration to be effective. The miscibility of the monomer VAc with alkanes indicates some affinity between them. The polymer PVAc is not soluble in alkanes but there could be sufficient affinity between the PVAc methylenic groups and the hydrocarbon tail of SDS to facilitate at least a partial penetration of the tail between neighboring polymer chains on the surface of the particles. Initially, they might "glue" the chains together but as more tails penetrate, the ionic sulfate groups will repel each other and this could force the chains apart, exposing the subsurface layers. Penetration of single species, if it did occur, would be expected to be approximately linear with SDS concentration rather than having a critical minimum value of 4.5 mM [SDS].

Alternatively, ordinary submicellar aggregates which are not stable in themselves and thus have a very short lifetime and are present in very low concentrations could interact with surface PVAc chains. These could thereby form "subPMCs", the equilibrium would be shifted so that more submicelles would form, and the process would proceed. Another possibility is that PMCs could form by SDS molecules associating with the adsorbed SDS or finding suitable sites (which may be a sequence of VAc units present as a loosely attached chain end or loop in the surface of the particle). Along the path to forming complete PMCs it must be possible for smaller groups of SDS molecules to associate with a shorter sequence of VAc units in the same way as submicellar units build up to form ordinary micelles at the cmc. Since the reversal and shrinkage of the particles is so rapid when the SDS concentration is reduced, *e.g.*, by dilution, it may be assumed that the interchange of SDS molecules between solution and PMCs is relatively fast (as for oridinary micelles) and that the PMCs are in dynamic equilibrium. If the SDS molecules do not penetrate the particles, the PMCs which are formed in the first instance must be in contact with the aqueous phase surrounding the still unswollen particles and each is accompanied by its corona of sodium counterions. An isolated PMC or incomplete PMC in the aqueous phase at the surface of a single particle may not be able to exert enough force to separate a portion of its attached chain or chains away from the surface of the particle, especially since the rest of the chain is likely to be buried in the unswollen particle or otherwise intertwined with other chains. When the [SDS] is high enough, PMCs will be present close enough together on a surface to be mutually repulsive, and this can be expected to provide a far greater force overcoming the van der Waals attractions and allowing the solution to penetrate under the outer layer. Another adsorbed layer and then PMCs form deeper in than the original surface. They are accompanied by sodium counterions and water, and it is the water that is responsible for almost all (96%) of the ultimate increase in size. Once PMCs form beneath the original surface, there would be a sufficient concentration of ionic species to provide the osmotic pressure that causes the particles to swell. If a critical density of PMCs is necessary on an individual particle, according to the above postulate, not all particles will start to swell at precisely the same SDS concentration and this will result in the observed curlup just past the point where swelling is first observed in the plot of swelling volume ratio against SDS concentration in Figure 2. Alternatively, the curlup could be attributed to a measure of polydispersity in the aggregation number for SDS molecules in the PMCs. The outermost several layers are loosened as quickly as is the surface layer, which suggests that there is nothing special concerning the surface. This all happens below the ordinary cmc.

Limitations to Swelling. The process slows down as separation or disentanglement of segments becomes more difficult. Such slowing down could mean that the mesh of already expanded material is providing constraints inhibiting further expansion or that there are more structures in the core of the particle than in the periphery which are difficult to loosen or relax. Along with the reversibility of the swelling, this indicates that unaffected parts of the chain may still be intertwined with other chains and that these will remain in microdomains of entangled chain ranging from a simple pair of loops to a knotted region. As these relax, during swelling or with time, further sites will appear along the chains, interact with SDS, and be seen as further swelling due to repulsion between the charged micellar complexes and to the ingress of solution. Finally, an apparent limit is approached, at least over the several months that we have followed the process. There will be a balance between the osmotic pressure difference within and outside the particle and the constraints provided by the entanglements. Where there is not an excess of SDS, an equilibrium or quasi equilibrium will be established at long times, according to the SDS concentration. The molecular SDS concentration will then have fallen to 4.5 mM, which is below the limit for formation of more PMCs. Swelling in 6–8 mM SDS (Figure 1) probably proceeds a layer at a time and stops at the point when the molecular SDS concentration falls below 4.5 mM.

Reversibility and Integrity. The swollen PVAc particles are very stable to shearing forces—prolonged high speed/high shear stirring (Ultraturrax, Janke and Kunkel KG) and exposure to ultrasonic treatment had no apparent effect on them. We are unable to tell whether this resistance to shear is due to a certain rigidity in the particle despite their open structure and high (96%) water content or more likely to a flexibility which allows the particle to deform to minimize the stress and then recover. We suggest that the power to recover is conferred by the opposing forces due to the repulsion between neighboring charged PMCs stretching the chains on the one had and on the other hand the collapsing of the chains because the vinyl acetate units are in water, a poor solvent.

At the SDS concentrations reported in these investigations, the swelling is reversible; on warming or on dilution of the SDS (Figures 7 and 9), the particles revert very rapidly to approximately the original size. The high initial swelling rate shows that there is a ready access of the aqueous phase to the interior of the swollen structure. A small residual shrinkage takes longer and this may mean that the collapsed outer layers either impede equilibration between the aqueous solution and the still swollen core or that it takes time for the fully relaxed disposition to be assumed.

On raising the SDS concentration again, the same rate of reswelling is obtained (Figure 8), showing that the particles have not lost their integrity. We believe that microdomains of entanglements provide this integrity.

Nature of the Microdomains. It is possible that the microdomains have structures which are so configured as to be unfavorable to the adsorption of SDS or to the formation of the PMCs. For example, there may be insufficient free and mobile segments of the chains at that location to loop at the surface of the PMCs providing the necessary thermodynamic driving force and stability. This of course implies some restrictions on the movement of the chains.

It seems unlikely that in the initial stages, a three-dimensional network could be formed by two or more chains being attached onto the one micelle as postulated for cellulose ether/SDS complexes.[36] The SDS of the PMCs would be expected to be in dynamic equilibrium with the SDS in the solution and thus should readily dissociate and be unlikely to give rise to a structure with any stability.

This leaves as the species responsible for the stable microdomains the intrinsic entanglements which were formed during the polymerization process or during subsequent diffusional movements and which cannot be loosened by the SDS. One example of these could be simple or complex knots formed as the end of the polymer chain grew during propagation or simply diffused subsequently so that it crossed back on itself. The theory of knotting of polymer chains dissolved in solvents is still being developed[41] and self-avoiding random walk Monte Carlo calculations have shown that fewer knots can be expected in good solvents than in poor solvents. Undoubtedly similar considerations apply during polymerization. Scaling theory indicates that the number of knots per chain scales as the square root of the length of the chain. In a chain of $M_w = 784\,000$ at most one knot can be expected per chain. Since each chain is in the random coil conformation, it will be intertwined with about 100 others and several of these could be expected to be confined together by the one knot. They will be imprisoned if the knot is tightened before they can escape and this will be considered below. PVAc usually has a degree of chain branching[42] and this might be expected to inhibit unraveling.

Another form of entanglement could be generated by the diffusion of a loop through another loop giving an entanglement similar to that which is often found in coiled ropes or tangled fishing lines. A knitted garment is an example of an orderly and extensive network of interlocking loops. A much more limited structure is present in polymers and there will be several per long chain. This structure could be formed during polymerization before the mixture of polymer and monomer became too viscous or perhaps in the early stages of swelling. The microdomains which are involved here are unlikely to consist of simple pairs of interlocking loops comprised of two crossing chains. However, the PMCs are in dynamic equilibrium, forming and reforming readily, and the repulsion should not greatly slow down the diffusional sliding. Therefore such simple loops are unlikely to prevent total dissolution. One loop positioned through another and perhaps locked by a third would be much less likely to disentangle and is probably one of the structures reponsible for preventing the dissolution of the particles in SDS solutions.

In considering the nature of the microdomains, it must be borne in mind that they are not released by SDS solutions at concentrations up to at least 20 mM but apparently can be loosened by acetone and other solvents for PVAc. Consider a simple knot formed by a PVAc polymer chain. When exposed to SDS solution, PMCs will form on the two arms of the knot and will repel each other, exerting a tightening force on the knot. Another chain trapped inside the knot will find it difficult to escape. Similarly, PMCs formed on entangled loops could tighten some structures. It has been pointed out that entanglements which involve pairs of acute angle loops could tighten irreversibly if sudden tension were applied to the polymer chain.[43] The rapid swelling observed in this system may apply tension faster than the disentangling relaxation processes can release the increase in strain and thus give rise to the microdomains which prevent complete solubilization of the particles. However, experiments involving the slow addition of SDS solution or the slow evaporation of a dilute PVAc/SDS solution over several days showed that there was still approximately the same number of particles present that the swelling was not greatly different from that of the rapidly swollen particles, and that swelling was reversible. Since we have no idea of how slow tightening must be to avoid irreversible tightening, we cannot altogether dismiss sudden tightening as a contributor to the integrity of the particles and it could be possible that even the slowest swelling is accompanied by knot and loop tightening.

We now turn to the interlocking loops or the simple knot tied around a chain which is then exposed to a solvent. Molecules of the solvent wet the chains and can therefore penetrate the inside of the loop or knot. In a good solvent the polymer chains repel each other,[44] forcing the loop or knot open in the same way as a marlin spike does with rope. Any trapped loop or chain is now much freer to reptate and ultimately to escape while the knot can also undo.

Lower molecular weight material can be expected to have fewer entanglements per chain—perhaps no entanglements for the lowest molecular weight chains—and is thus able to escape from the other chains as the readily soluble material. In support of this contention, it should be noted that even linear polymers, which do not have permanent links between neighboring chains, have been found to behave as if they had cross-links and this has been attributed to temporary trapped entanglements.[45,46] The effect is greater with higher molecular weight polymer; anomalous viscosity effects for melts at 160 °C were found for PS above molecular weight ~20 000. Further, Wool[47] found a critical molecular weight for bridge network crossover to a high-viscosity entangled fluid at ~25 000 for PVAc melts and this increased with dilution. These values should be compared with our upper limit of $M_w = 180\,000$ for the readily soluble material.

Structure of Readily Soluble Material. Irrespective of whether the portions of the chains between the PMCs were ensheathed in adsorbed SDS and were thus hydrophilic in character or whether the bare VAc units found themselves in a thermodynamically unfavorable aqueous environment, we believe the expansive forces of the charges associated with the PMCs predominated and that the chains of the readily soluble material were in an extended conformation. The detached readily soluble PVAc had fewer restrictions on its movement or conformation than had that still remaining inside the particle and the chains were more accessible to the SDS in the solution; all potential sites for PMCs were available and the PMC adsorption should therefore follow the Hill–Langmuir isotherm relationship.[38] Because of the greater accessibility, the readily soluble PVAc may be associated with relatively more SDS than was the PVAc inside the particles but, since we are not able to evaluate this from our experiments, we will assume that the weight of SDS associated with unit weight of PVAc is in the same proportion as that found in the swollen particles, *viz.*, 0.9.

Below 4.5 mM total [SDS], such as at 2.5 mM, which was the final concentration of the dilution experiment (Figure 9), the PMCs will have reverted to molecular SDS. Since there are solubility limitations, even the low molecular weight chains will have collapsed and coagulated. Perhaps some will have become reattached to the deswelled particles and others will have clumped together to form new particles too small to be detected by the DLS technique.

Structure of the Complex. The postulated formation of polymer–micelle complexes indicates the possibility of a close correspondence between the dispositions of the nonpolar methylene groups of the polymer backbone and its slightly polar ester groups on the one hand and the hydrophobic and hydrophilic areas, respectively, of the SDS molecules as grouped in the PMCs. Breuer and Robb[7] listed polymers in the following order of increasing degree of interaction with anionic surfactants: PVAl < PEO < methylcellulose < PVAc $\leq$ PPO $\sim$ poly(vinylpyrrolidone). Thus PVAc is expected to behave in a fashion similar to these water-soluble polymers but to differ in degree.

Witte and Engberts[34] using a fluorescence quenching method measured the mean values of the aggregation numbers for PPO/SDS complexes, *viz.*, 16 at 10 mM [SDS], 23 at 15 mM [SDS], and 29 at 20 mM [SDS]. The average aggregation number increases with increasing SDS concentration because, at the higher concentrations when the complexation would be expected to be complete, ordinary micelles (aggregation number 53) are forming. PVAc is said to have an affinity for SDS similar to that of PPO[7] so we shall assume $n \approx 16$ for the PVAc/SDS system—the aggregation number increases with surfactant concentration. The size of the PMC is governed, in part, by the repulsion between the charged sulfate groups of the PMC in the same way as in ordinary micelles.

Using NMR and other evidence, Cabane[37] has developed representations of the ordinary SDS micelles and of the "mixed micelles" formed between SDS and the water-soluble polymer PEO. Other proposed structures of ordinary micelles have been reviewed by Chevalier and Zemb.[48] In the PEO "mixed micelle", Cabane found the SDS tails are also in the interior while the polymer chains are adsorbed in proximity to both sulfate and methylene regions of the surface and there is a stoichiometric equivalence indicating a preferred complex between surfactant and polymer. Cabane[37] deduced that ~10% of the length of the PEO chain was associated directly with the surfaces of PMCs and, since the interaction between PVAc and SDS is stronger than that between PEO and SDS,[7] it can be assumed that something like 20% will be associated in the PVAc/SDS system. On the basis of these assumptions, a simple calculation shows that there are approximately 16 VAc units associated with 16 SDS molecules in each PMC and there are ~60 VAc units strung between neighboring PMCs and partially collapsed to occupy a length of ~7 nm. We consider that short segments of the PVAc chains are adsorbed at the hydrocarbon areas of the surface of the PMCs or just below the surface, displacing water and acting in the same way as a cosurfactant such as the amphiphile octanol.

The picture we favor is similar to that illustrated in Figure 1B of the paper of Xia *et al.*,[49] namely, PMCs each having several monomer units of the polymer associated but with the VAc units in between having both collapsed and extended regions. Again in Figure 1 of the paper by Nagarajan[50] several SDS clusters are held close together by a chain of PEO when one would expect their mutual repulsion to separate them as in an earlier representation.[51] However, the latter shows the PEO chain "lassooing" the small SDS micelles whereas we would expect the methylenic groups of the polymer backbone to be stationed at the same depth as the outer methylenic groups of the SDS while the more polar groups of the polymer, *viz.*, oxide for PEO or acetate for PVAc, would be between the sulfate head groups of the SDS. This would have the effect—as does a cosurfactant—of pushing the head groups apart, thus giving the smaller radius of curvature at the surface necessary for smaller micellar sizes. (The PMCs are not necessarily spherical.) Since PVAc is not soluble in hydrocarbon solvents, the disposition of PMCs and polymer chains is certainly not like the representation in Figure 6 of the paper by Kokufuta *et al.*,[52] where the polymer chain appears to pass through the center of the micelle. The description "string of beads" often appears in the literature and this is unfortunate because it has the connotation that there are central holes through which the string (the polymer) passes.

Salt. Salt lowers the cmc and similarly lowers the "critical PMC concentration". Also, the higher the salt concentration, the higher is the aggregation number for ordinary micelles and for PMCs.[34] A further consequence is that, since the salt can pass readily into and out of the swollen particle, the higher ionic strength outside the particles is reflected inside, repressing the ionization of the SDS so less water is expected to be in the fully swollen particles and hence their swollen volume is less than in the absence of salt. The aggregation numbers for the PMCs of both PEO/SDS and PPO/SDS increase with salt concentration.[34] Thus the salt systems reach plateaus (Figures 2 and 10) at relatively low [SDS], perhaps because ordinary micelles start to form before PMCs can form on all potential sites.

Cross-Linking. Cross-linking limits swelling presumably by completely restricting the disentanglement of some of the intertwining chains. At low SDS concentrations (where we believe the outer layers only are involved in the swelling), the final values for radiation cross-linked material are similar to those for non-cross-linked latex (Figure 11). This suggests that the surface layers are not cross-linked and can be loosened by the SDS. At higher SDS concentrations, the final values are less, indicating that cross-linking is confined to the interior of the particle.

Monomer and Iodine. The presence of monomer probably saturates the sites at which the surfactant micelles become attached. If the SDS concentration is increased, some monomer is squeezed out. Monomer has high solubility in the interparticle water phase and could be associated with or solublized by the ordinary micelles and may swell out the PMCs so they cannot stick to the chain. Similarly, each molecule of iodine is probably associated with several vinyl acetate sites on the chains so in this respect iodine may act like a cross-linking agent. However, both monomer and iodine are able to penetrate into the interior of the particle.

Relationship to Earlier Work. Our observations and interpretations—surface adsorption, PMC formation, readily soluble material, importance of molecular weight, rapid and dynamic equilibrium between the components, reversibility, and role of entanglements—explain many puzzling features reported in this area in the literature.

The increase in viscosity reported in PVAc/SDS systems was attributed to the solubilization of the chains and to their acting like a polyelectrolyte.[3] This could be true in some cases but we have shown that over the [SDS] range 5–30 mM the increase could be thickening due to interaction between swollen particles (Figure 5) and that the readily soluble material, which was in equilibrium with SDS solution and thus carried its share of ionic charges, had very little effect on the viscosity. Edelhauser's correction[6] for the contribution of unsolubilized particles to viscosity is thus not likely to be valid. Based on the greater rate of hydrolysis of PVAc in the presence of surfactant[40] and other evidence, Edelhauser[6] considered that surfactant molecules penetrated into the interior of the particles bringing water with them and swelling the particles until at a sufficiently high surfactant ratio (and at surfactant concentrations much higher than we report here), the particles disintegrated, resulting in a clear solution. Meanwhile, polymer chains become disentangled and detached from the surface of the particles. He showed by centrifugation that the particles had swollen tremendously before they disintegrated. He found a "cmc" of 5 mM [SDS] and that corresponds to the concentration we found for the onset of PMC formation and of swelling. Further, the free surfactant concentration was 10 mM when the total [SDS] was 40 mM and the remainder was readily released from the latex. Here he was unknowingly dealing with a reversible swelling. He thus described many of the features of this system but failed to note the role of PMCs or of the reversibility of swelling. Similarly, a sudden increase in surfactant adsorption at ~5 mM [SDS] was reported by Vijayendran *et al.*[53] for the PVAc-*co*-butyl acrylate/SDS systems. Other authors were certainly working in the same swelling regime as we report here, *viz.*, 4–20 mM [SDS], and obtained similar experimental results. For example, Horin and Arai[54] did not realize that PVAc dissolution was incomplete for higher molecular weight PVAc.

In the earlier literature there was evidence for a solubilized stoichiometric complex between polymer and SDS, and in many of the subsequent investigations the results are reported in terms of the ratio SDS/PVAc. Our work has shown that, over the PVAc concentration range 62.5–2000 ppm and probably below and beyond, the onset of swelling occurs at ~4.5 mM [SDS], corresponding to the concentration usually called "T_1" for soluble polymer/SDS systems.[11] T_1 had been found to be independent of polymer concentration.

PVAl interacts with SDS to form PMCs to only a limited degree, and this is presumably because it is too polar or dimensionally unsuitable and the displacement of water from the surface of the chains by SDS is not favored thermodynamically as strongly as for PVAc.

Although attention was drawn many years ago[27] to the possibility of partial solubilization of PVAc—the material we have termed readily soluble—subsequent authors do not appear to have taken account of this in interpreting their results. Our observations suggest a technique for separating lower molecular weight material from PVAc latices.

Often in emulsion polymerization studies authors note the total concentration of added surfactant in relation to its cmc. In a recipe such as the one we have used producing 142 nm particles, the total SDS concentration is initially 13 mM and thus above the cmc at the commencement of polymerization. The PVAc concentration was 223 000 ppm so most of the SDS would be adsorbed on the surface of the final PVAc particles, leaving the SDS concentration in the solution well below the cmc and below the SDS concentration needed for onset of swelling. The surface of the unswollen particles is capable of adsorbing the equivalent of 44.6 mM SDS while the molecular SDS concentration is 4.5 mM, making a total of 49 mM SDS. At higher total concentrations of SDS the molecular concentration will remain approximately constant at 4.5–5 mM, the additional SDS being used to swell the particles until they form a gel.

The question of the microscopic mechanism involved in the loosening and ultimate untying and freeing of knots and entanglements when polymers—especially those of high molecular weight—are dissolved in good solvents does not appear to have been addressed anywhere in the literature. We have suggested a plausible mechanism.

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