

Polymer–Surfactant Interaction and Stability of Amorphous Colloidal Particles

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The behavior of mixtures of polymer and surfactant as peptizing agents for controlling Ostwald ripening and solvent-mediated phase transformations of amorphous colloidal particles is studied by equilibrium dialysis and electron spin resonance (ESR) spectroscopy using nitroxide spin-labeled compounds. It is found that amorphous phase stability is dependent on the interplay between polymer–surfactant complexation in the bulk fluid and the conformation of adsorbed molecules at the particle–fluid interface. Optimum stability is obtained over a range of compositions in which both polymer and surfactant are strongly bound to the surface of the particles. The conformation of the adsorbed polymer is characterized by a high fraction of train segments and relatively few loops. The shorter chain surfactant functions as a filler to fill vacancies on the surface. The results suggest that the combination of polymer and surfactant may provide a defect-free monolayer that offers better protection against solvent-mediated transformations than either polymer or surfactant alone.

Introduction

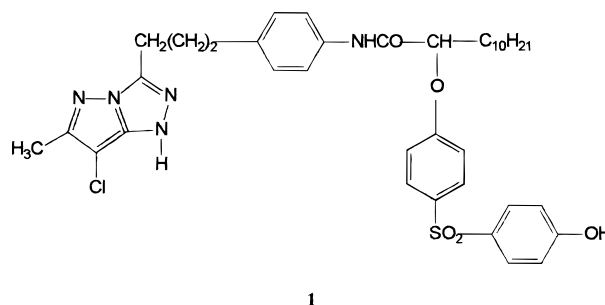
Both particle size and solid-state structure (amorphous or crystalline polymorphic form) of a dispersed component are important in many products and processes.¹ They influence chemical reactivity of a compound, solubility (bioavailability) of a drug, and flow properties of the dispersion, for example. Invariance of these features during storage of the dispersion is of critical importance. This paper is concerned with the synthesis and long-term preservation of colloidal particles of organic compounds in the amorphous form.

Nanoscale amorphous particles of organic compounds are a preferred form of materials for a number of applications because they are spherical and isotropic; dilute dispersions of these particles have well-defined flow. The higher solubility of these particles in comparison to crystalline forms may increase the bioavailability of relatively insoluble drugs.^{2,3} Furthermore, molecules undergoing chemical reaction have a greater mobility in the amorphous state (above the glass transition temperature) and may have a higher reactivity in this form compared to the crystalline state.⁴ However, the synthesis of these materials can be delicate. A common method of synthesis is by nucleation and growth from supersaturated solutions. In this process the initial precipitate is often amorphous but extremely unstable to particle growth by ripening and solvent-mediated phase transformations.^{5–9} Transformation to one of the crystalline forms may be rapid under normal conditions. However, extremely stable dispersions of amorphous nanoparticles are obtained by precipitation in the presence of a mixture of polymer and surfactant.^{10–13} But the mechanism of action of these agents is unknown. Here we show that amorphous phase stability is dependent on the structure of the adsorbed layer at the particle–fluid interface. The optimum structure is a close-packed composite of strongly bound segments of polymer and surfactant. Furthermore, for a given overall concentration of polymer, such a structure is realized over a limited range in the concentration of monomeric surfactant in the bulk aqueous fluid. The relationship between the latter and the total concentration

of surfactant in solution is mediated by polymer–surfactant assemblies. It is proposed that the above interfacial structure is characterized by a minimum of voids or vacancies, resulting in exceptional resistance to mass transport.

Results and Discussion

Compound **1** is an example of an incorporated dye precursor in color photographic film.¹⁴ When film is processed, it undergoes reaction with oxidized color developer to form dye.¹⁵



The compound is soluble in a mixture of aqueous base and a water-miscible organic solvent due partially to deprotonation under alkaline conditions. Aqueous dispersions of **1** may be prepared for incorporation in film by arrested precipitation from this medium. Typically, compound **1** (15 g of crystalline powder with a melting point of 162 °C) is dissolved in *n*-propanol (30 mL) upon heating to about 60 °C. Twenty milliliters of a solution containing 1 M sodium hydroxide in water is then added. The composition is allowed to cool to room temperature. It is then added slowly to a solution containing sodium dodecyl sulfate (SDS) (1.4 g) and poly(vinylpyrrolidone) (PVP) (7.5 g of Kollidon 30; $M_w \sim 30$ K and $M_w/M_n \sim 3.5$ from BASF) in 500 mL of water while stirring. The pH is adjusted to about 6.0 by the addition of a solution of acetic acid (15% w/w in water). The resulting dispersion is poured into dialysis membrane tubing (Spectra/Por 2 from Spectrum Medical Industries, Inc.) and washed with distilled water for 48 h to remove

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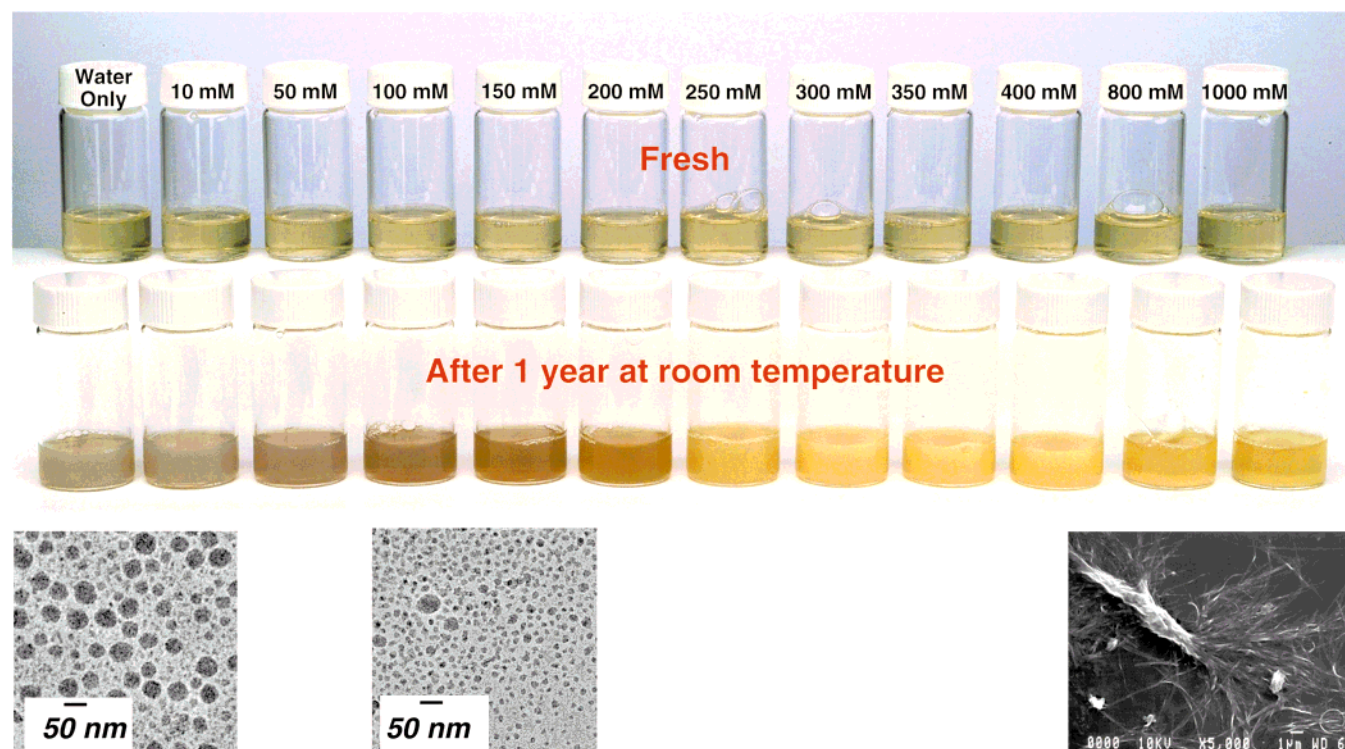


Figure 1. Influence of surfactant level on dispersions stabilized with PVP (0.5:1 by weight with respect to the active component). The upper row shows vials containing fresh dispersion (10 mL) to which an additional 1 mL of SDS solution has been added. The concentrations of the SDS solutions are displayed on the vials: (A) water only, (B) 10 mM, (C) 50 mM, (D) 100 mM, (E) 150 mM, (F) 200 mM, (G) 250 mM, (H) 300 mM, (I) 350 mM, (J) 400 mM, (K) 800 mM, and (L) 1000 mM. The lower row shows the same dispersions after storage at room temperature for 1 year along with electron micrographs of aged samples A, E, and L. Images of samples A and E were obtained by cryotransfer transmission electron microscopy (cryo-TEM).¹¹ The average particle size in these dispersions was determined separately by photon correlation spectroscopy (PCS) to be 47 and 16 nm, respectively. The average particle size in the fresh dispersion was found to be 10 nm. Image of sample L (air-dried on a silicon wafer) was obtained by scanning electron microscopy (SEM) using a Hitachi S4100 microscope (magnification 5000 \times). Analysis by X-ray diffraction¹² confirmed transformation of the dispersed phase from amorphous to crystalline in sample L. No sedimentation was observed in aged samples A–F. (Figure reduced to 73% for publication.)

n-propanol. The dispersion after washing contains about 2.5% w/v of **1** in the form of nanosized amorphous particles.

The upper row in Figure 1 shows several samples, each comprising 10 mL of the above dispersion to which has been added an additional 1 mL of pure SDS solution (containing no PVP) of varying concentration. The lower row shows the same samples after storage at room temperature for 1 year along with corresponding electron micrographs. It is clear that aged dispersions containing high levels of SDS exhibit the most dramatic change. In these samples one observes long threadlike crystals under the microscope; the amorphous phase is no longer dominant.¹⁶ Dispersions containing the lowest levels of SDS do not exhibit crystallinity but do show an increase in particle size. However, samples containing an intermediate level of SDS are surprisingly stable. These dispersions display minimal change in terms of particle size or physical state of the dispersed component even after 1 year! In previous work^{11,12} we found that dispersions of **1** prepared in the absence of PVP (using only an anionic surfactant sodium bis(2-ethylhexyl) sulfosuccinate) exhibit increases in particle size and crystallinity within 1 week after preparation under ambient conditions. To shed more light on the action of the polymer, we examine the influence of surfactant level on its conformation at the particle–fluid interface.

The conformation of polymers at interfaces is obtained by analysis of the electron spin resonance (ESR) spectra of molecules containing spin labels.¹⁷ The properties of spin labels based on the nitroxide free radical, such as the relationship between the motion of the spin label and its paramagnetic

resonance spectrum is well-known.^{18,19} Nitroxide spin-labeled PVP is prepared by polymerizing *N*-vinylpyrrolidone (55.6 g) and allylamine (5.7 g) using *tert*-butyl perbenzoate (0.97 g) as initiator and ethanol (100 mL) as solvent followed by reaction with 4-isothiocyanato-2,2,6,6-tetramethylpiperdinoxyl (0.75 g for 30 g of copolymer) in dichloromethane.^{20,21} The weight-average molecular weight of the polymer by size exclusion chromatography (SEC) is ~ 60 K. The inset in Figure 2a shows the ESR spectrum of the nitroxide group in spin-labeled PVP for polymer dissolved in water and in water containing SDS. In the former case the spectrum consists of three narrow lines, indicating relatively rapid near isotropic tumbling motion. Above a certain concentration of SDS, one observes broadening and loss in intensity characteristic of “weak immobilization” caused by attachment of portions of the polymer chain to SDS micelles. The main portion of the figure shows spectra of spin-labeled PVP in freshly prepared dispersions of **1** containing low, intermediate, and high levels of SDS. These samples were prepared in a manner analogous to the samples of Figure 1 using spin-labeled PVP in place of regular PVP. In each case the spectrum is composed of two major components: a pattern characteristic of slow motion (approaching “strong immobilization” or an anisotropic powder pattern) and a pattern representing freer rotation that depends on the level of SDS (similar to the inset). The former is attributed to spin labels attached to polymer segments that are in *direct contact* with the surface of the particles (trains) and the latter to spin labels in long loop and tail portions of polymers at the particle–water interface as well as those on molecules that are not adsorbed to the particles.

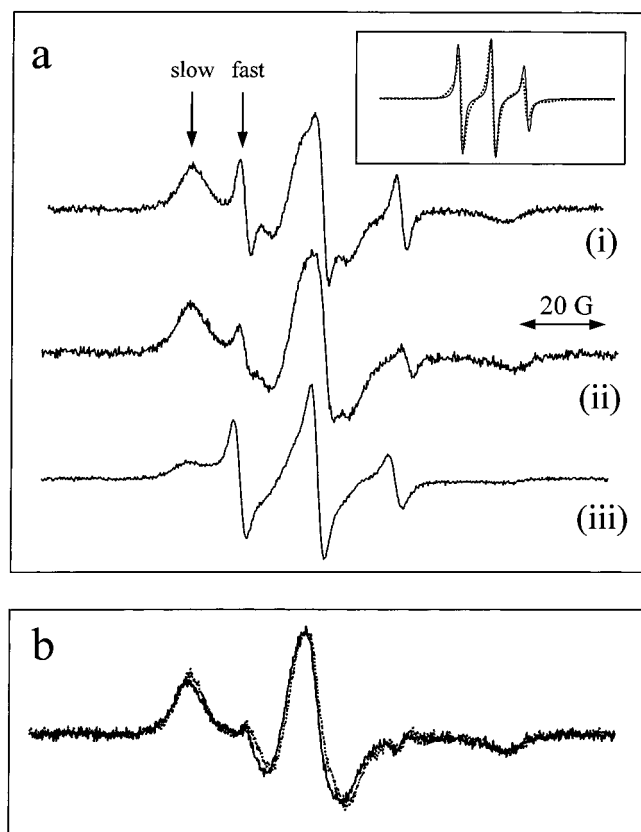


Figure 2. ESR spectra of spin-labeled PVP (PVP-TEMPO). (a) Spectra in freshly prepared dispersions containing (i) low, (ii) intermediate, and (iii) high levels of SDS corresponding to samples A, E, and L in Figure 1. The arrows indicate contributions from the slow moving and fast moving components. The inset shows the spectrum of 0.5% w/v PVP-TEMPO in water (full line) and water containing 0.5 M SDS (dotted line). The concentration of spin label in these samples was determined to be $\sim 10 \mu\text{M}$. A separate experiment was conducted using TEMPO (2,2,6,6-tetramethylpiperidino-1-oxy) at the same level to show that the nitroxide moiety has no affinity for the surface of the particles. (b) Comparison of the spectrum of the bound fraction of spins in samples containing low (full line) and intermediate (dotted line) levels of SDS. The decrease in intensity of the fast moving component at the intermediate level of SDS in part a is caused by association of polymer with SDS; i.e., the reference is now the dotted curve in the inset.

Analysis of these spectra indicates that at the low and intermediate levels of surfactant one has a very high fraction ($\sim 95\%$) of strongly immobilized spin labels. As shown in Figure 2b, the spectra of the "bound fraction" in both these cases (obtained after subtraction of the appropriate faster moving component) are identical in terms of intensity and line shape. The situation is different, however, at high levels of SDS. In this case there is a marked decrease in the fraction of strongly immobilized spin labels to $\sim 65\%$. These results are related to underlying changes in the concentration (or activity) of monomeric surfactant in the bulk aqueous fluid.

The inset in Figure 3 shows equilibrium dialysis measurements of the variation in concentration of monomeric surfactant as a function of the total surfactant concentration for SDS in water containing 35 mM sodium acetate. The level of sodium acetate is equivalent to that in the dispersion samples in Figure 1. For solutions that contain only surfactant, the concentration of the monomeric form is the same as the total surfactant concentration in the regime below the critical micelle concentration (cmc). In the presence of PVP one observes a deviation at about 1.5 mM, which marks the onset of association between surfactant and polymer.^{22,23} The concentration of monomeric

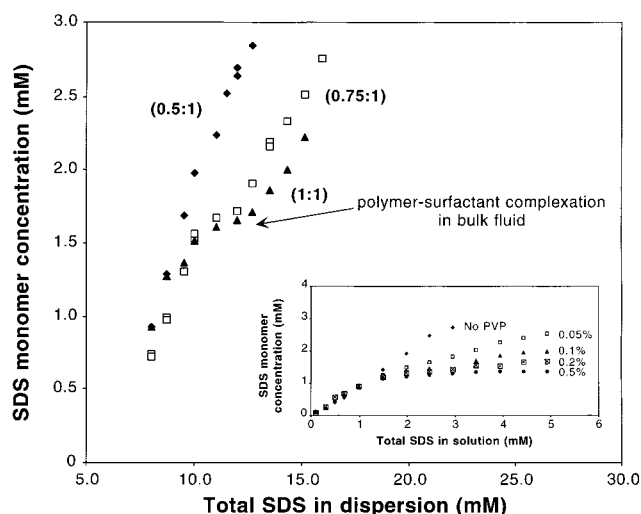


Figure 3. Equilibrium dialysis measurements of SDS monomer concentration. The inset displays the monomer concentration in aqueous solutions of SDS and PVP. The numbers on the figure indicate PVP concentration in % w/v. The main figure shows SDS monomer concentration in dispersions containing 0.5:1, 0.75:1, and 1:1 PVP with respect to the active component. In the first instance, the concentration of "free" polymer available for complexation with SDS is small ($\sim 0.05\%$ w/v). We estimate the amount of polymer adsorbed to the particles to be $\sim 0.8 \text{ mg/m}^2$. Upon increasing the amount of PVP to 0.75:1, the concentration of free polymer increases to $\sim 0.2\%$ w/v. The amount of polymer adsorbed to the particles increases slightly to $\sim 1.1 \text{ mg/m}^2$.

SDS shows relatively little change with increasing total SDS concentration until all polymer chains are saturated with surfactant. Beyond this point the concentration of the monomeric form increases more significantly until it reaches the region of the cmc, and free micelles are formed. As expected, the point of saturation (in terms of total concentration of SDS) shifts with the amount of polymer available for complexation. The main portion of the figure displays the concentration of monomeric SDS in the bulk aqueous fluid of freshly prepared dispersions of 1 containing varying levels of PVP as a function of the total amount of surfactant in the dispersion expressed on a molar basis. These curves exhibit the same pattern as the curves in the inset; of particular importance is the effect of polymer-surfactant assemblies on the concentration of monomeric SDS in the bulk fluid. The impact of this on the stability of the amorphous phase is shown in Figure 4. Here we compare the behavior of dispersions prepared with two different levels of polymer. It is apparent that the range of compositions corresponding to optimum long-term stability is determined by the concentration of monomeric surfactant in the bulk fluid. Note that the shift in the onset of optimum stability (in terms of total concentration of surfactant) at the higher level of polymer follows the shift due to polymer-surfactant complexation in Figure 3.

We summarize our findings as follows: To prepare a suspension of fine particles, one requires a high rate of nucleation coupled with a low rate of growth. On the basis of classical nucleation theory the rate of nucleation is proportional to $\exp(-\Delta G^*/k_B T)$ where ΔG^* is the free energy of formation of the critical nucleus.²⁴ The latter is given by

$$\Delta G^* = 16\pi\sigma^3/3\rho^2(k_B T)^2(\ln S)^2 \quad (1)$$

where σ is the interfacial energy, ρ is the density of the solid (amorphous) phase, and S is the relative supersaturation. Clearly, the rate of nucleation (for a given supersaturation) can be

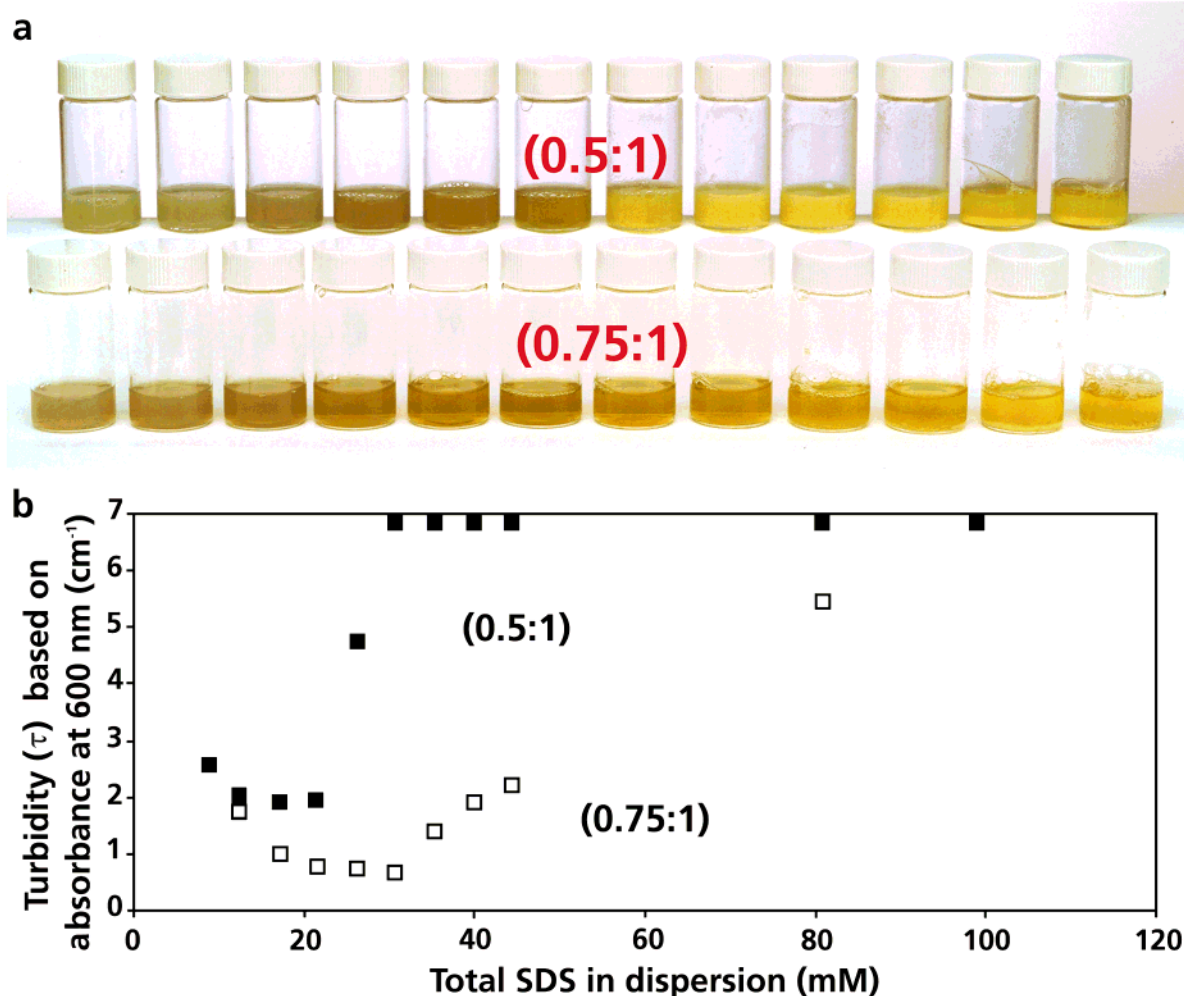


Figure 4. Influence of PVP on the stability of aged dispersions. (a) Aged dispersions containing two different levels of PVP; 0.5:1 with respect to the active component (upper row) and 0.75:1 (lower row). The surfactant levels are the same as in Figure 1. (b) Turbidity of aged dispersions as a function of the amount of surfactant. The turbidity is defined as $\tau = 2.303A/L$, where A is the absorbance and L is the path length of the cell in cm.

significantly enhanced by lowering the interfacial energy. A surfactant such as SDS is very effective in this regard. For example, SDS lowers the interfacial energy of a model interface such as the air–water interface by over 30 ergs/cm² at 25 °C. In contrast, the polymer PVP is able to reduce it by only 10 ergs/cm². Differences in dynamic interfacial energy changes²⁵ are likely to be more pronounced than these equilibrium values because of the slower diffusion of the polymer. As a consequence, in many cases it is not possible to prepare suspensions of small particles using PVP as the sole agent.^{26–28} The fate of the critical nucleus *after its formation* may be strongly dependent on the presence of the polymer. Assuming for the moment that the polymer is more efficient in controlling the growth of the nucleus by Brownian coagulation, Ostwald ripening or its conversion to thermodynamically more stable phases by a dissolution–growth process; the effectiveness of the polymer depends on its conformation at the particle–water interface. It would appear that a *flat conformation* is desirable to retard dissolution–growth processes. In other words, there should be a relatively large number of train segments in direct contact with the surfaces of the particles and relatively few loop segments (contrary to what is desired for steric stabilization^{29,30}). The conformation of the polymer depends on the concentration (or activity) of monomeric surfactant. If the latter is too high, train segments are displaced and the protective action of the polymer is compromised. But why do we obtain the best results

at an intermediate level of the surfactant? It is known that adsorbed monolayers containing relatively few defects are remarkably effective in retarding mass transport at the air–water interface.³¹ Our results suggest that under the right conditions the polymer functions similarly to provide a barrier at the particle–water interface. However, even in this situation one may expect some degree of looping (because of entropic considerations), giving rise to exposed areas at the surface.³² We postulate that over a regime in the activity of monomeric SDS, the conformation of adsorbed surfactant is such that it is able to effectively “plug” these “holes”, enabling an essentially defect-free monolayer at the particle–fluid interface. Confirmation of this is seen in the results of Figure 5. Here we show the ESR spectra of 5- and 16-doxylstearic acids (at a concentration of 10 μ M) in dispersions of **1** in the regime of interest. These molecules are similar in size and function to SDS and the variation in placement of the spin label along the chain is useful in analysis of conformation.^{18,19,33} It is clear that at both the low and intermediate levels of SDS the spectra of both compounds indicate significant motional restriction of the spin labels. We attribute the restricted motion to adsorption at the particle–water interface. Furthermore, the fact that the spectra of the 5- and 16-doxylstearic acids are very similar suggests that the environment is similar at both locations along the chain.³⁴ It is therefore reasonable to expect that *in this regime* a small molecule such as SDS will adsorb “flat” (with its chain

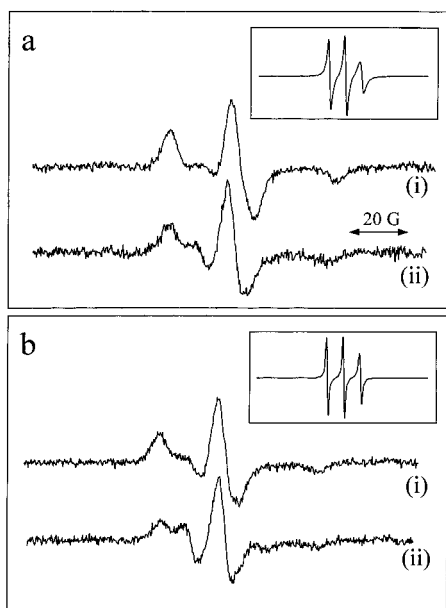


Figure 5. ESR spectra of 5- and 16-doxylstearic acids. (a) Spectra of 5-doxylstearic acid (10 μM) in (i) dispersion containing a low level of SDS (equivalent to (B) in Figure 1) and (ii) dispersion containing an intermediate level of SDS (equivalent to (E) in Figure 1). The inset shows the spectrum of 5-doxylstearic acid (100 μM) in water containing 11 mM SDS. (b) Spectra of 16-doxylstearic acid under the same conditions. The doxylstearic acid compounds were added to the dispersion as part of the additional SDS solution (Figure 1). It was determined by centrifugation and analysis of the supernatant that the amount of SDS adsorbed on the particles increases from $\sim 0.8 \mu\text{mol}/\text{m}^2$ to $\sim 1.7 \mu\text{mol}/\text{m}^2$ in going from (B) to (E).

resting on the surface of the particle) to fill vacancies left by the polymer as the amount adsorbed increases.³⁵ There is evidence that adsorbed surfactant molecules on planar surfaces undergo a conformational change to form aggregates at monomer concentrations approaching the cmc.^{36,37} Recent ^{13}C NMR experiments in our laboratory suggest a similar transition at the particle–fluid interface.³⁸ The influence of curvature of the interface on the formation of these aggregates and their impact on interfacial transport requires further investigation.

Although our study has been focused on particle size and solid-state structure of dispersed organic compounds, fundamentally similar behavior has been reported for inorganic compounds such as calcium carbonate or calcium phosphate, which are important constituents of biological tissue.³⁹ It is possible that our work may have significance in areas involving inorganic materials such as biomineralization^{40,41} and catalysis.⁴² Some of the ideas presented here may also be applicable to the stability of liquid in liquid emulsions.^{43–47}

Experimental Section

Materials. Sodium dodecyl sulfate (98% pure) was obtained from Acros Organics. The 5-doxylstearic acid and 16-doxylstearic acid were obtained from Aldrich Chemical Co.

Electron Spin Resonance (ESR) Spectroscopy. ESR spectra were obtained at room temperature on Varian E-12 and E-9 spectrometers operating at about 9.5 GHz. Spectra were measured with samples in quartz flat cells designed to handle lossy aqueous samples. Single scans of 1024 points obtained with a modulation amplitude of 5.0 G and a microwave power level of 10.0 mW gave spectra of sufficient resolution to allow semiquantitative analyses. Data were processed on WINEPR and WINEPR-SimFonia software packages from Bruker Instruments Inc.

Equilibrium Dialysis. The measurements were made as follows: 285 mL of dispersion was placed in a 600 mL beaker. An empty Slide-A-Lyzer membrane cassette with a molecular weight cutoff of 3.5 K from Pierce Chemical Co. was placed in the dispersion for approximately 5 min prior to injecting 5 mL of a 35 mM solution of sodium acetate into the cassette. The cassette was then reinserted into the dispersion and an additional 25 mL of pure surfactant solution of the required concentration was added to the dispersion. The samples were allowed to equilibrate for 48 h. The cassettes were then removed and the solution in the cassette analyzed for surfactant content by Epton titration.^{48,49} Experiments on aqueous solutions of polymer and surfactant were done similarly. As noted previously,⁵⁰ it was found that as the concentration of monomer got close to the critical micelle concentration (cmc) of SDS (~ 4 mM in this case), it became difficult to establish dialysis equilibrium. Measurements were therefore confined to the region below the cmc.

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- (45) In this paper we have taken the view that the combination of polymer and surfactant at the interface improves stability of the dispersion in a *kinetic* sense. However, it has been suggested^{46,47} that it might be possible to obtain *thermodynamically stable* dispersions of solids in liquids (similar to microemulsions) if the interfacial energy at the solid–liquid interface can be reduced to very low levels (zero or potentially negative) by adsorption of suitable molecules or ions. For example, Overbeek⁴⁶ has postulated that under these conditions growth of particles may be stopped and “even negative Ostwald ripening” might occur. While it is difficult to rule out this possibility without direct knowledge of the interfacial energy at the particle–water interface, we believe it is unlikely in our system. Measurements of interfacial energy at the air–water interface in solutions of PVP and SDS (with a low level of electrolyte)²⁶ indicate that the lowest value possible (obtained when the SDS monomer concentration is equal to the cmc) is about 37 ergs/cm². The same value is obtained both in the presence and absence of PVP. Although the magnitude of interfacial energy at a hydrocarbon–water interface will be much lower, we should expect the same trend. In other words, the lowest interfacial energy that is possible *may be obtained even in the absence of PVP*. But our dispersions are not stable without PVP. Furthermore, interfacial energies in the presence of PVP (over a range in concentration of SDS) are restricted by the formation of PVP–SDS aggregates in the bulk fluid. As noted by Overbeek,⁴⁶ in the case of thermodynamically stable microemulsions, one usually requires the combination of an aqueous soluble surfactant and an oil-soluble surfactant so that the activity of the surfactants is not restricted by the formation of mixed micelles in the aqueous phase.
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