Stabilization of High Ionic Strength Slurries Using Surfactant Mixtures: Molecular Factors That Determine Optimal Stability

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The successful formulation of particulate dispersions is often hindered by the presence of charged species dissolved in solution. If present at high enough concentrations, these species can reduce the screening length between particles to near zero, allowing rapid coagulation and destabilization. The addition of a mixture of ionic and nonionic surfactants has been shown in a previous publication (B. J. Palla and D. O. Shah, 2000, *J. Colloid Interface Sci.* **223,** 102) to stabilize alumina particles in the presence of high concentrations of charged species. The mechanism has been explained as enhanced adsorption of a nonionic surfactant using a strongly adsorbing ionic surfactant as a binding agent. In this work, the various factors that influence this stabilization mechanism are examined in detail. The factors are then verified by showing the same results for two different chemical environments, both of which are model slurries for chemical mechanical polishing (CMP) of metal surfaces. The stabilizing ability of the surfactant system is found to increase with increasing hydrophobicity of the nonionic surfactant and increasing hydrophobicity of the ionic surfactant. The effect of surfactant concentration on stabilizing ability is shown to have an optimum concentration range for a number of surfactants. The effect of the ratio of ionic to nonionic surfactant is also investigated for both chemical environments and is shown to have significant effects on stabilizing ability. All of the results are then compiled to present a concise picture of the factors that influence the stabilizing ability of mixed surfactant systems for high-ionic-strength slurries. © 2002 Elsevier Science (USA)

Key Words: dispersion stability; mixed surfactant synergism; chemical mechanical polishing (CMP); stabilization model.

INTRODUCTION

The stability of a dispersion is an issue in any industry in which settling of particles can result in poor performance. In most industrial applications, dispersions are complex formulations of particles (sometimes of multiple types) dispersed in an aqueous or organic phase, with chemical agents added to promote rheological behavior or some desired reaction or interaction with a substrate. Dispersion stability can have a significant effect on performance, resulting in insufficien fil thickness (1), poor adhesion, and insufficien reactivity (2), among many other problems depending on the application. Industries in which dispersion stability is a critical issue include paints and pigments, paper, ceramics, minerals, electronics, and biotechnology.

An important characteristic of many dispersions is that they are formed or are processed in severe environments. Severe environments include complex chemical environments that contribute to extreme pH or chemical reactivity conditions. Another type of severe environment has extreme pressure or temperature conditions. All of these severe environments can make the stabilization of dispersions a much more formidable challenge (3). This article focuses on the chemically complex type of severe environment. These systems pose a challenge for the technologist due to the effects of charge screening on the dispersed particles.

The presence of charged species in an aqueous solution results in the screening of surface charges on particles, which results in coagulation if the screening length is sufficientl reduced. The coagulation can often produce particles large enough to settle out of solution. Both coagulation and particle settling are stages of slurry destabilization, which can decrease process yield and reproducibility in addition to complicating slurry handling.

The work presented here focuses on dispersion stabilization and its application in CMP, so it is important to discuss the general approaches taken to stabilize dispersions. The two primary classes of molecules that are applied as stabilizing agents are surfactants and polymers. These two classes of molecules differ, sometimes significantl , in the way in which they bring about stabilization. To illustrate this point, the use of surfactants and polymers as stabilizing agents is shown schematically in Fig. 1.

Ionic surfactants are capable of producing a substantial opposite charge sufficien for stabilization in low-ionic-strength environments. Numerous investigations have focused on adsorption of ionic surfactants on oppositely charged particle surfaces. Such adsorption has been studied extensively by Somasundaran and Feurstenau (4), Gaudin and Feurstenau (5), and Somasundaran and Kunjappu (6), primarily for the system of sodium dodecyl sulfate (SDS) on alumina particles.

In contrast, nonionic surfactants have no charge associated with them. As a result, DLVO theory predicts that nonionic

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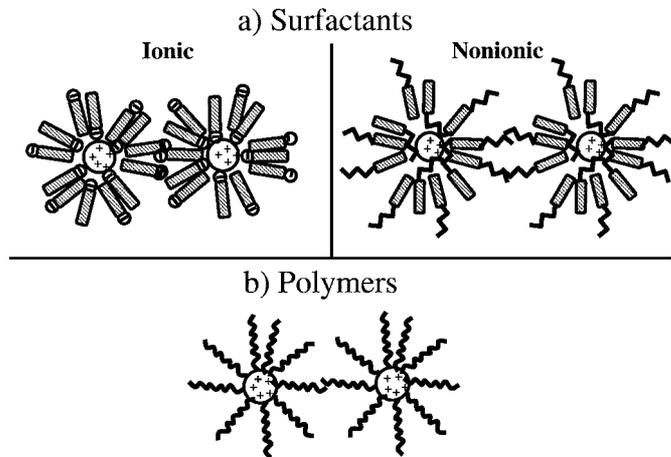E-mail: shah@che.ufl.edu

a) Surfactants

Ionic   **Nonionic**

b) Polymers

FIG. 1. Illustration of surfactants and polymers as stabilizing agents on hydrophilic particles.

surfactants will not provide a signif cant repulsive barrier to agglomeration. However, nonionic surfactants have been successfully applied as stabilizing agents in a number of applications due to their ability to effect steric stabilization. Nonionic surfactants differ from polymers when absorbed on a hydrophilic surface in aqueous solution in that, as shown in Fig. 1, they must form an aggregate structure such as a bilayer or hemimicelle. Within the aggregate structure, the hydrophilic portion of the

molecule is exposed to both the surface and the aqueous solution, similarly to the behavior of ionic surfactants. Nonionic surfactant molecules offer an advantage over polymers in that they are amphiphilic surfactant molecules and typically have a higher adsorption potential than an equal-chain-length polymer.

Steric stabilization occurs due to the presence of physical barriers adsorbed on particles that prevent the particles from coming close enough to allow the van der Waals attractive forces between particles to dominate (7, 8). The key to steric stabilization is to increase the closest distance of approach between particles in order to minimize van der Waals attractive forces (9, 10). Without steric stabilizing agents, the closest distance of approach is limited only by weak electrostatic forces, so the particles easily enter the strong potential well near the surface. With stabilizing agents, the attractive potential is greatly reduced at the closest distance of separation, making the barrier to agglomeration much easier to manipulate. Steric stabilization possesses at least three advantages over electrostatic stabilization: its relative insensitivity to high concentrations of electrolytes; the fact that high-solids dispersions display relatively low viscosities; and its equal effectiveness in both aqueous and nonaqueous dispersion media (11).

In previous work (12), it has been shown that synergistic mixtures of ionic and nonionic surfactants are capable of stabilizing slurries in which either ionic or nonionic surfactants are insuff - cient stabilizers. The stabilization mechanism has been proposed and is presented in Fig. 2. The two-step mechanism consists of
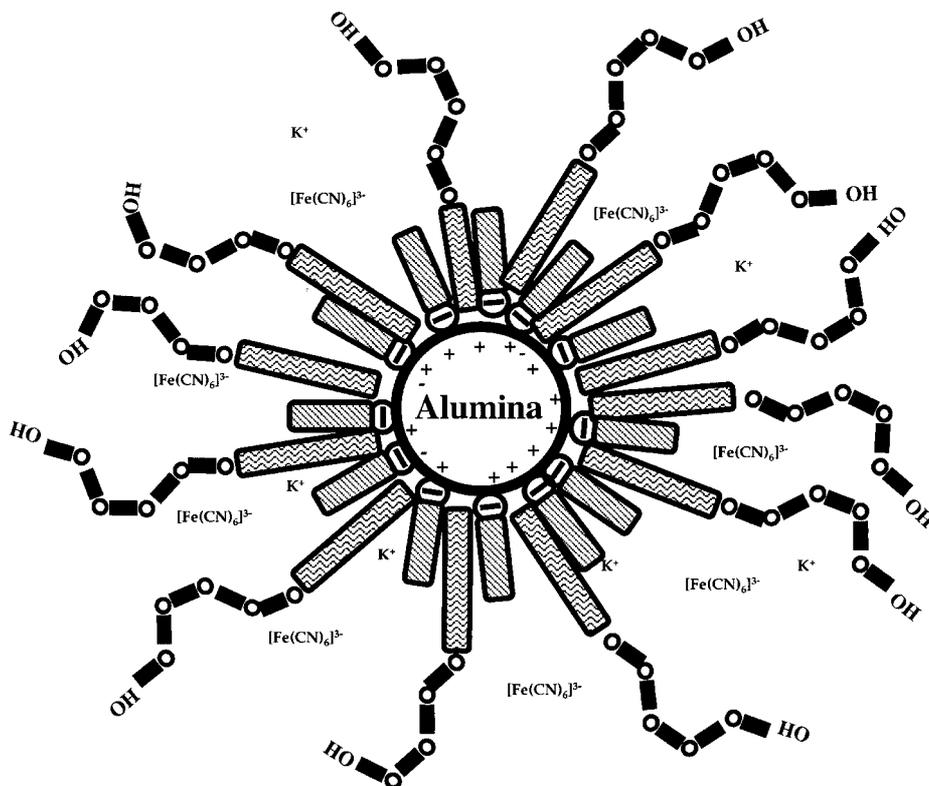

FIG. 2. The mechanism of high-ionic-strength slurry stabilization by the synergistic mixture of anionic and nonionic surfactants [from (12)].
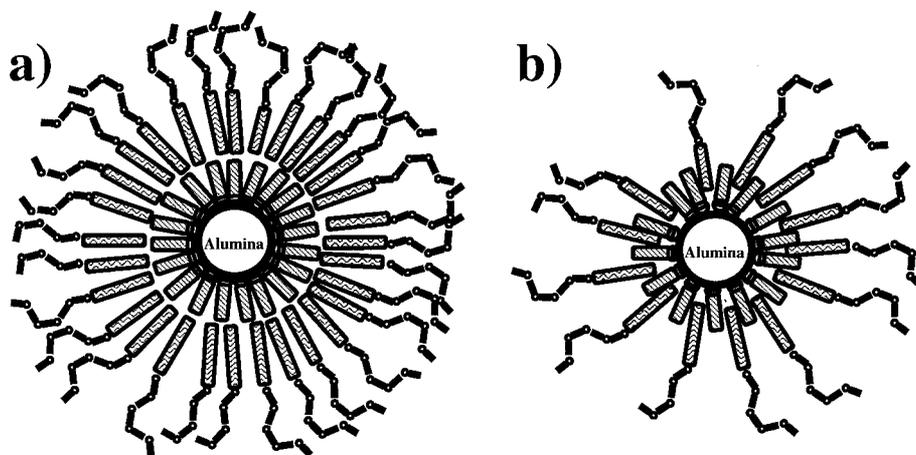
FIG. 3. Other possible conformations of stabilizing surfactant that result from the adsorption of a mixture of ionic and nonionic surfactants on particle surfaces. Conformations are (a) full bilayer and (b) penetrated bilayer.

(1) adsorption of ionic surfactant hydrophilic particles and (2) adsorption of nonionic surfactant onto the f lm of ionic surfactant via self-assembly. This self-assembly is driven by reduced free energy when the hydrophobic portions of the molecules are transferred from the solution to the interfacial aggregate via the hydrophobic effect (hereafter loosely referred to as hydrophobic chain interaction). This process results in the adsorption of a mixed surfactant bilayer onto the surface of the hydrophilic particles. The stabilization is then brought about by the steric barrier created by the mixed bilayer, due to both a tightly packed hydrophobic moeity and a hydrophilic moeity from the nonionic surfactant extending into the solution.

The mechanism in Fig. 2 only depicts one possible conformation of the adsorbed mixed surfactant layer, which in fact may be present as either a monolayer or a bilayer, as shown in Fig. 3. The conformation presented in Fig. 2 is a mixed monolayer conformation, in which the hydrocarbon chains of the two surfactants are lined up adjacent to each other, resulting in the lowest surfactant adsorption density of any of the conformation possible in this mechanism. Another possible conformation is the full bilayer illustrated in Fig. 3a, which shows that in this conformation the anionic surfactant has adsorbed in a full monolayer. The nonionic surfactant then adsorbs via hydrocarbon chain interactions as a full second monolayer, resulting in the highest surfactant adsorption density. The f nal type of conformation, a penetrated bilayer, is shown in Fig. 3b, which shows that the hydrocarbon chains of the nonionic surfactant penetrate the monolayer of anionic surfactant adsorbed onto the particle surface, but not completely. The degree of penetration of the nonionic surfactant will depend on the amount of space available between adsorbed anionic surfactant molecules, as well as the strength of the hydrocarbon chain interactions between adjacent molecules.

As discussed in Palla and Shah (12), this stabilization process is highly dependent on the choice of both ionic and nonionic surfactant. In the current investigation, the factors which affect the stabilization mechanism shown in Figs. 2 and 3 are investi-

gated. Specif cally, the types of surfactants which are preferred for this type of mechanism are determined, as well as the concentrations and ratios of surfactants which are necessary for the stabilization to be successful. Finally, this mechanism is applied to another slurry which utilizes chemistry for copper CMP applications, and the differences in surfactant type, concentration, and ratio for optimal stability are explained. With this knowledge, the formulator is given the ability to choose surfactants which will maximize stabilization, even in severe environments such as those considered here.

MATERIALS AND METHODS

Sedimentation experiments are used in this investigation to determine dispersion stability. The sedimentation method involves preparing a dispersion and allowing it to sediment undisturbed under gravity in a long vertical column such as a graduated cylinder (e.g., 100 ml volume) while monitoring the height of the dispersed phase. This method has been used conventionally as one of the primary means of determining stability in systems where destabilization occurs on macroscopic time scales and within a reasonable amount of time for measurement (e.g., 1 h to 30 days). The advantages of using sedimentation over alternative techniques such as centrifugation (13, 14) and light-transmittance measurements (15) include the ability to directly observe the entire sedimenting layer, thus allowing the experimenter to note unusual layer formation. The other advantage is that complete data are taken as a function of time, thus allowing any unusual kinetic behavior to be observed. With sedimentation, the volume of sedimented particles at the bottom of the cylinder can also be visually determined.

For the following investigation, all materials were used without further purif cation. The slurry particles used in this study were high purity AKP-50 α-alumina particles with particle size 100–300 nm obtained from Sumitomo Chemical Co., Ltd. Potassium ferricyanide, potassium iodate, potassium iodide, and

EDTA were obtained from Fisher, Inc. Sodium dodecyl sulfate (SDS) was obtained from Sigma Chemical Co. Tween 20, 21, 40, 60, 80, 81, and 85, Symperonic A4, A7, A11, and A20, Brij 30, 35, 52, 93, 97, 98, and 700, and Span 20 and 80 were obtained from ICI Surfactants. Ultrapure water was obtained from a Milli-Q Gradient A10 filtration system supplied by Millipore Corp.

Dispersions were prepared by first dissolving surfactants in the desired concentrations in water. Alumina particles in a concentration of 10 wt% were then added into the surfactant solution and the pH was coarsely adjusted to the desired value. In order to attempt to break up agglomerates that form either in the particle preparation process or when dry particles are stored in air (in plastic containers) for long periods of time, the dispersions were then sonicated in a DIW bath for 30 min with no observed air bubble formation. The oxidizing agent was then added and the pH was carefully readjusted to the desired value. For potassium ferricyanide slurries the pH range was 3.5–4.0, which was used to model CMP slurries used for tungsten polishing, which have been shown to have a high selectivity of tungsten over silicon dioxide in this range (16). For potassium iodate slurries, the desired pH range was 6.0–6.5.

Dispersion stability was then characterized by sedimentation testing. Sedimentation experiments were performed by thoroughly dispersing the slurries prior to pouring them into 100-ml graduated cylinders, where they were then left undisturbed throughout the length of the experiment. Room temperature was maintained at $25 \pm 1°C$ throughout the experiment time. The amount of settled slurry, as well as the sediment height, was recorded over time and converted to fractional volume to normalize the results. The amount of settled slurry was determined as the sum of (1) the amount of clear liquid on top and (2) a fraction of the amount of cloudy layer below the clear liquid. The cloudy layer was the transition region between fully dispersed slurry and clear liquid. Examples of this calculation procedure for total settled volume are given in Fig. 4 in order to make the procedure more clear. The fractions used for conversion of the

FIG. 4. Examples of sedimentation experiments along with the total settled volume determined using the procedure outlined below (f = fraction settled as defined in Table 1).

TABLE 1

Fractions Used for Determination of Total Settled Volume Based on Degree of Cloudiness in Sedimentation Experiments

Classification	Range of absorbance values	Fraction settled
Very cloudy	2.0–3.0 AU	0.1
Cloudy	1.0–2.0 AU	0.3
Hazy	0.3–1.0 AU	0.6
Slightly hazy	0.1–0.3 AU	0.8

cloudy layer to the clear liquid equivalent are given in Table 1. These fractions (f) are used to calculate the total settled volume in the examples in Fig. 4.

RESULTS AND DISCUSSION

In order to investigate the factors that influence the stabilization of high-ionic-strength slurries using mixed surfactant systems, the type of surfactant has been varied for a model tungsten CMP slurry and a model copper CMP slurry. The factors which influence stability were hypothesized in Palla and Shah (12) and are:

(1) Adsorption of ionic surfactant onto alumina surface with ample surface coverage. Both cationic and anionic surfactants are expected to work for this mechanism since charge screening allows adsorption of charged molecules of the same sign as the surface, although surface charge and heterogeneity will ultimately determine the adsorption density.

(2) Partitioning of nonionic surfactant out of the aqueous phase and into the surface aggregate by hydrocarbon chain self-assembly with the film of ionic surfactant. Hydrocarbon chain interactions have been shown to be maximal for equal chain lengths of ionic and nonionic surfactant (17–19). However, the driving force for partitioning of nonionic surfactant out of the aqueous phase and onto the surface increases with increasing hydrophobicity of nonionic surfactant according to a semiquantitative extension of Traube's rule (20) made by Freundlich (21). As a result, the adsorption affinity of the nonionic surfactant increases with long hydrocarbon chains or short hydrophilic segments of the nonionic surfactant.

(3) Steric stabilization via the mixed surfactant layer on adjacent particles. This depends primarily on the ability of the hydrophilic ethylene oxide (EO) segments of the nonionic surfactant to extend into the aqueous phase upon adsorption and not tend to form flocs. As discussed previously, steric stabilization occurs in mixed layers due to the presence of steric barriers from adsorbed nonionic molecules that prevent the particles from coming close enough to allow van der Waals attractive forces between particles to dominate (9, 10). However, the poly(ethylene oxide) segments must not interact attractively with segments on adjacent particles to induce flocculation, causing destabilization of the slurry. The tendency to flocculation will increase as the adsorption density of polymer segments is increased.
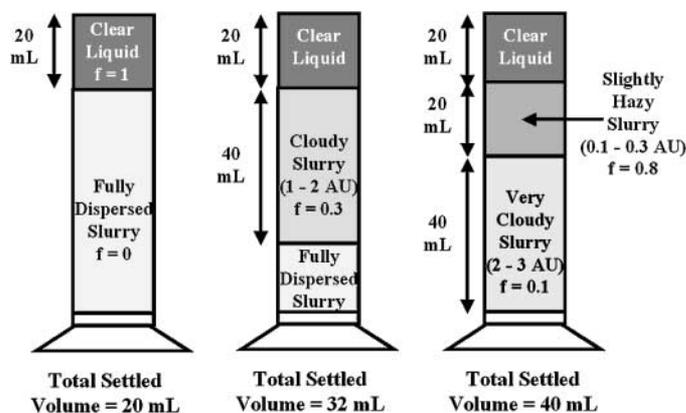
Optimization of Dispersion Stability Using Various
  Nonionic Surfactants for Tungsten CMP

For this investigation, a representative formulation of a tungsten CMP slurry has been used. This slurry contains 10 wt% alumina and 0.1 M potassium ferricyanide as oxidizing agent. A variety of commercially available nonionic surfactants have been mixed in a 1 : 1 molar ratio with SDS at a total surfactant concentration of 50 mm. Nonionic surfactants have been divided into groups with carbon chain lengths of 12 and 18. It is critical to note that these are commercially available nonionic surfactants with polydistributed mixtures of EO segments. Therefore, the number of EO groups is the average of the distribution cited by the manufacturer. In fact, the more hydrophobic components of the mixture (lower number of EO segments) will preferentially adsorb into the hydrophobic environments prior to the more hydrophilic components (22). Further, those surfactants with EO segment averages of less than 4 will have a signif cant number of unreacted reactant molecules with EO segments of 0. The sedimentation results for the mixtures investigated are given in Figs. 5 and 6 for C_{12} and C_{18} nonionic surfactants, respectively.

As can be seen for both the C_{12} and C_{18} surfactants, there appears to be some correlation between degree of polymerization, as indicated for each series, and dispersion stability. The most stable combinations in both Figs. 5 and 6 have only 2 EO groups (E_2) on the nonionic surfactant, while the highest degree of polymerization (E_{50} for C_{12} and E_{100} for C_{18}) results in the most unstable slurries. These two extremes show a general trend to increasing stability with decreasing degree of ethoxylation of the nonionic surfactant. Additionally, Span surfactants (E_0) are unstable in both f gures. However, in both Figs. 5 and 6 the Span surfactants show a substantial particle layer ($F = 0.4$) remaining in the unstable slurries. There also appears to be a signif cant variation with type of nonionic surfactant linkage, since for the C_{18} surfactants, Tween 80 (sorbitan linkage) and Brij 98 (ether
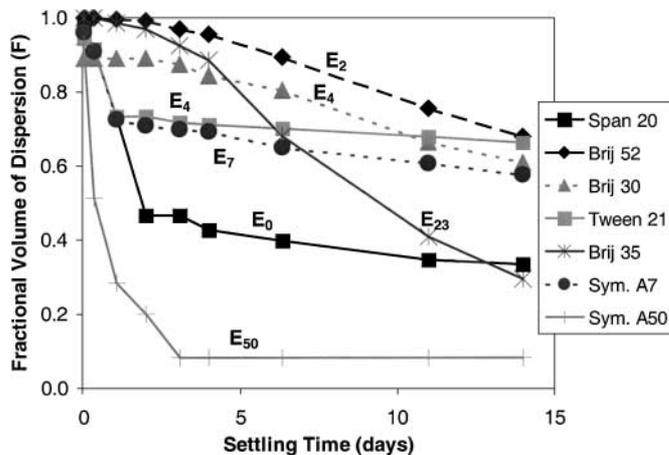

FIG. 6. Sedimentation results of dispersions with 1 : 1 mixtures of SDS and the C_{18} nonionic surfactant indicated. Oxidizing agent is 0.1 M potassium ferricyanide.

linkage) are E_{20} surfactants, but their results do not follow the same trend.

There appears to be some correlation of dispersion stability with the molecular factors of the surfactant, including the carbon chain length, degree of polymerization, and linkage segment in Figs. 5 and 6. All of these parameters contribute to the overall hydrophobicity of the surfactant, which can be summed up for surfactants using the empirical hydrophile–lipophile balance (HLB) number. HLB numbers are low for hydrophobic surfactants and high for hydrophilic surfactants, and an equal hydrophobic–hydrophilic balance corresponds to a value near 10 (23). The hydrophobicity of a nonionic surfactant is expected to be a signif cant factor in dispersion stability, since ultimately this factor and the surface architecture will determine the driving force for surfactant to leave the bulk and adsorb at the interface.

In order to show the effect of hydrophobicity of nonionic surfactant on dispersion stability, the data in Figs. 5 and 6 have been plotted in Fig. 7 as a function of the HLB number of the

FIG. 5. Sedimentation results of dispersions with 1 : 1 mixtures of SDS and the C_{12} nonionic surfactant indicated. Oxidizing agent is 0.1 M potassium ferricyanide. E_x represents the mean number of ethoxy groups on the nonionic surfactant molecule.
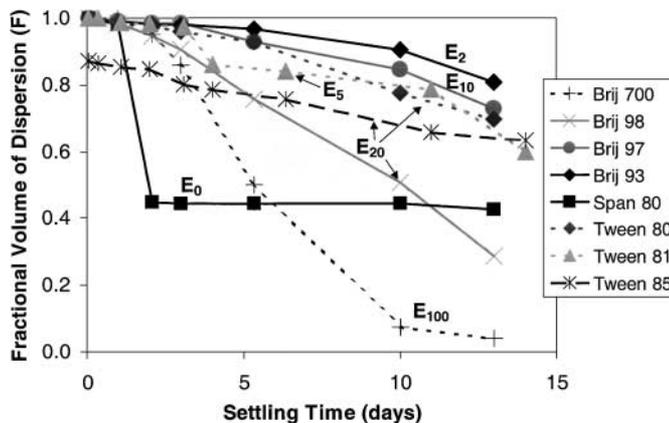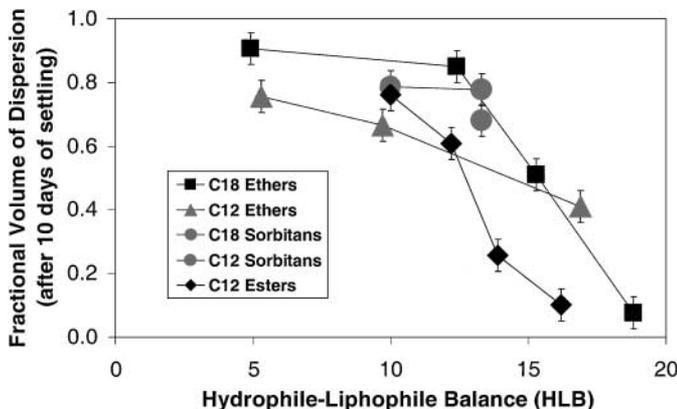

FIG. 7. Correlation of dispersion stability with hydrophobicity of nonionic surfactant, as given by its HLB number. Data are from 50 mM 1 : 1 mixtures of SDS and the given nonionic surfactant adsorbed on 10 wt% AKP-50 particles in 0.1 M $K_3Fe(CN)_6$ at pH 4.

nonionic surfactant. The surfactants are grouped in this figure according to both linkage type and chain length (C_{12} or C_{18}). Figure 7 shows that both C_{12} and C_{18} ethers and the esters (all C_{12}) show a decrease in dispersion stability with an increase in HLB number of nonionic surfactant. The sorbitan surfactants remain stable at HLB numbers greater than 15, but it is expected that if it were possible to obtain very high HLB number sorbitan surfactants, they would also show a decrease in dispersion stability at higher HLB numbers. The data in Fig. 7 show that increasing hydrophobicity of nonionic surfactant leads to increased dispersion stability.

Verification of Results for Model Copper CMP Slurry

In order to determine the generality of the trends presented above, the effect of nonionic surfactant on dispersion stability was determined using similar sedimentation experiments for a type of slurry with applications in copper CMP. This slurry contains primarily monovalent ions, unlike the trivalent ferricyanide ion. The slurry is composed of 10 wt% alumina particles and 0.1 M KIO_3, 0.01 M KI, and 0.01 M EDTA. This slurry combination has been shown to provide substantial oxidation of the copper surface due to KIO_3 while the corrosion is inhibited by the presence of I^- from KI, which forms a surface layer on Cu. Finally, the driving force for removal of copper is maximized by addition of the complexing agent EDTA (24).

Figure 8 shows the trend of dispersion stability for this copper CMP slurry with HLB number of nonionic surfactant for all of the nonionic surfactants investigated in Fig. 7. In this figure, the surfactants are grouped according to carbon chain length (C_{12} and C_{18}), and the C_{12} surfactants are investigated at total surfactant concentrations of both 50 and 100 mM to observe any differences. The data in Fig. 8 appear to be very well correlated with the HLB number of the nonionic surfactant. For both C_{12}
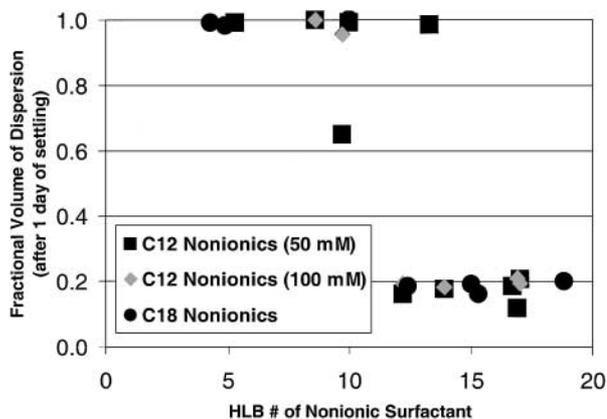
and C_{18} surfactants, there appears to be a rapid stable–unstable transition in a range of HLBs from 10 to 12. It is important to note that these stability data are presented after only 1 day of settling, indicating that the settling in the unstable slurries is rapid. However, the stable slurries with HLB numbers less than 10 are fully stable after a period of 10 days, indicating a high degree of stability.

The primary outlier point is a C_{12} nonionic surfactant with an HLB number of 13.3, which yields a stable dispersion. This surfactant is Tween 21, which has a sorbitan linkage, unlike most of the C_{12} surfactants investigated. It appears that, as in Fig. 7, the sorbitan linkage contributes more significantly to steric stabilization at high HLB numbers than its ether or ester counterparts. The results for the dispersions at concentration 100 mM mimic those at concentration 50 mM, indicating that there is no change in stability in this concentration range. The effects of surfactant concentration on dispersion stability will be discussed in greater detail. The results of Fig. 8 verify the robust nature of the stabilizing scheme presented in this investigation. The general trend of increasing dispersion stability with decreasing HLB number of nonionic surfactant holds for both the tungsten and copper CMP slurries investigated, indicating that the underlying stabilization mechanism is the same in both systems.

The results in Fig. 8 do include the Span surfactants (E_0), which produce stable slurries, in contrast to the results in Figs. 5 and 6. This is true even though the Span surfactants have 0 EO groups, and hence their hydrophilic segment is composed of only the sorbitan linkage. This contrasting element will be considered and explained in the next section after an explanation of the general trend of increasing stability with decreasing HLB number of nonionic surfactant.

Correlation of Dispersion Stability with HLB Number of Nonionic Surfactant

The trend that stands out in both Figs. 7 and 8 is that increasing hydrophobicity of nonionic surfactant, with all other factors constant, brings about increasing dispersion stability. This is contrary to the popular thought that longer EO chains should provide better dispersion stability due to increasing size of the steric barrier to particle approach (23). A schematic of the environment in which a hydrophilic nonionic surfactant with a long polymer chain is present in solution is presented in Fig. 9a, while the same situation with a hydrophobic short-chain surfactant is presented in Fig. 9b.

The reason for the greater degree of stabilization with the hydrophobic (low HLB) surfactant is clearly the number of surfactant molecules present on the surface. With the hydrophobic surfactant, the driving force to place monomers onto the particle surface is higher than for the more hydrophilic surfactant. As a result, the hydrophilic surfactant, although capable of greater steric stabilization if adsorbed, does not adsorb in sufficient quantity to stabilize the particles. The key to understanding this stabilization mechanism is that there are opposing forces
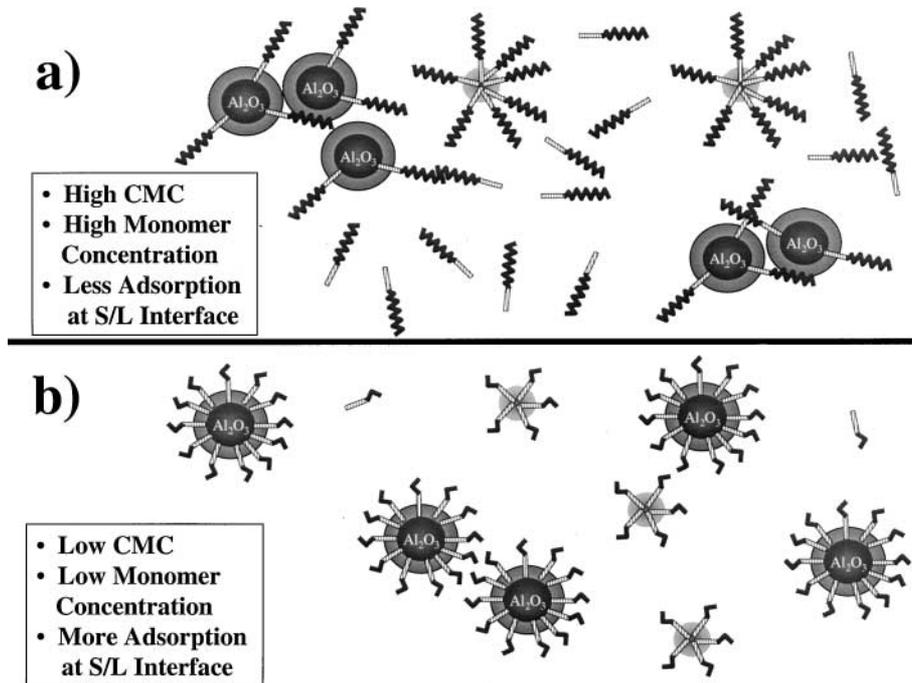

FIG. 8. Variation in dispersion stability vs HLB number of nonionic surfactant for a model copper CMP slurry containing 0.1 M KIO_3, 0.01 M KI, and 0.01 M EDTA (nonionic surfactants are Span 80, Brij 93, Brij 52, Span 20, Brij 30, Symperonic A4, Tween 81, Symperonic A7, Brij 97, Tween 21, Symperonic A11, Tween 80, Brij 98, Tween 20, Brij 35, Symperonic A50, and Brij 700).

FIG. 9. Schematic of dispersion environment showing adsorption density differences between (a) high HLB (hydrophilic) nonionic surfactant and (b) low HLB (hydrophobic) nonionic surfactant.

governing the choice of nonionic surfactant—the driving force to adsorb vs the degree of polymer extension into solution once adsorbed. Clearly in the example slurries presented in Figs. 7 and 8, the repulsive barrier is suff cient with only 2 or even 0 E groups on the surface.

This leads to the discussion of the contrasting element between Figs. 7 and 8. The Span surfactants (E_0) stabilize the KIO_3 slurries but not the $K_3[Fe(CN)_6]$ slurries. The reason is that in the KIO_3 slurries the charge screening effects are not as overwhelming as in the $K_3[Fe(CN)_6]$ slurries. Quantitatively, the Debye length ($1/\kappa$) in an electrolyte solution containing 0.1 M KIO_3 and 0.01 M KI is 9.17 Å, while in solution containing 0.1 M $K_3[Fe(CN)_6]$ it is only 4.30 Å (25, 26). Therefore, the alumina particles in KIO_3 dispersions experience a greater electrostatic barrier, and this combined with the steric barrier provided by the surfactant leads to greater dispersion stability in KIO_3 dispersions. The strongly adsorbed hydrophobic Span (E_0) surfactants in KIO_3 dispersions provide a suff cient steric barrier to impart stability. The $K_3[Fe(CN)_6]$ slurries, with a trivalent counterion, provide more complete charge screening and therefore reduce the electrostatic barrier to agglomeration and increase the requirements of the steric barrier needed. The E_2 or E_4 surfactants, however, are considerably more hydrophilic than the E_0 surfactants and possess the polymer chain necessary to provide steric repulsion in these slurries. Since the hydrophobicity of these surfactants is also suff ciently high, they provide ample surface coverage and maximum stabilization for the $K_3[Fe(CN)_6]$ environment.

Effect of Total Surfactant Concentration on Dispersion Stability

The results in Figs. 7 and 8 are for a total surfactant concentration of 50 mM, but the dispersion stability is expected to vary signif cantly with surfactant concentration. As a result, the surfactant concentration has been varied in sedimentation experiments presented in Fig. 10. In this f gure, the dispersions are 10 wt% AKP-50 alumina at pH 4 with 0.1 M potassium ferricyanide and the surfactant in these systems is a mixture of SDS and the indicated nonionic surfactant in a 1 : 1 molar ratio.
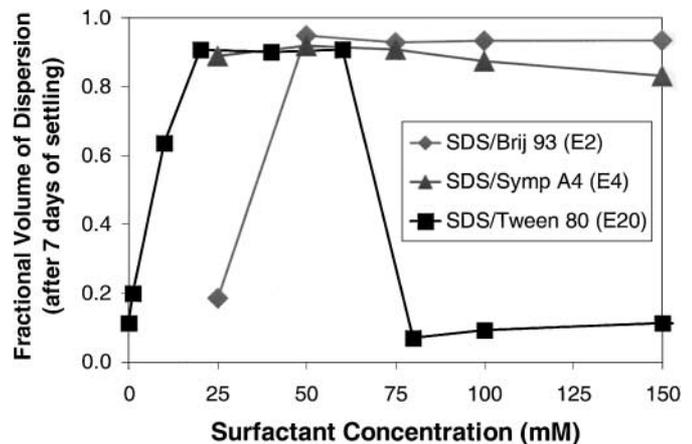

FIG. 10. Sedimentation experiments showing dependence of dispersion stability on surfactant concentration in 0.1 M potassium ferricyanide slurries at pH 4.

The results in Fig. 10 show interesting, unexpected results, particularly for the SDS/Tween 80 surfactant mixture. The data show that, as expected, a minimum surfactant concentration is needed for stabilization, indicative of the large surface area of the particles that must be suff ciently covered with surfactant to achieve stabilization. The unexpected result is that the dispersion stability once again decreases at high concentrations of SDS/Tween 80. This result may be due to a number of factors, the f rst being the formation of nonionic surfactant domains or micelles lining the adjacent particles. The Tween 80 domains formed by E groups then serve as glue (adhesive) connecting the particles in a loose agglomerate or f oc. This mechanism will be explained in detail in a later section. The other possible explanation for this result is that multilayer effects are dominant in this system, resulting in the adsorption of a third surfactant layer of either SDS or Tween 80 at high concentrations. This third layer, with hydrophobic chains extending into solution, makes the particles once again susceptible to agglomeration due to hydrophobic interactions between adjacent particles.

The results of the other surfactant systems (SDS/Brij 93 and SDS/Symperonic A4) which are shown in Fig. 10 do not show the same trends as the SDS/Tween 80 results. Although SDS/Brij 93 mixtures do show a minimum concentration required for stability, there is no decrease in dispersion stability at higher concentrations. However, it is important to note that Brij 93 is only slightly soluble in water due to its hydrophobicity. The solubility of Brij 93 is signif cantly enhanced by the presence of SDS, but there is some cloudiness present at high concentrations (>75 mM), indicating that the solubility limit has been reached. As a result, it is expected that the reason the SDS/Brij 93 mixtures do not become unstable at higher concentrations is that not enough Brij 93 surfactant is solubilized to cause instability at high concentrations. The SDS/Symperonic A4 mixture is likewise less soluble than the SDS/Tween 80 mixture, so the results for this system are expected to be similar to those of the SDS/Brij 93 system, as shown in Fig. 10.

The effects of surfactant concentration on dispersion stability have also been investigated for the copper CMP slurry consisting of 0.1 M KIO_3, 0.01 M KI, and 0.01 M EDTA. It is important to note that the SDS/Tween 80 mixture does not signif cantly stabilize this slurry, so a direct comparison with the $K_3Fe(CN)_6$ slurry results is not possible. However, the effects of concentration are given in Fig. 11 for two mixtures that have been found to provide optimum stabilization for this slurry at 50 mM concentration.

This f gure shows that both the SDS/Symperonic A4 and SDS/Tween 21 mixtures impart stability to alumina particles in the KIO_3 environment at concentrations as low as 25 mM, but at concentrations higher than 75 mM, both dispersions are clearly unstable. This result is similar to the result for the SDS/Tween 80 mixture in Fig. 10. The SDS/Symperonic A4 mixture shows these high concentration effects in a KIO_3 environment but not in a $K_3Fe(CN)_6$ environment because the solubility of the SDS/Symperonic A4 mixture is greater in KIO_3 solution than in $K_3Fe(CN)_6$ solution since the prevalent ion is monovalent, not trivalent. Both mixtures of SDS/Symperonic
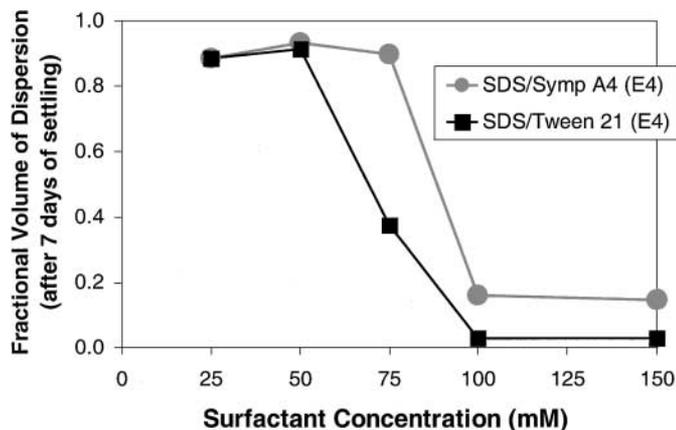

FIG. 11. Effect of surfactant concentration on dispersion stability in 0.1 M KIO_3, 0.01 M KI, and 0.01 M EDTA slurries at pH 6.

A4 and SDS/Tween 21 in KIO_3 solution become cloudy at concentrations greater than 100 mM, indicating that the solubility limit has been reached, but not before high concentration effects cause instability of the dispersion.

The results presented in Figs. 10 and 11 show that surfactant concentration is a parameter which can signif cantly affect dispersion stability. The results have shown the presence of a maximum in dispersion stability over a concentration range which depends upon a number of factors. The results have also shown that mixtures of surfactants will show a solubility limit that depends upon the ion concentration and valence as well as the hydrophobicity of the surfactant system. Finally, the results have shown that the solubility limit of the surfactant may keep the surfactant from dissolving at high enough concentrations to cause instability.

Effect of Ratio of Surfactants in Mixtures on Dispersion Stability

The f nal parameter regarding the surfactant mixture in the complex systems that have been investigated is the ratio of ionic to nonionic surfactant. To this point, all of the mixtures investigated have been at a 1 : 1 molar ratio. However, it has been shown in Palla and Shah (12) that ionic or nonionic surfactant alone yield unstable slurries, so there is expected to be at least two stable–unstable transitions on a plot of stability versus fraction of one component. This parameter has therefore been studied in order to make this investigation of the molecular factors inf uencing stabilization complete.

For the $K_3Fe(CN)_6$ chemistry, ratios of SDS : Tween 80 and SDS : Symperonic A4 have been investigated using 50 mM total surfactant and 10 wt% AKP-50 particles. The sedimentation results are given in Fig. 12 for these systems as a function of mole fraction of SDS in the total mixture.

Both systems investigated are unstable when only one surfactant is used (SDS, Tween 80, or Symperonic A4 alone), as illustrated at the endpoints in Fig. 12. The SDS/Tween 80 mixture is shown to impart stability to dispersions at mole fractions of SDS at or greater than 0.5 and all the way up to 0.97 (corresponding
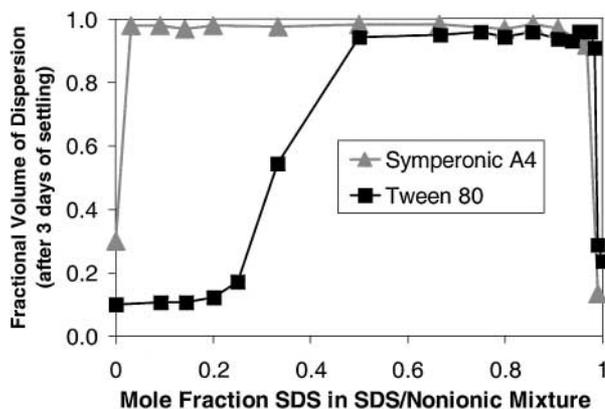
FIG. 12. The effect of ratio of surfactants on dispersion stability for slurries containing 0.1 M $K_3Fe(CN)_6$ at pH 4. Total surfactant concentration is 50 mM.

to a molecular ratio of 30 : 1 between SDS and Tween 80). At ratios that favor Tween 80, these dispersions are unstable. The SDS/Symperonic A4 mixture is shown to be unstable only at the endpoints (mole fractions of 0 and 1), while it is stable throughout the range of ratios investigated.

The differences in behavior between SDS/Tween 80 and SDS/Symperonic A4 mixtures is presumably due to the inability of low ratios of SDS/Symperonic A4 to produce nonionic surfactant domains which act as adhesive between particles. This explanation is feasible since the mechanism, which is discussed in the next section, depends on long hydrophilic polymer segments on the nonionic surfactant aggregating to form the domains responsible for instability. Since Symperonic A4 is an E_4 surfactant and Tween 80 is an E_{20} surfactant, the tendency for Tween 80 systems to exhibit this behavior is much greater than for Symperonic A4 systems.

The effect of ratio of surfactants in mixtures has also been investigated for the copper CMP slurry based on KIO_3 chem-

istry stabilized with SDS/Symperonic A4 mixtures. The results of these experiments show trends similar to the results of SDS/Symperonic A4 mixtures used in the model tungsten CMP slurry in Fig. 12, as expected.

Explanation of Observed Instability in Surfactant Mixtures at High Concentrations and at Ratios Favoring Nonionic Surfactant

The results of dispersion stability as a function of concentrations and ratios of SDS/Tween 80 mixtures in Figs. 10 and 12, respectively, both exhibit unexpected instability in the dispersions. Likewise, the results of dispersion stability as a function of concentration for the KIO_3 chemistry shown in Fig. 11 shows instability at high concentrations. The results will be explained in terms of the SDS/Tween 80 system, but the same mechanism applies to other systems for the KIO_3 chemistry. The observed instability is presumably due to a change in the conformation of the adsorbed polar segments of Tween 80 in the presence of excess Tween 80. Since Tween 80 is an E_{20} surfactant, any change in the conformation of these steric stabilizing segments could lead to a change in stabilization behavior to a greater extent than for the surfactants with lower degrees of ethoxylation. This is presumably the reason that in Fig. 12 the SDS/Tween 80 mixture exhibits instability in the ratio of surfactant results, but the SDS/Symperonic A4 mixture does not. Similarly, in the concentration of surfactant results, the SDS/Tween 80 mixture exhibits instability in the $K_3Fe(CN)_6$ solution while the other mixtures, with lower degrees of ethoxylation, do not.

The change in conformation of adsorbed Tween 80 segments is presumably due to a greater flocculation potential between adjacent particles at higher concentrations of Tween 80. This type of flocculation, however, is of a different origin than normal
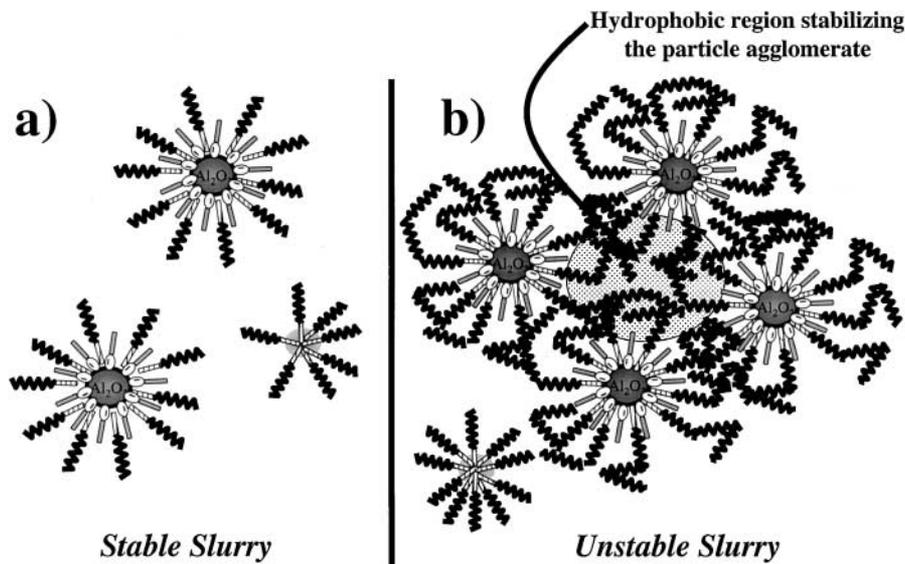

FIG. 13. The proposed mechanism of induced instability in mixed surfactant systems: (a) low concentrations/ratios of nonionic surfactant and (b) high concentrations/ratios of nonionic surfactant.

f occulation, which is favored in systems using low concentrations of high-molecular-weight polymers that are not well solvated. High concentrations of the highly solvated Tween 80 molecules can lead to the formation of admicelles, or nonionic surfactant domains, of Tween 80 near the particle surfaces. These admicelles are aggregates of adsorbed Tween 80 and Tween 80 in bulk solution that interacts with the adsorbed molecules. When two particles surrounded by these nonionic surfactant domains approach one another, the Tween 80 molecules have a tendency to aggregate with Tween 80 molecules on the adjacent particles, causing a loose f oc to form, with the region between particles having a high density of Tween 80 molecules. This type of f occulation is illustrated in Fig. 13. The region between particles may or may not include additional Tween 80 molecules bound to the f oc as shown in Fig. 13b. If additional Tween 80 molecules are bound to the f oc, adsorption measurements should show a high ratio to adsorbed Tween 80 to SDS, which is the subject of a future publication.

SUMMARY

The addition of ionic and nonionic surfactant mixtures to high-ionic-strength slurries has been shown in a previous publication (12) to be capable of slurry stabilization. The stabilization is steric in nature and occurs by nonionic surfactant hydrophobic chain self-assembly with a f lm of adsorbed ionic surfactant. The factors inf uencing this stabilization mechanism have been discussed. The strong adsorption of ionic surfactant on particles is extremely important, while the nonionic surfactant must then be capable of adsorption via hydrocarbon chain interactions with the ionic surfactant. This adsorption is governed by two factors: the ability of the nonionic surfactant to partition out of the aqueous solution, which will favor more hydrophobic nonionic surfactant, and the strength of the interactions between adjacent adsorbed molecules, which will be strongest if the chain lengths are equal. Finally, the nonionic surfactant must conform to allow steric stabilization, which is not generally an issue with the use of ethoxylated nonionic surfactant in aqueous solution.

The molecular factors that inf uence this stabilization mechanism have been considered. The type of nonionic surfactant has been shown to have a major effect on the degree of stabilization by measuring sedimentation of dispersions containing numerous nonionic surfactants mixed with anionic surfactant. The results show a trend of increasing dispersion stability with decreasing HLB number of nonionic surfactant. This result is explained as due to the fact that the tendency of lower HLB (hydrophobic) nonionic surfactants to partition out of the aqueous phase and onto the particle surface is much greater than that of high HLB (hydrophilic) nonionic surfactants. This same trend has been observed for a model copper CMP slurry chemistry. This observation verif es the robust nature of the stabilizing scheme and its applicability to numerous environments, including severe environments.

The dependence of dispersion stability on surfactant concentration has been investigated for a number of mixed surfactant systems. The results show that a range of concentrations are capable of providing maximum stabilization, although some systems do not show instability at higher concentrations. The differences are due to the solubility of some mixtures being too low to experience instability at high concentrations. The dependence of dispersion stability on the ratio of ionic to nonionic surfactants has also been investigated. For most systems, stability is high in most regions except near the pure component endpoints. This is not true in the sodium dodecyl sulfate (SDS)/Tween 80 system, which is unstable with ratios having less SDS. This result is due to insuff cient driving force for the relatively hydrophilic nonionic surfactant to attach to the lower number of adsorption sites created by SDS adsorption. With this investigation, the factors inf uencing robust dispersion stability by using synergistic mixtures of ionic and nonionic surfactants have been determined.

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