

The Dispersion Properties of Precipitated Calcium Carbonate Suspensions Adsorbed with Alkyl Polyglycoside in Aqueous Medium

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The zeta potentials and dispersion properties of precipitated calcium carbonate suspensions adsorbed with alkyl polyglycosides in aqueous medium were investigated. Within the investigated pH ranges, the adsorption curves of alkyl polyglycosides on calcium carbonates show sigmoidal shapes, and the zeta potential decreases as the amount of adsorption increases. At positively charged surfaces of low pH, the adsorption amounts were greater than those at negatively charged surfaces, indicating that alkyl polyglycosides were negatively charged in aqueous solutions. At low concentrations of alkyl polyglycosides, the dispersion stabilities of suspensions were very poor and showed no linearity with zeta potentials over the entire range of pHs, which may be attributed to the onset of hydrophobic interaction between particles due to the adsorption of surfactant molecules. This destabilization continued until monolayer coverage by the surfactant layer was complete. Based on the classical DLVO theory, there may be a strong hydrophobic interaction between particles. Beyond monolayer adsorption, the dispersion stability increases, probably by the formation of hemimicelle or admicelle. Therefore, it is believed that ionization of alkyl polyglycosides and admicelles of surfactants on particle surface plays a key role in the stability of dispersions and the abrupt increase in adsorption. © 2000 Academic Press

Key Words: alkyl polyglycoside; precipitated calcium carbonate; suspensions; dispersion stability; zeta potential; DLVO theory.

INTRODUCTION

Alkyl polyglycosides are widely known as environment-friendly surfactants derived from sugars, due to their excellent surface activity as well as their mildness and biodegradability. Alkyl polyglycoside surfactants exhibit greater tolerance toward electrolytes and temperature than traditional nonionic surfactants do (1, 2). These properties are desirable for a number of commercial applications such as detergency, emulsification, dispersion, wetting, and solubilization. Also, alkyl polyglycosides have potential in biological and pharmaceutical applications and are used in biological studies for solubilization of membrane proteins without denaturation (3, 4).

Alkyl polyglycoside surfactants are prepared from a reaction of excess fatty alcohol with dextrose under strong acid conditions (5). The reaction of a fatty alcohol and dextrose yields a nonionic surfactant where the alkyl chain is attached to the anhydrous glucose ring through an ether linkage. In chemical terms, alkyl polyglycosides are polymeric acetals of glucose and fatty alcohols, although the average degree of polymerization of compounds of industrial importance is very low at $n < 2$, where n is the number of glucose rings in the alkyl polyglycoside. A great deal of work has been devoted to understanding how alkyl polyglycoside surfactants behave in aqueous solutions. Surface and interfacial tension measurements (6, 7), phase behavior and rheological data (8), micellar aggregation numbers (9), and microemulsion systems (10) have been reported.

Although there are a number of articles on the solution behavior of these surfactants, information on adsorption of alkyl polyglycoside on solid substrates is limited. Smith *et al.* (11) measured the adsorption isotherms of three alkyl polyglycosides on titanium dioxide. Smith *et al.* postulated that the hydroxyl groups on the alkyl polyglycoside surfactant are slightly acidic in nature and can have hydrogen bonding with the basic OH groups on the surfaces of TiO₂ particles. Once a sufficient number of surfactant molecules adsorb to render the particle surface hydrophobic, a second layer of surfactant adsorbs with the head groups directed out toward the bulk aqueous solution. Zhang *et al.* (12) measured the effect of pH on the adsorption of *n*-dodecyl- β -D-maltoside on alumina and reported that the maltoside adsorption is not affected by the change in pH and so the electrostatic interaction is not a dominant factor in determining the adsorption of *n*-dodecyl- β -D-maltoside on alumina. Zhang *et al.* also showed that the zeta potentials of alumina and titania are not altered significantly by the adsorption of maltoside surfactant.

From this point of view, the adsorption characteristics of alkyl polyglycoside on solid particles are different from other ethoxylated surfactants. The aim of this work was to investigate the effect of alkyl polyglycoside on the dispersion state of calcium carbonate in water and to elucidate the mechanism of the effect. Calcium carbonate was used as the model particulate material

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since it is widely used in many industrial products such as paints, inks, papers, and plasticizers.

EXPERIMENTAL

Materials

Alkyl polyglycoside was obtained from Henkel Corporation and was used without further purification. The alkyl chain was in the range C₈–C₁₀. Its degree of polymerization was 1.8 (average alkyl chain length was 9.1) and its HLB (hydrophile–lipophile balance) was 15.5. The average molecular weight of alkyl polyglycoside used in this study was about 449.3.

The precipitated calcium carbonate (PCC) particles were prepared from a calcium hydroxide solution of 27.8 g/l by bubbling a mixture of CO₂ and air. The calcium hydroxide solution was stirred for 3 h, and then a mixture of 30% CO₂ in air (v/v) was blown into the solution with a flow rate of 5 l/min. A photograph of calcium carbonate particles is shown in Fig. 1. The shape of the prepared particles was cubic and nearly monodisperse. The surface area determined by the BET method using nitrogen was 19.3 m²/g and the average particle diameter calculated from electron microscopic observation was about 0.09 μm. The isoelectric point (IEP)—the point at which the zeta potential is zero—of calcium carbonate was known to be around 8.2 (13). The potential-determining ions of calcium carbonate are Ca²⁺, HCO₃⁻, CO₃⁻, H⁺, and OH⁻. Therefore, deionized water was used to eliminate the effects of ions in all experiments.

The calcium carbonate particles were dewatered and dried at 75°C for 5 days. The dried powder was pulverized and sealed from water.

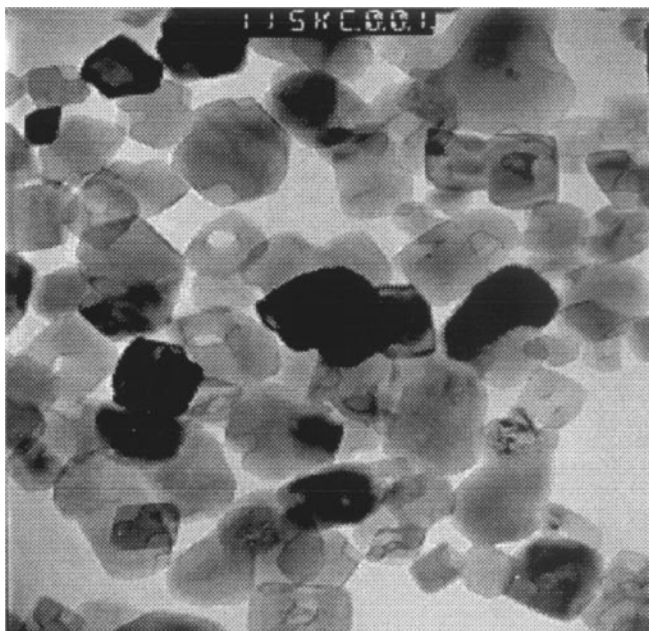


FIG. 1. TEM photograph of precipitated calcium carbonate particles prepared under experimental conditions.

Methods

In 100 ml of water, 5 g of calcium carbonate powder was dispersed and stirred for about 3 days. During this dissolution procedure, the solution pH of the suspension reached around 8.4, which is nearly the isoelectric point (IEP) of calcium carbonate suspension.

The pH of the suspensions was adjusted to 6, 8, and 12 with standard solutions of 0.1 N HCl and NaOH. After alkyl polyglycoside was solubilized in 50 ml water, calcium carbonate suspensions were added, keeping the total solid weight fraction in the suspension at about 3.3% (w/w).

The amount of surfactant adsorbed onto the calcium carbonate particles was determined from measurements of the difference in concentrations of the surfactant solutions before and after the suspensions were equilibrated with surfactant solution. After equilibrium was reached, the solution was centrifuged at 12,000 rpm for 30 min, which was sufficient for the complete sedimentation of all the particles. The clear supernatant was decanted for measurement of the surfactant concentration. The concentration of alkyl polyglycoside in the supernatant was determined by UV/vis spectrophotometry at a wavelength of 221.8 nm.

The zeta potentials were measured with a Zeta Plus instrument (Brookhaven Instruments Co.). Once the electrophoretic mobility was measured, the zeta potential value was calculated using the Smoluchowski equation. Each zeta potential reading was averaged from at least 15 measurements. Four or five replicates were determined for each sample. All measurements were performed at 20°C.

The dispersion stabilities of calcium carbonate suspensions were determined by the sedimentation method. Calcium carbonate suspensions adsorbed with alkyl polyglycoside were stirred vigorously for 3 h to maintain the homogeneity of suspensions and then were poured into 25-ml cylindrical test tubes. Before measurement, the cylinders were turned end over end 20 times. Stability was determined directly by measuring the settling time, $T_{1/2}$, defined by the time required for the settling plane to move to half of the height of the suspension volume (14).

Finally, the size of CaCO₃ particle aggregates in an aqueous medium was measured using a Pamas particle size analyzer. The suspension (3.3 wt% solid concentration) of 0.5 ml was diluted with 300 ml deionized water and stirred for 15 min. Several numbers of replicates were determined for each sample.

RESULTS AND DISCUSSION

Adsorption Isotherm of Alkyl Polyglycoside on CaCO₃ Particles

Figure 2 shows the adsorption isotherm for alkyl polyglycoside adsorbed at three different pH's. The isotherms show sigmoidal curves in all cases. The amounts of saturation adsorption are dependent on the initial suspension pH; that is, the amounts adsorbed at pH 6 and 8 (below IEP—positively charged surface) are much larger than the amounts adsorbed at pH 12 (above

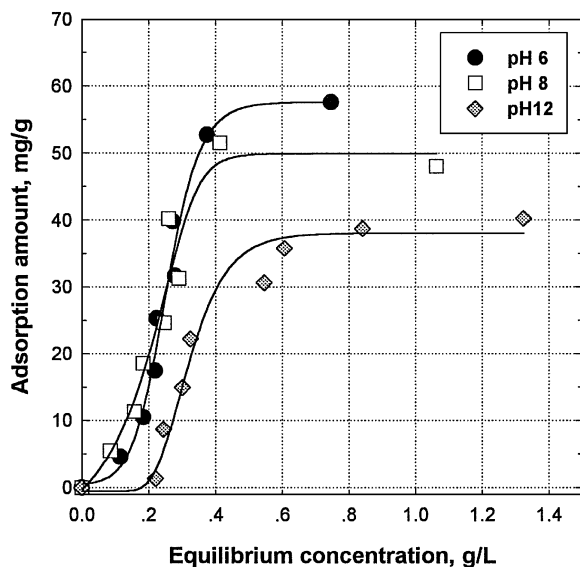


FIG. 2. Adsorption isotherm of alkyl polyglycoside on calcium carbonate particles at different suspension pH.

IEP—negatively charged surface). Therefore, it is believed that a negative electric charge is developed on the alkyl polyglycoside interface. Such a result, that alkyl polyglycoside molecules have a negative charge in the solution, is in accord with Balzer's observations (15). In fact, this negative charge inhibits the adsorption of alkyl polyglycoside on calcium carbonate surfaces at pH 12. These adsorption isotherms suggest that the electrostatic interaction between surfaces and adsorbents is an important factor in determining the adsorption of alkyl polyglycoside on the surface of CaCO_3 .

Figure 2 also shows that the adsorption amount increases abruptly at the equilibrium concentration between 0.20 and 0.25 g/l at pH 6 and 8. At these concentrations, a monolayer of surfactant at the solid/liquid interface has been formed, and rapid increase in the adsorption density can probably be attributed to the onset of lateral interactions between the hydrocarbon chains. By this interaction, the surfactants begin to associate in a form of two-dimensional patchwise surfactant aggregate such as hemimicelles or admicelles (adsorbed micelles) on solid surfaces (16, 17). However, as can be seen from Fig. 2, clear changes in the slope of the adsorption isotherm, giving rise to different isotherm regions, were not observed in the present work.

Change in Zeta Potential

Figure 3 shows that the zeta potentials of aqueous suspensions of calcium carbonate can be affected by adsorbed alkyl polyglycoside at various pH's. The zeta potentials of calcium carbonates at pH 6 and 8 are initially positive. As the adsorbed amounts increase, the potentials show a steep decrease from positive to negative, passing the different points of zero charge, but show plateaus at the adsorption amount of about 40 mg/g. The decrease in zeta potential with increasing adsorption density at pH 12 was smaller than that observed at pH 6 and 8.

Evidently, the negatively charged alkyl polyglycoside molecules are easily attached to the positively charged surface of calcium carbonate at pHs of 6 and 8. Once a sufficient number of surfactant molecules adsorb to render the particle surface hydrophobic by electrostatic force, hemimicelles or admicelles begin to form on the solid/liquid interface. At pH 12, the surface potential of the bare surface is initially negative, but the adsorption of alkyl polyglycoside occurs on the surface with a negative charge. The zeta potential does not decrease significantly in spite of the increase of the adsorption of surfactant, because this initial adsorption of surfactant would be attributed to the acid–base interaction between the basic hydroxyl groups present on the surface of the calcium carbonate particles and negatively charged alkyl polyglycoside. Hydroxyl ions are among the potential-determining ions for calcium carbonate and are adsorbed onto the surface of calcium carbonate (11). The primary and secondary hydroxyl groups on the glucose ring in alkyl polyglycoside molecules are slightly acidic in nature. So the interaction between the OH groups on the surface of calcium carbonate and hydroxyl groups on alkyl polyglycoside drives initial adsorption of surfactant onto the surfaces of particles. A similar mechanism was reported for the adsorption of sodium dodecyl sulfate onto TiO_2 (18) and onto alumina (19). But it is concluded that a gradual displacement of counterions from the Stern layer by adsorbing surfactant molecules shifted the adsorption and the zeta potential of calcium to the saturation after a certain concentration of alkyl polyglycoside.

The Effect of Zeta Potential on Dispersion Stability

Figures 4, 5, and 6 show the settling times of calcium carbonate suspensions and zeta potentials as a function of surfactant concentrations at different pHs. In Figs. 4 and 5, the CaCO_3 suspension not having an alkyl polyglycoside adsorbed layer

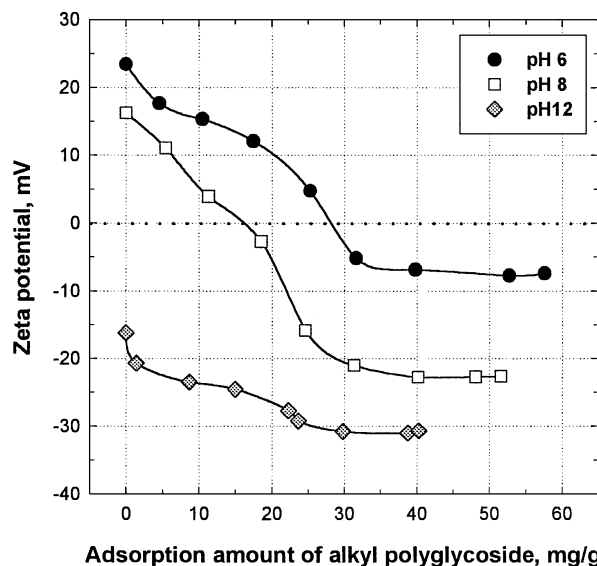


FIG. 3. Change in zeta potential of calcium carbonate suspensions as a function of equilibrium concentration at different suspension pH.

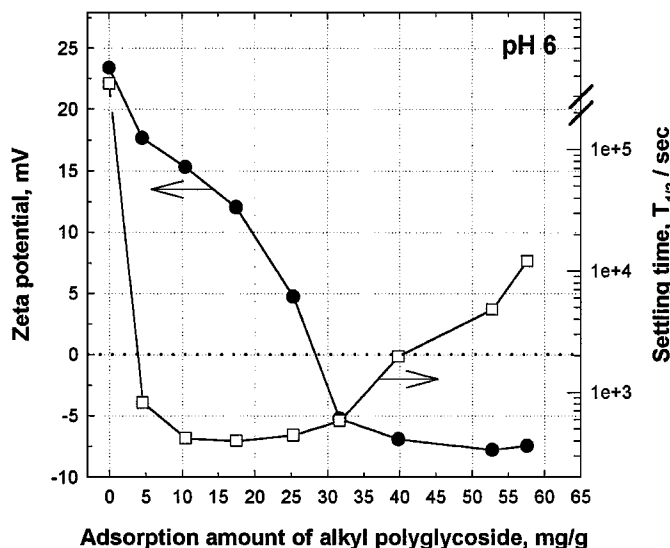


FIG. 4. Change in zeta potential (●) and dispersion stability (□) of calcium carbonate suspensions adsorbed with alkyl polyglycoside at pH6.

exhibits very good stability (over 100 h of settling time), apparently because of the high surface potential. As alkyl polyglycoside adsorbs slightly, the stability of suspension rapidly decreases up to an adsorption amount of about 30 mg/g at pH 6 and 8. (At pH 12, it is about 22 mg/g.) The stabilities apparently have no direct relationships to the zeta potentials of particles in the small adsorption amount region. For example, the zeta potentials are relatively high, in the range of 25 and 30 mg/g at pH 8, but the dispersion stabilities are very poor. A similar observation is obtained at pH 12.

The changes of dispersion stabilities would be explained by changes in the surface properties of calcium carbonate. As the adsorption of surfactant increased, the suspensions were destabi-

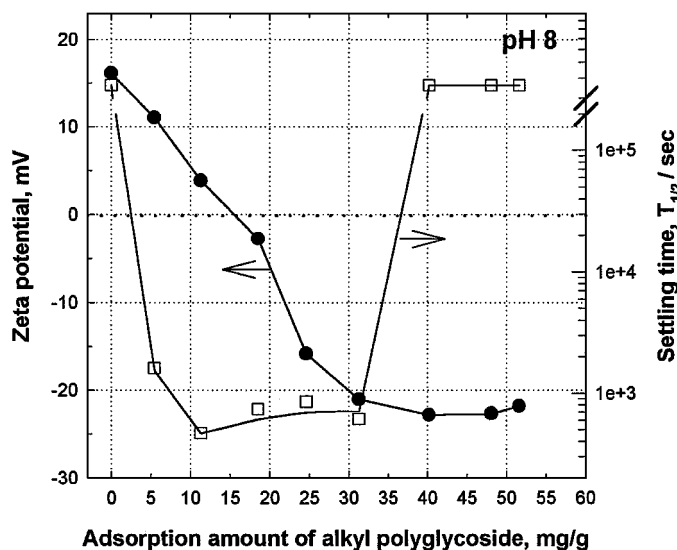


FIG. 5. Change in zeta potential (●) and dispersion stability (□) of calcium carbonate suspensions adsorbed with alkyl polyglycoside at pH8.

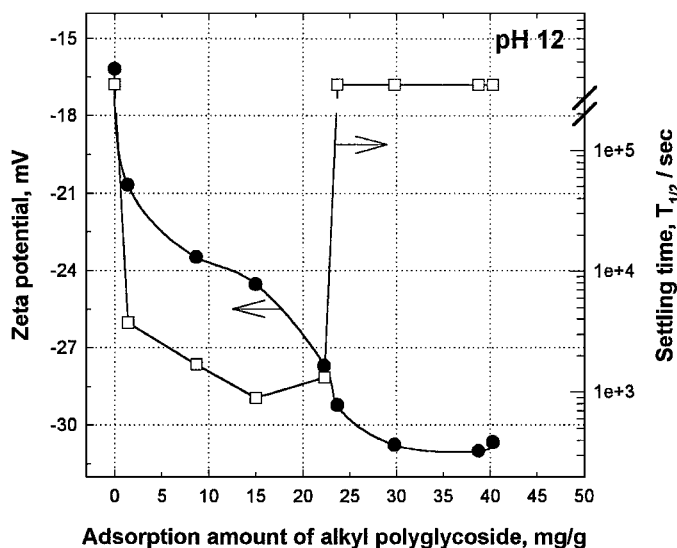


FIG. 6. Change in zeta potential (●) and dispersion stability (□) of calcium carbonate suspensions adsorbed with alkyl polyglycoside at pH12.

lized due to the change in hydrophilicity. That is, the surfaces of calcium carbonate particles changed from hydrophilic to hydrophobic. The hydrophobic interaction between particles or the potential energy of hydrocarbon chain association abruptly increased, and the stability of the suspension showed a rapid decrement, until the monolayer saturation of surfactant molecules on the solid/liquid interfaces were saturated. When the particle surfaces became hydrophilic again by the formation of admicelles, the stability showed a sharp increment for the suspensions at pH 8 and pH 12. At pH 6, however, this abrupt change of dispersion stability was not observed because the surface potential was relatively small. When the solid surface became hydrophilic, the zeta potentials played a key role in the dispersion stability of calcium carbonate suspensions at pH 8 and pH 12.

From the observation of the adsorption amounts, the zeta potentials, and the dispersion properties of calcium carbonate suspensions, it seems that the adsorption amount of about 30 mg/g is the onset point for the formation of admicelles on solid/liquid interface below pH 8.2, which is the IEP of calcium carbonate in aqueous solution. That is, the monolayer of surfactant molecules reached saturation at this adsorption amount. Above the IEP, the amount adsorbed is about 22 mg/g. Using the surface area of $19.3 \text{ m}^2/\text{g}$ by BET method, the adsorption density at the monolayer coverage of alkyl polyglycoside can be determined to be $3.46 \times 10^{-6} \text{ mole/m}^2$ below the IEP and $2.54 \times 10^{-6} \text{ mole/m}^2$ above the IEP.

Computation of Total Potential Energy

Generally, the total interaction energy, U_T , is given by the sum of the repulsive electrostatic interaction energy, U_R , and the attractive London-van der Waals energy, U_A :

$$U_T = U_R + U_A. \quad [1]$$

The repulsive energy of interaction, U_R , between two spheres of materials 1 and 2 in a third medium 3, for two dissimilar particles (with surface potential ψ_1 and ψ_2) and unequal sizes (radii R_1 and R_2 , respectively), has been formulated by Hogg *et al.* (21) for the case of constant potential upon approach,

$$U_R = \frac{\varepsilon R_1 R_2 (\psi_1^2 + \psi_2^2)}{4(R_1 + R_2)} \left\{ \frac{2\psi_1 \psi_2}{(\psi_1^2 + \psi_2^2)} \ln \left[\frac{1 + \exp(-\kappa H_0)}{1 - \exp(-\kappa H_0)} \right] + \ln[1 - \exp(-2\kappa H_0)] \right\}, \quad [2]$$

where ε is the dielectric constant of the medium; κ is the Debye–Hückel reciprocal length parameter; and H_0 is the nearest distance between the surfaces of the particles. Under the condition that $\psi_1 = \psi_2 = \psi$ and $R_1 = R_2 = R$, Eq. [2] can be reduced to the following form:

$$U_R = \frac{\varepsilon R \psi^2}{2} \ln[1 + \exp(-\kappa H_0)]. \quad [3]$$

In computation, $\kappa^{-1} = 10^{-6}$ cm is used for the 1% aqueous surfactant solution (32) and R is 4.5×10^{-6} cm from electron microscopic measurement. The dielectric constant, ε , is expressed as the product $\varepsilon_r \varepsilon_0$, where ε_r is the usual dimensionless dielectric constant, being 78.3 for water at 25°C, and ε_0 is the permeability of free space, having a value of 1.11×10^{-12} CV⁻¹ cm⁻¹ (22).

The attractive energy of interaction, U_A , can be calculated from the equation

$$U_A = -\frac{A_{132}}{6} \left\{ \frac{2R_1 R_2}{[H_0^2 - (R_1 + R_2)^2]} + \frac{2R_1 R_2}{[H_0^2 - (R_1 - R_2)^2]} + \ln \frac{[2(R_1 + R_2) + H_0]H_0}{(2R_1 + H_0)(2R_2 + H_0)} \right\}, \quad [4]$$

where A_{132} is the Hamaker constant for the materials 1 and 2 in medium 3. The Hamaker constant for the calcite particles in water has the value of 3.364×10^{-19} J (23). For the interaction between two identical spheres of the same material in water ($R_1 = R_2 = R$), Eq. [4] is reduced to

$$U_A = -\frac{RA_{131}}{12H_0}. \quad [5]$$

The potential energy curves for electrical repulsion and London–van der Waals attraction and the total potential energy curves were obtained from Eqs. [1], [3], and [5] and shown in Fig. 7. Curves 1 and 2 are the electrical repulsive energies with zeta potentials of 30 and 24 mV. Curve 3 is the attractive energy with no adsorbed layer. Curves 4 and 5 are the total potential energies obtained by combining curves 1 and 3 and curves 2 and 3, respectively. When the zeta potential is around 24 mV, the electrical repulsive energy is sufficiently high to overcome the attractive energy. According to the DLVO theory, an energy barrier of 15 kT is sufficient to produce a highly stabilized dispersion system (29). Therefore, the initial high stabilities of suspensions

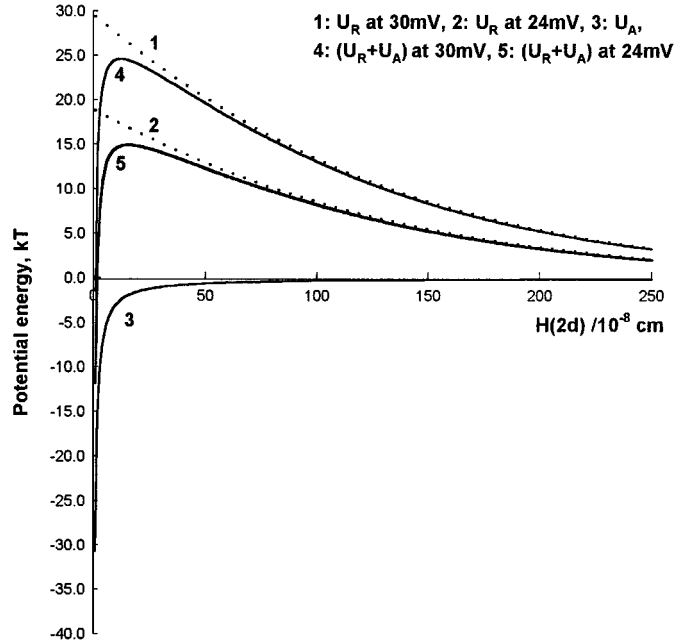


FIG. 7. Potential energies between calcium carbonate particles with no adsorbed surfactant layer.

were reasonable because its surface charge was high enough. At pH 12, a strong attractive force between the surfactant-coated calcium carbonate particles is observed in the region of 10–22 mg/g of adsorption amount, and at pH 8, the instability region is in the region of 25–30 mg/g of adsorption amount in spite of high surface potentials. In these regions, the hydrophobic interaction between particles would be developed in addition to the electrostatic repulsive force.

The total potential energy, U_T , between two hydrophobic particles can be represented by two additional terms describing the potential energy of hydrophobic interaction,

$$U_T = U_A + U_R + U_{H1} + U_{H2}, \quad [6]$$

where U_{H1} is the potential energy of hydrophobic interaction and U_{H2} is the potential energy of hydrocarbon chain association. Based on the measurement of the force between approaching hydrophobic mica surfaces, Israelachvili (24) and later Claesson *et al.* (31) found that the distance of hydrophobic interaction can reach 25 nm and that the potential energy of hydrophobic interaction U_{H1} decays exponentially with distance. The new results obtained by Rabinovich and Derjaguin (30) on hydrophobic silica filaments in water indicated that the hydrophobic attractive force may occur even at much longer distances (20–60 nm). An empirical formula for U_{H1} is represented as (24, 30)

$$U_{H1} = -2.51 \times 10^{-3} R l_0 Q \exp\left(-\frac{H_0}{l_0}\right), \quad [7]$$

where R is the radius of the spherical particles, l_0 the decay length, and Q the coefficient of hydrophobicity of the surface. However, many researchers have proposed different values of

the decay length (25–27). The value of the decay length for an aqueous calcium carbonate suspension was estimated by Zygmunt (23) to be 12.2 nm. For strong hydrophobic surfaces, the value of Q must lie close to 1.

The chain association interaction is similar to micelle formation. The potential energy of hydrocarbon chain association can be calculated according to the formula

$$U_{H2} = uV \left(\frac{16R^2\sigma n_c}{3(R + L_0)^3 - R^3} \right). \quad [8]$$

The term u is the association energy of one $-\text{CH}_2-$ group and is equal to 2.2×10^{-21} J (28). In this equation, R is the radius of the spherical particles. n_c is the carbon number of the hydrocarbon chain of the surfactant molecule (for the alkyl polyglycoside used in this experiment, the average carbon number of the hydrocarbon chain is 9.1). σ is the average surface distribution density of the adsorbed surfactant molecules, and L_0 is the thickness of the adsorbed layer. When the adsorbed surfactant molecules create a monolayer, L_0 is the length of the surfactant molecule (for alkyl polyglycoside in this work; L_0 is about 1.7 nm by a geometrical optimization using the Hyperchem molecular modeling program (Hypercube, Inc. and Autodesk Inc.). The surface distribution density of surfactant molecules in the adsorption layer, σ , can be calculated from the surface excess, Γ , equivalent to 3.46×10^{-6} mol/m². V represents the overlapping volume of two approaching surfactant layers, and can be described as follows:

$$V = \frac{1}{3}(L_0 - H_0)^2(3R + 2L_0 - H_0). \quad [9]$$

Figure 8 shows the total interaction energy at a monolayer-saturated surface with a surface charge of -30 mV. As can be

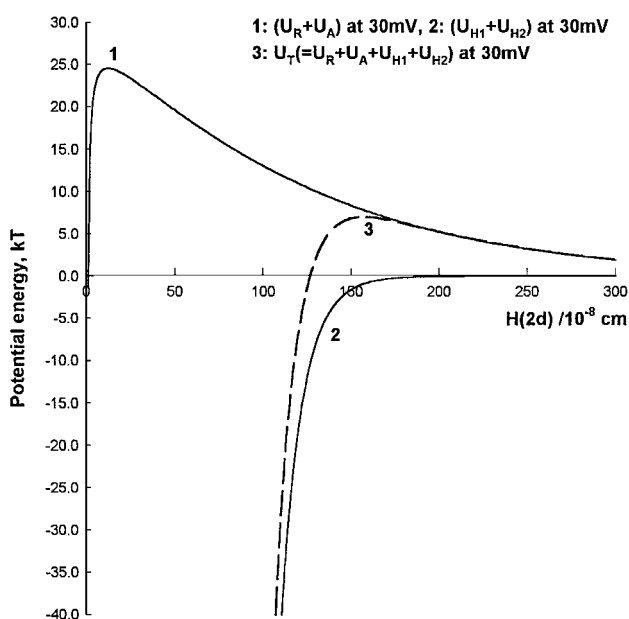


FIG. 8. Potential energies between calcium carbonate particles containing monolayer of surfactant at 30 mV surface charge.

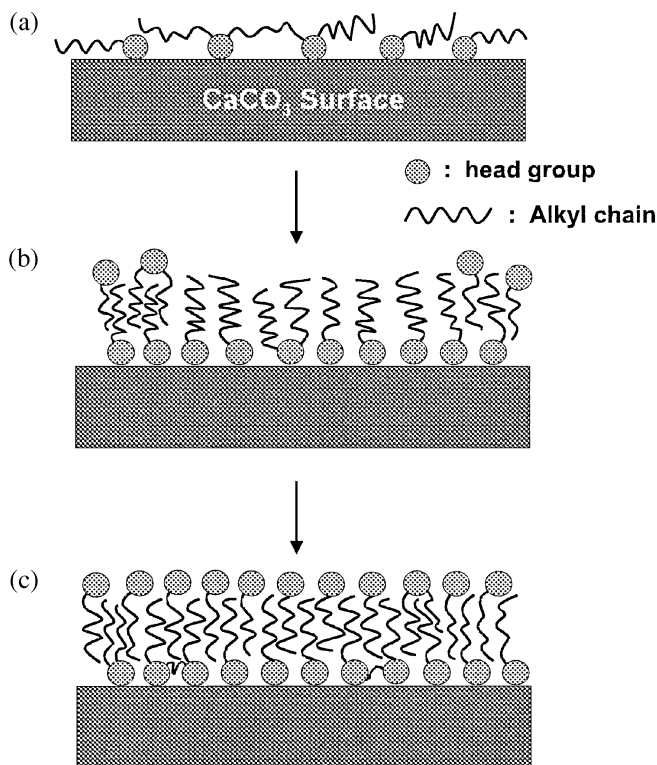


FIG. 9. Proposed orientation model for the adsorption of alkyl polyglycoside on calcium carbonate surfaces, showing the conformation of surfactant at the surfaces: (A) at low adsorption amount of surfactant, (B) at medium adsorption amount of surfactant, and (C) at high surfactant concentration.

seen, when hydrophobic energies U_{H1} and U_{H2} are taken into account, the total potential energy indeed becomes strongly attractive and the aggregation of particles occurs spontaneously in spite of high surface potentials, because the potential energy between calcium carbonate particles is smaller than the maximum energy barrier ($15kT$). Therefore, an abrupt decrease of stability at the hydrophobic surface by the adsorption of alkyl polyglycoside is expected.

In Fig. 9, an orientation model for the adsorption of alkyl polyglycoside on calcium carbonate surface is proposed including the conformation of surfactant at the surfaces. The adsorption of surfactant on CaCO_3 solid particles can be divided into three regions: (A) The surfactant is adsorbed on the solid surface individually due to the electrostatic attraction force between surface and alkyl polyglycoside, and the dispersion stability decreases due to the hydrophobicity of surface in this region. Finally, the hydrophobic interaction attains a maximum at the end of monolayer saturation. (B) Interactions between surfactant chains take place and hemimicelles or admicelles begin to form, leading to a steep rise in adsorption. The dispersion stability increases very sharply from this point. (C) The adsorption completes a bilayer with hydrophobic chains interpenetrating each other.

Using a specific surface area of CaCO_3 and adsorption amount at monolayer surface coverage (30 mg/g), the surface area per molecule adsorbed below pH 8.2 (IEP of calcium carbonate)

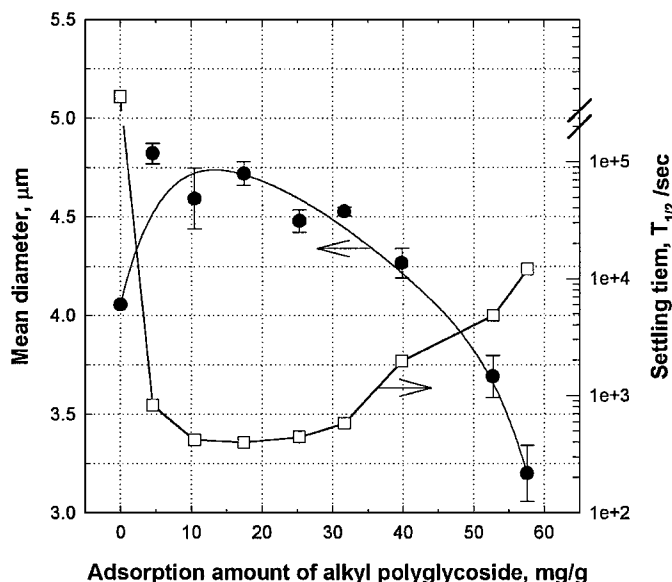


FIG. 10. Influence of adsorption amount of alkyl polyglycoside on aggregate size (●) and dispersion stability (□) of calcium carbonate particles at pH 6.

is estimated to be less than 48.0 \AA^2 , which is consistent with 48.5 \AA^2 (12) from the surface tension at the solution–air interface.

Mean Aggregate Size of Diluted CaCO_3 Suspension

Figure 10 shows that the mean diameters of particle aggregates and the settling times of suspensions change with the adsorption amount of alkyl polyglycoside at pH 6. Aggregates of particles without an adsorbed alkyl polyglycoside layer were not initially formed due to the high surface potentials. The size of aggregates of calcium carbonate particles rapidly increased in the range of small amount of adsorption, which may be attributed to the reduction of surface potential and hydrophobic interaction between particles. Beyond 30 mg/g, the aggregate size decreased significantly in spite of the small change of surface potential, consistent with the change of settling time (dispersion stability). This is because the surfaces of the solid particles became hydrophilic above this concentration, and therefore the electrostatic repulsion again played an important role in the dispersion of particles. The aggregate sizes of calcium carbonate particles also vary along with the adsorption isotherm and zeta potential (20).

CONCLUSION

The amounts of alkyl polyglycoside adsorbed onto calcium carbonate particles in an aqueous medium depend on the surface nature of the solid. The amount of alkyl polyglycoside that was adsorbed onto the surface increased with increasing positive surface charge. Further, the zeta potentials of calcium carbonate particles markedly decreased. This indicates that alkyl polyglycoside molecules have a negative charge in the solution. In pH

6 and 8, the electrostatic attraction force drives the adsorption of alkyl polyglycoside onto the surface. In pH 12, the initial adsorption may be attributed to the hydrogen bonding between the hydroxyl groups present on the surface and on the glucose ring.

At the low concentration of alkyl polyglycoside, the dispersion stability of suspensions did not show linearity with zeta potentials at the entire range of pH and exhibits very poor stabilities. Such poor dispersion stabilities may be attributed to the hydrophobic interaction between particles, which is caused by the adsorption of alkyl polyglycoside. The destabilization concentrations extended until monolayer coverage was complete, equivalent to an adsorption amount of 30 mg/g. The total potential energy at monolayer coverage, calculated by the DLVO theory, indeed becomes strongly attractive, and the aggregation of particles will occur spontaneously in spite of high surface potentials (at pH 12), probably because the potential energy between particles is smaller than the minimum energy barrier ($15kT$).

Beyond a monolayer, the adsorption amount abruptly increased owing to the formation of hemimicelles (further adsorption occurred by the formation of bilayer of surfactant on surface) and the suspension showed good stabilities due to the electrostatic repulsion between particles. It is believed that the change of surface hydrophilicity due to formation of admicelles of surfactants on the particle surface plays a key role in the stability of dispersions and the abrupt increase of adsorption amount. Finally, the surface area per alkyl polyglycoside molecule at the saturated monolayer was calculated to be 48.0 \AA^2 .

REFERENCES

1. Salka, B., *Cosmet. Toiletries* **108**, 89 (1993).
2. Siracusa, P. A., *Tappi* **29**, 100 (1992).
3. Helenius, A., McCaslin, D. R., Fries, E., and Tanford, C., *Methods Enzymol.* **56**, 734 (1979).
4. Stubbs, G. W., Smith, H. G., Jr., and Litman, B. J., *Biochim. Biophys. Acta* **425**, 46 (1976).
5. Hill, K., Rybinski, W. von, and Stoll, G., in "Weinheimer Jahrbuch, 1977."
6. Aleksejczyk, R. A., Allen, C. B., and Counts, M. W., paper presented at the American Oil Chemists' Society, May 1990.
7. Aleksejczyk, R. A., and Counts, M. W., paper presented at the American Oil Chemists' Society, May 1991.
8. Balzer, D., *Tenside Surfactants Deterg.* **28**, 419 (1991).
9. Parker, W. O., Jr., Genova, C., and Carignano, G., *Colloids Surf.* **72**, 275 (1993).
10. Stubenrauch, C., Paepow, B., and Findenegg, G. H., *Langmuir* **13**, 3652 (1997).
11. Smith, G. A., Zulli, A. L., Grieser, M. D., and Counts, M. C., *Colloids Surf.* **88**, 67 (1994).
12. Zhang, L., Somasundaran, P., and Maltesh, C., *J. Colloid Interface Sci.* **191**, 202–208 (1997).
13. Somasundaran, P., and Agar, G. E., *J. Colloid Interface Sci.* **24**, 433 (1967).
14. Moriyama, N., *Colloid Polym. Sci.* **254**, 726 (1976).
15. Balzer, D., *Langmuir* **9**, 3375 (1993).
16. Kunjappu, J. T., and Somasundaran, P., *J. Colloid Interface Sci.* **175**, 520 (1995).
17. Somasundaran, P., and Krishnakumar, S., *Colloids Surf.* **93**, 79 (1994).
18. Ma, C., and Xia, Y., *Colloids Surf.* **68**, 171 (1992).

19. Chandar, P., Somasundaran, P., and Turro, N. J., *J. Colloid Interface Sci.* **117**, 31 (1987).
20. Hong, J. J., Yang, S.-M., Choi, Y.-K., and Kim, M. S., *Colloids Surf. B Biointerfaces* **7**, 221 (1996).
21. Hogg, R., Healy, T. W., and Fuerstenau, D. W., *Trans. Faraday Soc.* **62**, 1638 (1966).
22. Wiese, G. R., and Healy, T. W., *Trans. Faraday Soc.* **66**, 490 (1970).
23. Zygmunt, S., *Powder Technol.* **80**, 93 (1994).
24. Israelachvili, J. N., and Pashley, R., *Nature* **30**, 243 (1982).
25. Israelachvili, J. N., and Pashley, R. M., *J. Colloid Interface Sci.* **92**, 500 (1984).
26. Claesson, P. M., and Christenson, H. K., *J. Phys. Chem.* **92**, 1650 (1988).
27. Rabinovich, Ya. J., and Derjaguin, B. V., *Kolloidn. Zh.* **49**, 682 (1987).
28. Lu, S., and Song, S., *Colloids Surf.* **57**, 49, 61 (1991).
29. Rosen, M. J., "Surfactants and Interfacial Phenomena," p. 256. Wiley, New York, 1978.
30. Rabinovich, Ya. I., and Derjaguin, B. V., *Colloids Surfaces* **30**, 243 (1988).
31. Claesson, P. M., Blom, C., Herder, P. C. and Ninham, B. W., *J. Colloid Interface Sci.* **114**, 234 (1986).
32. Hachisu, S., *Shikizai Kyokaishi* **38**, 523 (1965).