

# Mixtures of Anionic and Cationic Surfactants with Single and Twin Head Groups: Adsorption and Precipitation Studies

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**ABSTRACT:** This research reports on the adsorption and precipitation of mixtures of anionic and cationic surfactants having single and twin head groups. The surfactant mixtures investigated were: (i) a single-head anionic surfactant, sodium dodecyl sulfate (SDS), in a mixture with the twin-head cationic surfactant pentamethyl-octadecyl-1,3-propane diammonium dichloride (PODD)—adsorption was studied on negatively charged silica; and (ii) a twin-head anionic surfactant, sodium hexadecyl-diphenyloxide disulfonate (SHDPDS), and the single-head cationic surfactant dodecylpyridinium chloride (DPCI)—adsorption was studied on positively charged alumina. Whereas the mixed surfactant system of SHDPDS/DPCI showed adsorption on alumina that was comparable to that of SHDPDS alone, the mixed surfactant system of SDS/PODD showed increased adsorption on silica as compared with PODD alone. The adsorption of the SDS/PODD mixture increased as the anionic and cationic system approached an equimolar ratio. Precipitation diagrams for mixtures of single- and twin-head surfactant systems showed smaller precipitation areas than for single-head-only surfactant mixtures. Thus, the combination of single- and double-head surfactants helps reduce the precipitation region and can increase the adsorption levels, although the magnitude of the effect is a function of the specific surfactants used.

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**KEY WORDS:** Alumina, anionic surfactant, cationic surfactant, mixed surfactant, precipitation, silica.

Mixtures of anionic and cationic surfactants act synergistically, as evidenced by ultralow critical micelle concentrations (CMC), increased surface activity (1,2) and improved detergency performance (3). The main disadvantage of mixed an-

ionic and cationic surfactant systems is their tendency to form precipitates or liquid crystal phases (4). Precipitation negatively affects surfactant use in many applications, such as detergency performance and subsurface remediation of oil contamination (4,5).

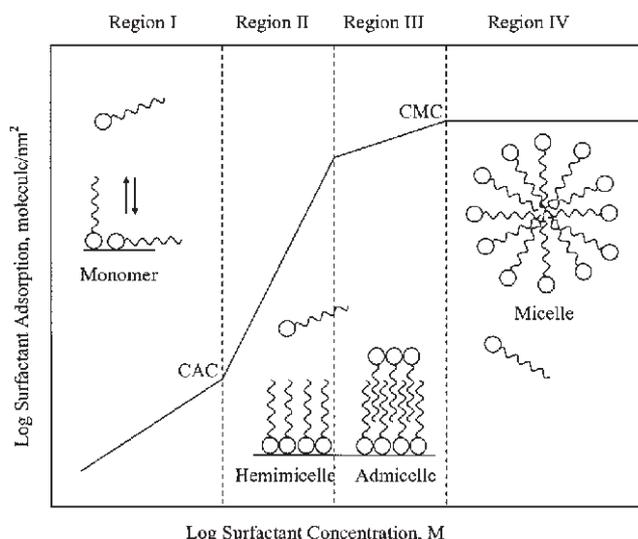
The main goals of this work are to evaluate synergism of surfactant adsorption onto solid surfaces by using anionic and cationic surfactant mixtures, and to determine how properties of these adsorbed mixtures affect the co-adsorption or adsolubilization of different types of solutes. While of secondary interest, we also evaluate the precipitation of anionic/cationic surfactant mixtures to define isotropic concentration regimes in which to conduct the adsorption studies.

We hypothesize that by using mixtures of anionic and cationic surfactants we will observe a synergistic adsorptive behavior as evidenced by having higher surfactant adsorption at sub-CMC surfactant concentrations and by reaching the adsorption plateau (Region IV) at lower surfactant concentrations compared with single surfactant systems; this hypothesis is based on the lower CMC observed for mixtures of anionic and cationic surfactants compared with mixtures of similarly structured surfactants. We also hypothesize that an increased level of plateau surfactant adsorption will result because of the tighter packing density in adsorbed aggregates of these mixed surfactants owing to a reduction in charge repulsion between adjacent adsorbed surfactants compared with single surfactant systems.

Figure 1 presents a typical adsorption isotherm of an ionic surfactant on an oppositely charged mineral surface, which can be divided into four regions (6). At very low surfactant concentration in Region I, or the Henry's Law region, adsorption is proportional to surfactant concentration. In Region I, adsorption density is so low that negligible interaction occurs between adsorbed molecules. Region II is characterized by a rapid increase in adsorption due to tail-tail interactions and the onset of bilayer coverage or admicelle formation. In Region II, adsorption increases with concentration as successively less energetic patches fill with admicelles. In Region III, the adsorption increases more slowly with concentration than

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Abbreviations: CMC, critical micelle concentration; DPCI, dodecylpyridinium chloride; IASR, Institute for Applied Surfactant Research; PODD, pentamethyl-octadecyl-1,3-propane diammonium dichloride; SDHS, sodium dihexyl sulfosuccinate; SHDPDS, sodium hexadecyl-diphenyloxide disulfonate.



**FIG. 1.** Adsorption isotherm of a surfactant onto a solid surface (modified from Ref. 6). CMC, critical micelle concentration; CAC, critical admicelle concentration.

in Region II, likely owing to lateral hindrances between adsorbed surfactants and also to heterogeneities in surface potentials. Region IV is the plateau adsorption region where adsorption is constant because the surfactant concentration exceeds the CMC.

From adsorption experiments by solution depletion, the amount of the surfactant adsorbed onto silica and alumina surface is obtained by Equation 1 (7):

$$\Gamma = \frac{V_L(C_1 - C_2)}{m} \quad [1]$$

where  $\Gamma$  is the adsorption of surfactant on the solid surface in mol/g,  $V_L$  is the volume of the liquid phase in L,  $C_1$  is the concentration of surfactant before adsorption in mol/L,  $C_2$  is the concentration of surfactant at adsorption equilibrium in mol/L, and  $m$  is the mass of the adsorbent in g. Alternatively, the adsorption can be expressed on a unit area basis (mol/m<sup>2</sup>) by dividing  $\Gamma$  from Equation 1 by the adsorbent surface area (m<sup>2</sup>/g).

To date, only a limited number of adsorption studies have been conducted with mixtures of anionic and cationic surfactants, largely due to precipitation limitations and analytical challenges (8–13). Thus, while adsorption is the primary focus of this research, we also conducted precipitation studies to identify regions in which we could conduct our adsorption studies and avoid precipitation. In this work we take advantage of the smaller precipitation region, which results from using a combination of single-head and twin-head ionic surfactants, which results in a larger isotropic concentration regime in which adsorption can be studied (14).

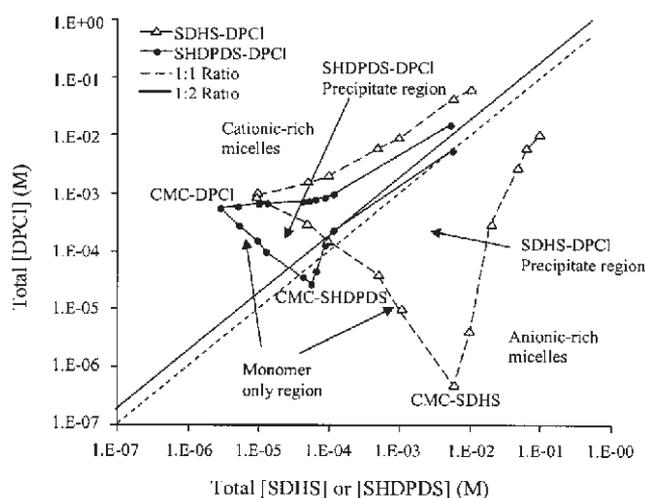
To understand surfactant precipitation, it is helpful to recognize that at low concentrations, anionic and cationic surfactants exist as dissociated surfactant monomers. As the surfactant concentration increases, micelles begin forming at

the CMC (15,16). For anionic and cationic surfactant systems, when the monomer concentrations equal or exceed their solubility limit, precipitate will form (17). Below the CMC, all of the surfactant is present as monomer; and as the concentration of one of the surfactants increases, a lesser concentration of the oppositely charged surfactant is needed to cause precipitation. This equilibrium (17) is modeled using the solubility product as shown in Equation 2:



where  $A^-$  is the concentration of the anionic surfactant monomer,  $C^+$  is the concentration of the cationic surfactant monomer,  $AC$  is the precipitate, and  $K_{sp}$  is the concentration-based solubility product of the precipitate. Activity coefficients are omitted from Equation 2 since they vary little over the concentration range of interest and can be difficult to evaluate for micellar systems.

The monomer, precipitate, and micelle phase boundaries for the surfactant mixtures hexadecyl-diphenyloxy disulfonate (SHDPDS) and dodecylpyridinium chloride (DPCl), and sodium dihexyl sulfosuccinate (SDHS) and DPCl are presented in Figure 2. Three precipitation boundaries are apparent in Figure 2; the first one occurs at low concentrations of both surfactants and corresponds to the monomer–precipitate equilibrium described by Equation 2. The right-hand side of the phase boundary corresponds to the equilibrium between anionic-rich micelles and the precipitate. The left-hand phase boundary corresponds to the equilibrium between the cationic-rich micelles and the precipitate. The vertices of the phase diagram correspond to the CMC of the surfactant mixtures. By looking at the precipitation phase diagram in Figure 2, it is apparent that the precipitation region in the system



**FIG. 2.** Precipitation diagrams for mixed surfactant systems, sodium dihexyl sulfosuccinate and dodecylpyridinium chloride (SDHS/DPCl), and sodium hexadecyl-diphenyloxy disulfonate and dodecylpyridinium chloride (SHDPDS/DPCl), 0.15 M NaCl, 25°C (adapted from Ref. 14). For other abbreviation see Figure 1.

SHDPDS/DPCI is smaller than the precipitation of the system SDHS/DPCI (14). Doan *et al.* (14) suggested that the twin-head structure of SHDPDS increased its resistance to precipitation and thus accounted for the smaller precipitation region. In this work we evaluate the precipitation of a twin-head cationic surfactant (pentamethyl-octadecyl-1,3-propane diammonium dichloride—PODD) with an oppositely charged and single-head anionic surfactant (sodium dodecyl sulfate—SDS); we expect that this combination will be more resistant to precipitation and can thus be formulated over a wider range of concentrations than a combination of two oppositely charged single-head surfactants (SDS/DPCI).

By reducing the precipitation potential of anionic and cationic surfactant mixtures we seek to exploit the potential synergism for these systems to produce ultra-low CMC values, to enhance oil solubilization and microemulsion formation, and to enhance adsorption. In this research we are especially interested in the possibility of increasing the adsorption of surfactant mixtures onto mineral surfaces (silica and alumina) for use as adsorbent materials for organic molecules.

## EXPERIMENTAL PROCEDURES

**Materials.** The cationic surfactant pentamethyl-octadecyl-1,3-propane diammonium dichloride (PODD, or Duoquad<sup>®</sup> T50) was donated by Akzo Nobel Surface Chemistry LLC (McCook, IL) as a 50% solution in isopropanol; although PODD is mainly octadecyl (38% C18:1 and 25% C18:0), PODD is also 29% hexadecyl, with the remaining 8% being C14:0, C14:1, C16:1, and C18:2. The isopropanol was evaporated by cyclic heating at 80°C under vacuum. The purified

sample was re-diluted and titrated until the remaining alcohol was <1%. The anionic surfactant SHDPDS (Dowfax 8390), which is a mixture of mono-hexadecyl and di-hexadecyl diphenyloxide disulfonate (80 and 20%, respectively) (18), was obtained from Dow Chemical Company (Midland, MI) (36% active). Dodecylpyridinium chloride (DPCI, 98% active) and SDS (98% active) were purchased from Aldrich Chemical Company (Milwaukee, WI) and used as received. The chemical properties of the surfactants are shown in Table 1. Alumina (Al<sub>2</sub>O<sub>3</sub>), mesh size 150, was purchased from Aldrich Chemical Company and was supplied as having a point of zero charge of 9.1 and a measured specific surface area of 133 m<sup>2</sup>/g. Silica Hi-sil<sup>®</sup> 233, donated by PPG Industries Inc. (Monroeville, PA), is reported to have a point of zero charge in the range of 2 to 4 and a measured specific surface area of 143 m<sup>2</sup>/g.

The BET specific surface area of the mineral oxides was determined by using a Micromeritics model Flow Sord II 2300 instrument (Norcross, GA). The samples were prepared by heating while simultaneously evacuating or flowing gas (nitrogen as the adsorbed gas and helium as the carrier gas) over the sample to remove the liberated impurities. The prepared samples were then cooled with liquid nitrogen and analyzed by measuring the volume of gas adsorbed at specific pressures (19).

Anionic and cationic surfactant concentrations were measured using a Dionex ion chromatograph in reversed-phase mode using an IonPac NS1 column (Dionex, Sunnyvale, CA) with a water/acetonitrile mixture as a mobile phase containing either 10 mM of tetrabutyl ammonium hydroxide or 10 mM of methane sulfuric acid as coupling agents for anionic

**TABLE 1**  
Chemical Properties of Surfactants

Chemicals	Molecular structure	Molecular weight, g/mol	CMC, mM
Pentamethyl-octadecyl-1,3-propane diammonium dichloride <sup>a,b</sup> (PODD)		463.62	1.3 <sup>c</sup> (0.01 M NaCl)
Sodium dodecyl sulfate (SDS)	CH <sub>3</sub> (CH <sub>2</sub> ) <sub>11</sub> SO <sub>4</sub> Na	288.38	6.8 <sup>d</sup> (0.15 M NaCl)
Dodecylpyridinium chloride (DPCI)		283.88	4.0 <sup>d</sup> (0.15 M NaCl)
Sodium hexadecyl-diphenyloxide disulfonate (SHDPDS)		642	6.3 <sup>e</sup> (0.15 M NaCl)

<sup>a</sup><http://surface.akzonobelusa.com/cfm/2page2.cfm?PID=100> (accessed July 21, 2005).

<sup>b</sup>[http://www.lion.co.jp/laco/e/prod/p/44dqad\\_e.htm](http://www.lion.co.jp/laco/e/prod/p/44dqad_e.htm) (accessed July 21, 2005).

<sup>c</sup>Inferred from onset of Region IV in Figure 5 at 0.01 M NaCl adsorption experiment.

<sup>d</sup>Stellner *et al.* (20).

<sup>e</sup>Rouse *et al.* (18).

and cationic surfactants, respectively. The individual coupling agent forms a neutral complex with the oppositely charged surfactant, which is then chromatographically separated from the other surfactant in the column. The effluent from the column is contacted with either an anionic suppressor (ASRS, 4 mm; Dionex) or a cationic suppressor (CSRS, 4 mm; Dionex), causing the complex to decouple; the decoupled surfactant is then detected using a CD-25 conductivity detector. All calibration runs resulted in linear fits with good correlations ( $R^2 > 0.99$ ).

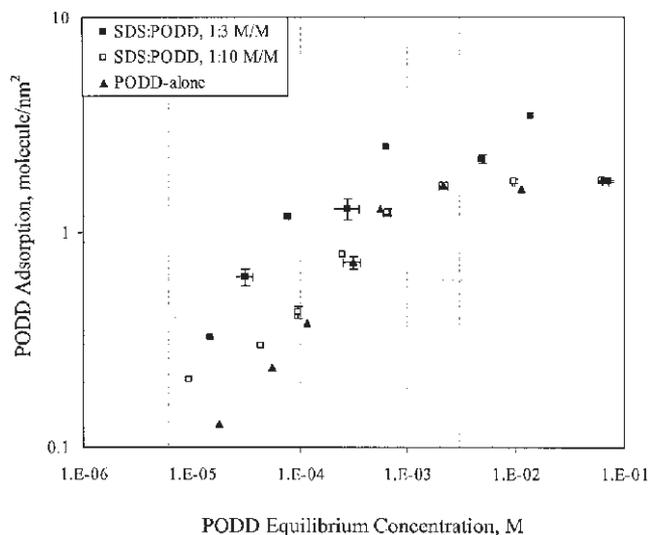
The solution for all experiments contained 0.01 M or 0.015 M NaCl to maintain a constant ionic strength for mixed SDS/PODD and mixed SHDPDS/DPCI systems, respectively. All of the experiments in this research were conducted in at least duplicate, and error bars of SD are plotted where appropriate.

**Methods.** (i) *Adsorption experiments.* The adsorption of SDS and PODD was evaluated individually and in mixtures (initial ratios 1:3 and 1:10, cationic-rich) at various initial concentrations in 40-mL vials. The vials were shaken for 2 d to reach equilibrium at  $25 \pm 1^\circ\text{C}$ . The pH of the solution was checked and adjusted in the range of 6 to 7 by using NaOH and HCl solutions; if pH adjustment was required, the vials were shaken again for 1 d. Five milliliters of the supernatant sample was taken from each vial after centrifuging at  $500\text{--}700 \times g$  for 30 min. The samples were subsequently measured for both anionic and cationic surfactants by high-performance liquid chromatography. The surfactant adsorption was calculated according to Equation 1. A similar procedure was used for SHDPDS and DPCI, individually and for SHDPDS/DPCI mixtures at ratios of 3:1, 10:1, 30:1, anionic-rich.

(ii) *Precipitation studies of SDS and PODD.* In studying their precipitation, surfactant systems were prepared in 20-mL vials with Teflon-lined caps, with either 0.01 or 0.15 M NaCl (the latter for comparison with data from previous research). The solutions were supercooled at  $0^\circ\text{C}$  for 2 d to prevent supersaturation effects. The samples were then placed in a water bath shaker at constant temperature ( $30.0 \pm 0.1^\circ\text{C}$ ) for 4 d. The precipitation phase boundaries were determined by visual inspection according to the procedure described by Stellner *et al.* (20).

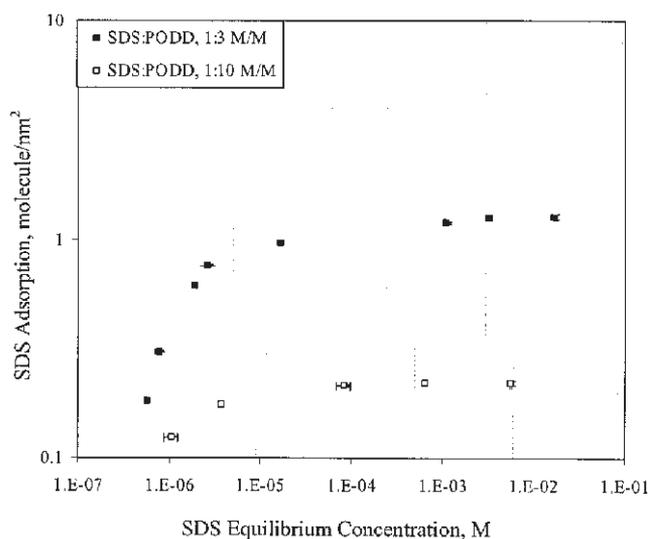
## RESULTS AND DISCUSSION

*Adsorption experiments.* The adsorption isotherms for PODD and SDS individually and SDS/PODD mixtures on silica are shown in Figures 3–5, respectively (in 0.01 M NaCl at  $25^\circ\text{C}$ ). Adsorption experiments of SDS/PODD were evaluated at initial ratios of 1:3 and 1:10, whereas SHDPDS/DPCI adsorption was studied at initial ratios of 3:1, 10:1, and 30:1 (in 0.015 M NaCl at  $25^\circ\text{C}$ ); these ratios were selected to avoid precipitation, as documented in the next section of this paper. Analytical detection limits prevented measurement of surfactant concentrations in Region I and rendered the distinction between Regions II and III difficult at best (see Fig. 3). Selected points were measured in triplicate to

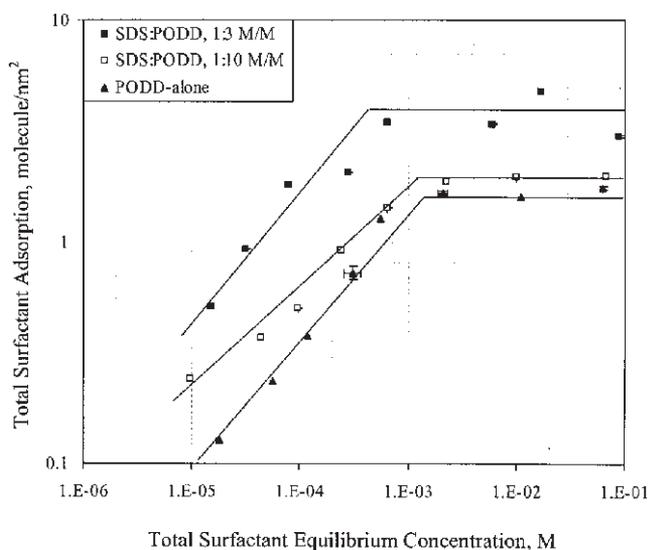


**FIG. 3.** Adsorption of the cationic surfactant pentamethyl-octadecyl-1,3-propanediammonium dichloride (PODD) onto silica for PODD alone and PODD mixed with sodium dodecyl sulfate (SDS) (0.01 M NaCl,  $25^\circ\text{C}$ ).

assess the magnitude of the experimental precision; the resulting error bars proved to be similar in magnitude to the size of the data symbols ( $\pm 4\text{--}7\%$ ). For PODD concentrations greater than  $1 \times 10^{-4}$  M, the adsorption of PODD is virtually the same when using PODD alone or at an initial ratio of 1:10 SDS/PODD; thus, adding a small concentration of SDS did not significantly affect the adsorption of PODD. However, when using an initial SDS/PODD ratio of 1:3, a measurable increase in the total adsorption was observed over the PODD alone; thus, a minimum amount of the oppositely charged surfactant (SDS) is necessary to reduce the charge repulsion between adjacent surfactant molecules



**FIG. 4.** Anionic surfactant (SDS) adsorption onto silica for mixed SDS/PODD system (0.01 M NaCl,  $25^\circ\text{C}$ ). Note: SDS-alone adsorption on silica was negligible. For abbreviations see Figure 3.



**FIG. 5.** Total surfactant (SDS and PODD) adsorption onto silica for PODD-alone and mixed SDS/PODD system (0.01 M NaCl, 25°C). Note: SDS-alone adsorption on silica was negligible. For abbreviations see Figure 3.

(PODD) and thus increase the adsorption density of the PODD, as demonstrated in previous research (21).

Figure 4 shows SDS adsorption on silica when SDS coexists with PODD. Data for SDS alone are not shown because SDS adsorption was negligible on silica, as expected since both the SDS and silica are negatively charged at neutral pH [silica is reported to have a point of zero charge of 2–4 (22)]. However, SDS co-adsorbs when present with PODD and shows increased adsorption at higher initial surfactant ratios (SDS/PODD, 1:10 and 1:3).

Figure 5 presents the total surfactant adsorption isotherms (PODD plus SDS). An initial SDS/PODD ratio of 1:10 has only a minor effect on the adsorption isotherm, but a stronger adsorption synergism is observed at an initial ratio of 1:3, as evidenced by both higher plateau adsorption (4.0 vs. 1.8 molecule/nm<sup>2</sup>—see Table 2) and attainment of that plateau adsorption at a lower surfactant concentration (0.60 vs. 2.3 mM). The fact that the plateau adsorption occurs at a

lower surfactant concentration is expected from the lower CMC of mixed anionic-cationic surfactant systems.

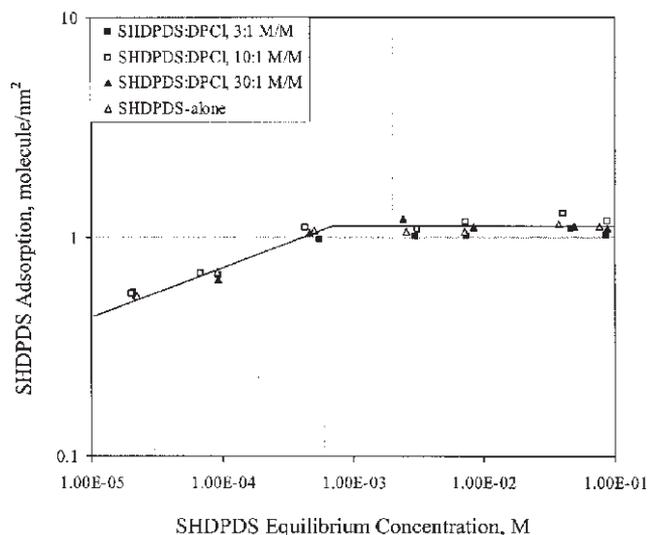
Figures 6–8 show surfactant adsorption on alumina for SHDPDS, DPCL, and combined SHDPDS/DPCL, respectively. Another relevant characteristic of the curves in Figure 6 is that the addition of the cationic surfactant DPCL did not significantly affect the adsorption of SHDPDS, even when present at ratios as high as 3:1. The reason for the lack of SHDPDS adsorption synergism is unclear, but the extreme reduction in the precipitation region for SHDPDS (see below) suggests steric hindrances that may also limit synergism in adsorption. In Figure 7, DPCL adsorption results are only shown for the ratio of 3:1 and 10:1 because the ratio of 30:1 showed insignificant adsorption (less than 0.1 molecule/nm<sup>2</sup>). It is interesting to note that, even though SHDPDS did not show enhanced adsorption in the presence of the DPCL, the DPCL did co-adsorb with SHDPDS, as SDS did in mixtures with PODD above. Thus, whereas the surfactant adsorption itself did not show significant synergism, the co-adsorption of DPCL with SHDPDS may still alter the properties of the adsorbed layer.

*Precipitation studies.* Although adsorption studies were the focus of this research, precipitation studies were conducted to ensure we evaluated adsorption outside the precipitation region. Nonetheless, while not comprehensive, the precipitation studies do provide some valuable insights that are worthy of discussion. Figure 9 shows the precipitation phase diagrams for the SDS/PODD system with NaCl concentration of 0.01 and 0.15 M and for 25 vs. 30°C, respectively. At 0.15 M NaCl and 30°C, the SDS/PODD system did not exhibit precipitation, and there was only a very small region of liquid crystal formation; this region did not exist at 25°C. This is in contrast to the precipitation region observed for SDS/PODD at the lower salt concentration of 0.01 M and 25°C, and the much larger precipitation regime for SDS/DPCL at 0.15 M NaCl and 30°C. In the SDS/DPCL system, both anionic and cationic surfactants have linear hydrophobic groups of the same length (12 carbons), and we refer to this system as symmetric-linear. Two characteristics of PODD are relevant: It is branched in the hydrophobe and it has two cationic head groups, so the SDS/PODD sys-

**TABLE 2**  
Adsorption of Mixed and Single Surfactant Systems

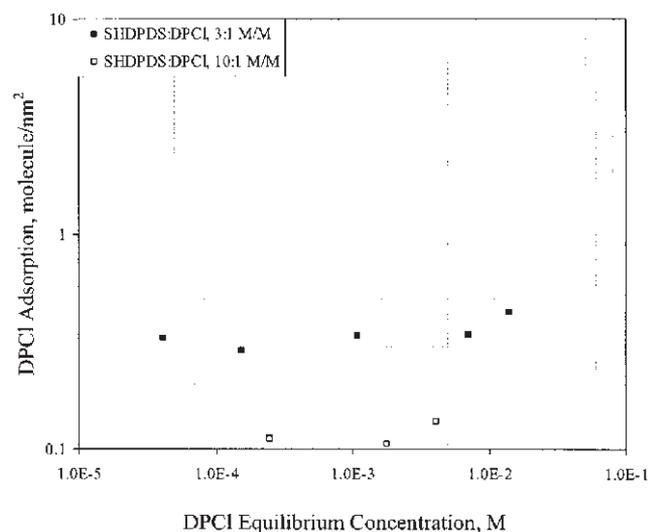
Medium	Structure, initial concentration ratio	Plateau adsorption								
		Cationic surfactant			Anionic surfactant			Total surfactant		
		molecules/nm <sup>2</sup>	nm <sup>2</sup> /molecule	mol/g	molecules/nm <sup>2</sup>	nm <sup>2</sup> /molecule	mol/g	molecules/nm <sup>2</sup>	nm <sup>2</sup> /molecule	mol/g
Silica	SDS/PODD, 1:3	2.8	0.36	6.6 × 10 <sup>-4</sup>	1.2	0.8	2.8 × 10 <sup>-4</sup>	4.0	0.25	9.5 × 10 <sup>-4</sup>
	SDS/PODD, 1:10	1.9	0.53	4.5 × 10 <sup>-4</sup>	0.20	5.0	4.7 × 10 <sup>-5</sup>	2.1	0.48	5.0 × 10 <sup>-4</sup>
	PODD alone	1.8	0.56	4.3 × 10 <sup>-4</sup>	NA <sup>a</sup>	NA	NA	1.8	0.56	4.3 × 10 <sup>-4</sup>
Alumina	SHDPDS/DPCL, 3:1	0.36	2.8	7.3 × 10 <sup>-5</sup>	1.0	1.0	2.0 × 10 <sup>-4</sup>	1.4	0.74	2.8 × 10 <sup>-4</sup>
	SHDPDS/DPCL, 10:1	0.13	7.7	2.6 × 10 <sup>-5</sup>	1.1	0.88	2.3 × 10 <sup>-4</sup>	1.3	0.79	2.6 × 10 <sup>-4</sup>
	SHDPDS/DPCL, 30:1	0.05	20.0	1.0 × 10 <sup>-5</sup>	1.1	0.91	2.2 × 10 <sup>-4</sup>	1.2	0.87	2.3 × 10 <sup>-4</sup>
	SHDPDS alone	NA	NA	NA	1.1	0.92	2.2 × 10 <sup>-4</sup>	1.1	0.92	2.2 × 10 <sup>-4</sup>

<sup>a</sup>The adsorption of like-charged surfactant alone and media was below detection limits. NA, not applicable; for other abbreviations see Table 1.

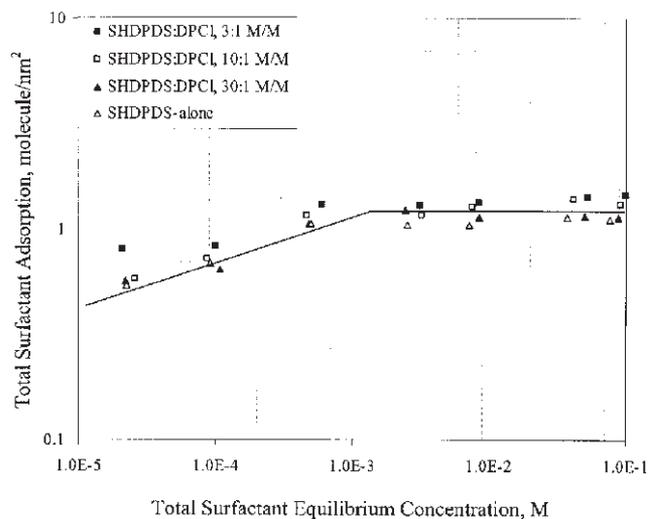


**FIG. 6.** Anionic surfactant (SHDPDS) adsorption onto alumina for mixed SHDPDS/DPCI system (0.015 M NaCl, 25°C). For abbreviations see Figure 2.

tem is both asymmetric and nonlinear. In previous work, as shown in Figure 2, we used a branched monovalent anionic surfactant (SDHS) or a branched divalent anionic surfactant (SHDPDS) with a linear cationic surfactant (DPCI). Below the CMC, the SHDPDS/DPCI system has even less tendency to precipitate than the SDS/DPCI system, and the SDHS/DPCI system even less tendency to precipitate (compare Figs. 2 and 9). Precipitation phase boundaries for SDS/DPCI have been compared with these with smaller alkyl chains in the anionic surfactant ( $n = 8$  and 10 compared with 12) (23), and the tendency to precipitate below

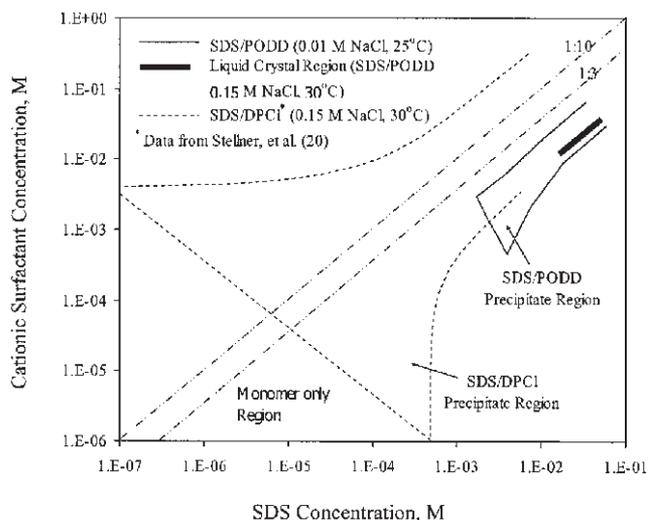


**FIG. 7.** Cationic surfactant (DPCI) adsorption onto alumina for mixed SHDPDS/DPCI system (0.015 M NaCl, 25°C). Note: Adsorption results for the initial ratio of 30:1 and for DPCI-alone are not shown because they were negligible. For abbreviations see Figure 2.



**FIG. 8.** Total surfactant (SHDPDS and DPCI) adsorption onto alumina for SHDPDS-alone and for mixed SHDPDS/DPCI systems (0.015 M NaCl, 25°C). For abbreviations see Figure 2.

the CMC is less as  $n$  decreases. It is not clear how much of this effect is due to the mismatch (asymmetry) between the alkyl chain lengths of the anionic and the cationic surfactant (24) and how much is due to the smaller size of the hydrophobe. There is a significant reduction in precipitation for the SDS/PODD system in Figure 9. Although we cannot attribute specific effects to alkyl chain branching, to asymmetry due to the dissimilar surfactant alkyl chain lengths, or to valency effects below the CMC, we can greatly reduce the precipitation with a model anionic surfactant by using a



**FIG. 9.** Precipitation diagram of asymmetric ionic head group mixed surfactant SDS/PODD at 0.01 M NaCl. [Data for the SDS/DPCI precipitation diagram from Stellner et al. (20) at 0.15 M NaCl are shown for comparison]. The lines labeled 1:10 and 1:3 correspond to constant 1:10 and 1:3 molar ratios of SDS/cationic surfactant, respectively, for varying surfactant concentrations. For abbreviations see Figures 2 and 3.

multiply charged, asymmetrically branched cationic surfactant.

Above the CMC, the tendency to precipitate is a consequence of two competing forces: the solubility product and the tendency to form micelles. These can lead to contrasting trends to those below the CMC. For example, above the CMC, the SDHS/DPCL system has a much broader precipitation region than SHDPDS/DPCL (Fig. 2) indicating that the branching of the anionic surfactant can reduce the tendency to form micelles more than the effect on the  $K_{sp}$ . For systems with varied alkyl chain lengths for alkyl sulfate/DPCL, the precipitation phase boundaries above the CMC are not greatly altered. For both the SHDPDS/DPCL system in Figure 2 and the SDS/PODD system in Figure 9, the precipitation region above the CMC is considerably less than for the SDS/DPCL system. Therefore, while the nuances of the effect of surfactant structure on precipitation are not totally clear, it appears that using either anionic or cationic surfactants with multiple charges tends to shrink the precipitation phase boundary greatly above the CMC.

It should be noted that in Figure 9 we include data from Stellner *et al.* (20) for SDS/DPCL; those experiments were conducted at 0.15 M NaCl whereas the present work with SDS/PODD was carried out at 0.01 M NaCl. The additional NaCl in the experiments of Stellner *et al.* with the SDS/DPCL system will tend to lower the CMC for this system and thus shrink the precipitation regime; nonetheless, the SDS/DPCL system still demonstrates a much larger precipitation diagram than the SDS/PODD system. The smaller size of the precipitation region allows the formulation of systems with ratios that more closely approach equimolar concentrations, where the maximal synergism is typically observed for anionic and cationic mixtures. As an example, for 1 mM PODD, as much as 3 mM SDS can be added without precipitation, but for the SDHS/DPCL system at 1 mM of DPCL, the addition of 3 mM of SDS results in precipitation (see Fig. 9).

Based on the precipitation data in Figure 9, adsorption experiments of SDS/PODD were evaluated at initial ratios of 1:3 and 1:10, while SHDPDS/DPCL adsorption was studied at initial ratios of 3:1, 10:1, and 30:1, respectively, in order to avoid precipitation. Although the precipitation work is at 30°C and the adsorption data are at 25°C, the adsorption studies are carried out far enough from the precipitation boundaries to render this difference insignificant.

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