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Influence of Solvents on Adsorption of Ionic Surfactants on Highly Dispersed Silicas

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Abstract □ The adsorption of cationic and anionic surfactants on three hydrophilic silicas and one hydrophobic (methylated) colloidal silica was studied in the presence of organic solvents. Cationic surfactants (alkylpyridinium chlorides and alkyltrimethylammonium chlorides) are strongly bound by hydrophilic silicas in a weak polar solvent (CHCl_3). While pyridinium and ammonium as the head group have no marked influence upon adsorption, the hydrocarbon chain length (in the range C_4 – C_{10}) determines the surface areas occupied by adsorbed surfactant molecules. Homologs with longer hydrocarbon chains (C_{12} – C_{18}) all occupy equal areas in the saturated adsorption layer. Polar organic solvents (alcohols) reduce the adsorption of cationic surfactants on hydrophilic silicas. In the presence of dimethyl sulfoxide, no adsorption is observed. Maximum adsorption of dioctyl sodium sulfosuccinate is attained in the presence of carbon tetrachloride. Solvents with hydrogen-bonding abilities (dimethyl sulfoxide and dioxane) prevent adsorption of anionic surfactants (dioctyl sodium sulfosuccinate and sodium alkyl sulfates). It is suggested that the silanol groups on the surface, which are capable of hydrogen bonding and electrostatic interactions, are the active adsorption sites of the silica. If their number is reduced, the adsorption is diminished to the same extent.

Keyphrases □ Adsorption of ionic surfactants on highly dispersed silicas—solvent effect □ Silicas, highly dispersed—solvent effect on adsorption of ionic surfactants □ Surfactants, ionic, adsorption on silicas—solvent effect □ Solvent effect—adsorption of ionic surfactants on highly dispersed silicas

Flame-hydrolyzed colloidal silicas¹ and ionic surfactants are widely used as important agents in pharmaceutical preparations. Interactions between these substances may influence the stability, the colloidal chemical behavior, and the drug release from dosage forms. Striking effects on these properties result from

Table I—Silicas under Investigation

Hydrophilic Silicas	BET Surface ^a , m. ² /g.
Silica A ^b	234
Silica B ^c	129
Silica C ^d	58
Hydrophobic silica	
Silica D ^e	79

^a The surface measurements were carried out after drying the samples at 120°, 10⁻³ torr for 10 hr. by N₂ adsorption after the method of Brunauer, Emmett, and Teller. ^b Aerosil 200. ^c Aerosil 130. ^d Aerosil Ox 50. ^e Aerosil R 972.

the adsorption of surface-active substances on colloidal silica in aqueous media (1–3).

However, there is no detailed information concerning the adsorption of ionic surfactants in nonaqueous media (4, 5). In this study, some organic liquids were chosen as models to elucidate the interactions between modified silica surfaces and ionic detergents in the presence of organic solvents with different polarity.

MATERIALS

Solvents used were of analytical grade and stored over molecular sieve (4 Å): dimethyl sulfoxide, methanol, ethanol, isopropanol, *n*-butanol, dioxane, chloroform, and carbon tetrachloride. Dioctyl sodium sulfosuccinate came from a commercial source².

Alkylpyridinium salts³, with the chain length from C₁₀ to C₁₈, were recrystallized in ethyl acetate. The homologs from C₄ to C₈ were prepared by reaction of the corresponding alkyl chlorides with

¹ Aerosils.

² E. Merck, Darmstadt, W. Germany.

³ Obtained from Henkel & Cie, Duesseldorf, W. Germany.

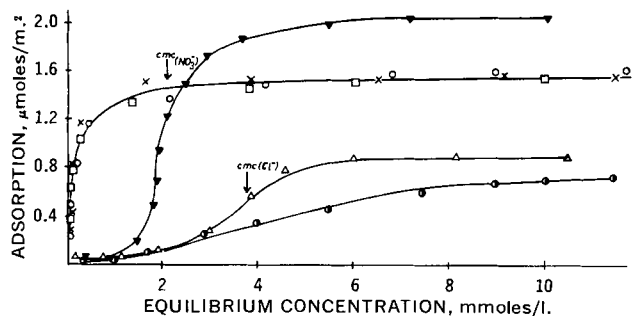


Figure 1—Adsorption of cationic surfactants on silica A in water, chloroform, and isopropanol. Key: Δ , tetradecylpyridinium chloride in water; ∇ , tetradecylpyridinium nitrate in water; \times , tetradecylpyridinium chloride in chloroform; \circ , tetradecylpyridinium nitrate in chloroform; \bullet , tetradecylpyridinium chloride in isopropanol; and \square , hexadecyltrimethylammonium chloride in chloroform. The arrows mark the corresponding CMC of the surfactants in water.

pyridine and recrystallized in acetone-ethyl acetate. Alkyl sulfates (C_{12} - C_{16}) were also used⁴. Silicas⁵ under investigation are listed in Table I.

EXPERIMENTAL

To exclude water vapor from silicas (after drying at 120° , 10^{-3} torr), solutions, and solvents, all processes were carried out in a dry box with an N_2 atmosphere (dried by P_2O_5). For the adsorption isotherms, a concentration range of the surfactants between 1×10^{-4} and 2.5×10^{-2} mole/l. was provided. To get the single initial concentration of the surfactants, the procedure was as follows.

Silica, 0.5 g., was placed in a stainless steel tube of an ultracentrifuge⁶. An aliquot of stock solution of the surfactant (2.5×10^{-2} mole/l.) was then added, and the volume was adjusted with pure solvent to 50.0 ml. The well-closed tubes were shaken for 12 hr. at $20 \pm 0.1^\circ$. After centrifugation at 15,000 r.p.m. for 30 min., the unadsorbed amounts of the solute were determined from aliquots of the supernatant liquids. Dioctyl sodium sulfosuccinate and the alkyl sulfates were measured by a two-phase titration according to Carkhuff and Boyd (6). The concentration of alkylpyridinium homologs was monitored by UV spectrophotometry⁷.

RESULTS

Cationic Surfactants—Cationic surfactants are strongly adsorbed in chloroform by hydrophilic silica A⁸ (Fig. 1). In this weak polar solvent, adsorption of tetradecylpyridinium chloride, tetradecylpyridinium nitrate, and hexadecyltrimethylammonium chloride can be expressed by one adsorption isotherm. This is in contrast to aqueous media, where a sudden rise in the region of the CMC characterizes the adsorption isotherms of cationic surfactants on colloidal silica (7). The plateau regions of the isotherms indicate saturation of adsorption or "limited adsorption" (8) at the silica surface.

By assuming formation of monolayers, the capacities of the adsorption layer and the areas per adsorbed molecule can be calculated. The differences in the cationic head groups have no remarkable effect upon adsorption. There is, however, a relation between the hydrocarbon chain length of the hydrophobic part in the surfactant molecules and the corresponding saturation values of adsorption: in the homologous series of alkylpyridinium chlorides, the surface area per molecule of surfactant increases linearly with the hydrocarbon chain length from C_4 to C_{10} (Fig. 2). The alkylpyridinium chlorides with longer nonpolar chains (C_{10} - C_{18}) all show the same saturation value of $1.5 \mu\text{moles/m}^2$ for the adsorption layer. Thus, it may be concluded that there is no further increase in surface area occupied by adsorbed surfactant molecules with hydrocarbon chains longer than C_{10} .

⁴ Obtained from Dehdag, Duesseldorf, W. Germany.

⁵ Obtained from Degussa, Frankfurt am Main, W. Germany.

⁶ Beckman Spinco.

⁷ With a Zeiss PQMII.

⁸ Aerosil 200.

Table II—Saturation Values of Adsorption of Surfactants on Silica D in the Presence of Organic Dispersants

	Dispersant				
	CCl_4	$CHCl_3$	Di-oxane	Bu-tanol	Di-methyl Sulf-oxide
Dioctyl sodium sulfosuccinate adsorbed, $\mu\text{moles/m}^2$	0.011	0.009	— ^a	— ^a	— ^a
Tetradecylpyridinium chloride adsorbed, $\mu\text{moles/m}^2$	Insoluble	0.23	0.05	0.04	— ^a

^a Adsorption levels are below the sensitivity of the analytical method.

While the surfactants show differences in the adsorption pattern, the hydrophilic silica samples A, B, and C (Table I) are characterized by the same adsorption capacity per surface unit (m^2). With the hydrophobic silica D (Table I), the adsorption of cationic surfactants is restricted to $0.23 \mu\text{mole/m}^2$. This methylated surface (3) has only 15% of the adsorption capacity in comparison to the hydrophilic silica surfaces (on the basis of surface unit) (Table II).

Polar organic solvents reduce the adsorption of cationic detergents on hydrophilic colloidal silicas (Table III). In alcoholic media, the adsorption of tetradecylpyridinium chloride is reduced from $1.11 \mu\text{moles/m}^2$ in butanol to $0.02 \mu\text{mole/m}^2$ in methanol. Adsorption in the presence of dimethyl sulfoxide is below the range of analytical accuracy.

Anionic Surfactants—The anionic surfactant dioctyl sodium sulfosuccinate is strongly bound by hydrophilic silica A in the presence of the nonpolar carbon tetrachloride (Fig. 3). Saturation on the silica surface is obtained at $2.1 \mu\text{moles/m}^2$. In chloroform as dispersant the adsorption capacity is reduced to $0.94 \mu\text{mole/m}^2$. In butanol the maximum adsorption is reduced to $0.04 \mu\text{mole/m}^2$; in dioxane, ethanol, and dimethyl sulfoxide, no adsorption is observed. Alkyl sulfates with hydrocarbon chains from C_{12} to C_{16} are not adsorbed by hydrophilic silica in alcohols, dioxane, and dimethyl sulfoxide. On hydrophobic silica D the adsorption of dioctyl sodium sulfosuccinate is very low in organic liquids. For example, the saturation value in chloroform is limited to $0.009 \mu\text{mole/m}^2$, while polar solvents prevent the adsorption totally (Table II).

DISCUSSION

The adsorption of ionic detergents on highly dispersed silica surfaces is controlled by interactions between surface adsorption sites—the silanol groups—(3) and solute and solvent molecules. If the solute and the solvent molecules possess polar groups, which are, for example, capable of hydrogen bonding with the silanol groups, they compete for these adsorption sites. In the surfactant solutions under investigation, the solvent molecules are in great excess of those of the solute. Thus, it appears that the adsorption of the detergent will be suppressed if the interactions of the solvent and the solute with the surface are of the same magnitude in this respect. This can be observed with dioctyl sodium sulfosuccinate in

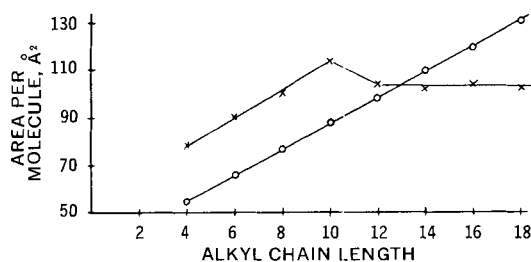


Figure 2—Areas occupied by adsorbed alkylpyridinium chloride molecules on the surface of silica A. Key: \circ , theoretical values, assuming flat, close-packed monolayers; and \times , experimental values, derived from maximum amounts of adsorption.

Table III—Saturation Values of Adsorption of Tetradecylpyridinium Chloride on Hydrophilic Silica A in the Presence of Various Solvents

	Solvents						
	Dimethyl Sulfoxide	Methanol	Ethanol	Isopropanol	Butanol	Chloroform	Water
Surfactant adsorbed $\mu\text{moles/g.}$	0.1	5	100	200	260	318	220
$\mu\text{moles/m.}^2$	0.004	0.02	0.428	0.865	1.11	1.39	0.9
Area per molecule, \AA^2	—	(9000)	—	190	150	123	—

dimethyl sulfoxide and dioxane, where adsorption of the detergent is below analytical sensitivity. Adsorption of dioctyl sodium sulfosuccinate becomes effective only in weak polar solvents like carbon tetrachloride (9). White (10) found that the adsorption of this solvent (CCl_4) on silica is due to weak dispersion forces. Therefore, the solvent molecules can be easily displaced by the solute. The adsorption isotherm indicates a saturation value of $2.1 \mu\text{moles/m.}^2$ corresponding to an area of $79.5 \text{\AA}^2/\text{molecule}$ dioctyl sodium sulfosuccinate in the adsorption layer (Fig. 3). This value favors the view of a close packing in the monomolecular layer of the surfactant on the silica surface (11).

In chloroform dispersions, saturation (= limited adsorption) on hydrophilic silicas is obtained at $0.94 \mu\text{mole/m.}^2$ for dioctyl sodium sulfosuccinate. The corresponding area of a dioctyl sodium sulfosuccinate molecule in the adsorption layer is 177\AA^2 . This value cannot be attributed to the saturation of the fixed number of adsorption sites on the silica surface (3) nor to a close packing of dioctyl sodium sulfosuccinate molecules comparable with the arrangement in adsorption layers on other sorbents (11).

The loose packing of dioctyl sodium sulfosuccinate in the surface phase in chloroform dispersions may be caused by an incomplete displacement of solvent molecules on the one hand and solvation effects around the adsorbed molecules on the other hand. This view is confirmed by the well-recognized hydrogen-bonding properties of chloroform (12), the high solubility of dioctyl sodium sulfosuccinate in chloroform, and the difference between the heats of solution of the surfactants with respect to carbon tetrachloride⁹.

The adsorption of cationic surfactants on hydrophilic silicas in organic liquids is induced by Coulombic forces between the silica surface and the polar head groups of the organic cations, which are part of solvated ion pairs in solution (13). As in the case of dioctyl sodium sulfosuccinate, solvation effects around the surfactant molecules and competition for adsorption sites on the silica control the adsorption process.

The arrangement of the surfactant molecules in the adsorption phase may be discussed using two models:

1. Surfactant molecules lying flat on the silica surface. Assuming an orientation of the molecules with their hydrocarbon chains parallel to the surface, the area per molecule in the adsorption layer should increase linearly with the hydrocarbon chain length.

2. Surfactant molecules oriented perpendicularly to the surface, thus occupying the same area per molecule for all of the homologs.

Experimental data for alkylpyridinium chlorides with hydrocarbon chains from C_4 to C_{10} —increasing surface area per molecule

with increasing chain length—support the view of flat-lying surfactant molecules. However, the experimental surface areas per homologous molecules are 25\AA^2 higher than expected from close-packed monolayers. This may be caused by solvent adsorption on the silica and by solvation effects around the adsorbed surfactant molecules.

The apparent surface areas of alkylpyridinium chlorides with chains longer than C_{10} show no further increase with increasing chain length. This favors the view of a perpendicular orientation in the adsorption layer. Moreover, interactions by van der Waals' forces come into play in an adsorption layer where long hydrocarbon chains ($>\text{C}_{10}$) are parallel to each other. Therefore, the adsorption of alkylpyridinium chlorides in the presence of chloroform may be caused by a dynamic equilibrium between these two states of adsorption, with the longer species preferring a perpendicular orientation.

Solvents with strong hydrogen-bonding abilities diminish the adsorption of cationic surfactants on hydrophilic silicas (Table III). In this respect, water is an exception, because in aqueous systems hydrophobic bonding determines the adsorption behavior (14).

The surface of the hydrophobic silica D, where about 80% of the surface hydroxyls are methylated, is a weak adsorbent for surfactant molecules in organic liquids. The results indicate (Table II) that the residual silanol groups interact mainly by electrostatic forces (with cationic surfactants), while hydrogen bonding is almost completely reduced (dioctyl sodium sulfosuccinate).

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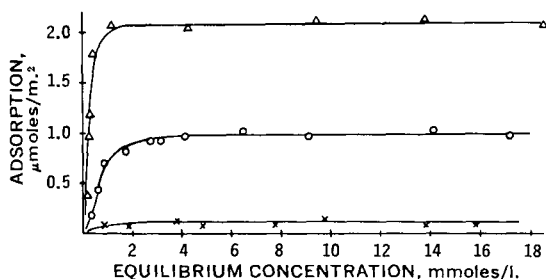


Figure 3—Adsorption of dioctyl sodium sulfosuccinate on silica A in organic solvents. Key: \times , n-butanol; \circ , chloroform; and Δ , carbon tetrachloride.

⁹ Difference in the heat of solution for dioctyl sodium sulfosuccinate in chloroform and carbon tetrachloride, evaluated by adiabatic calorimeter at 20° :

$$\Delta H_{\text{CCl}_4} - \Delta H_{\text{CHCl}_3} = -1.8 \text{ kcal./mole}$$