

CCA-752

541.183.2:661.185
Conference Paper

Sulfonate Adsorption and Wetting Behavior at Solid—Water Interfaces*

K. Osseo-Asare and D. W. Fuerstenau

Department of Materials Science and Engineering, University of California,
Berkeley, California 94720, U. S. A.

Received November 20, 1972

The electrophoretic mobilities of silver iodide sol particles have been measured as a function of pAg in the presence of various concentrations of C_5 , C_8 , C_{10} , C_{12} and C_{14} sodium alkyl sulfonates at constant ionic strength and temperature. Contact angles in the solid-air-solution system both in the absence and in the presence of the C_{14} sulfonate have also been determined. These results have been compared with previously reported work on the effect of alkyl sulfonates on the electrokinetic and wetting behavior of alumina. Application of the Stern-Grahame model of the electrical double layer allows delineation of the various mechanisms contributing to the adsorption phenomena. In the case of the alumina-sulfonate system the adsorption process is purely physical, *viz.* electrostatic and hydrocarbon chain-chain interactions, while for the AgI -sulfonate system both physical and chemical processes are involved, *viz.* electrostatic, hydrocarbon chain-solid, chain-chain, and solid-polar head interactions.

INTRODUCTION

Adsorption phenomena at solid—water interfaces are dependent on the physico-chemical properties of the adsorbing species, the composition of the aqueous solution and the nature of the solid. The adsorption behavior of a surfactant results essentially from its amphipathic nature, namely the presence in the same species of both polar (the headgroup) and non-polar (the hydrophobic chain) character. The nature, of the polar head on the adsorbing ion or molecule determines whether there is any coulombic or chemical interaction with the solid, while the structure of the hydrocarbon chain controls the extent of the interaction of the species with the aqueous medium. The nature of the solid may enter into the adsorption process in a number of different ways. Chemisorption may result if there is direct chemical reaction between the adsorbing species and metal ions in the surface. If the surfactant is ionic, the electrical double layer at the interface may significantly affect adsorption, and the concentration of potential-determining ions in the aqueous solution then controls adsorption because these ions determine the sign and magnitude of the surface charge. In terms of wettability, surfaces such as those of oxides and the salt-type minerals are basically hydrophilic while others such as graphite and polyethylene are hydrophobic. In general, a given material may exhibit both hydrophobic and hydrophilic characteristics, with

* Based on a lecture presented at the *III International Summer School on the Chemistry of Solid/Liquid Interfaces*, Rovinj, Yugoslavia, July 1—5, 1972.

the result being that the adsorption of surfactants at the solid—water interface may involve a complex interplay of electrostatic, chemical and hydrophobic interactions.

This paper is a contribution to the study of the inter-relationship between these various interactions. New results on the effect of alkyl sulfonates on the electrokinetic and wetting behavior of silver iodide are presented and these are compared with previous results for the alkyl sulfonate-alumina system¹⁻³.

Background

Hydrogen and hydroxyl ions are potential-determining ions for oxides, such as alumina. Somasundaran¹ has clearly demonstrated that adsorption of alkyl sulfonates only occurs at pH values less than 9, the point of zero charge (pzc), *i. e.* under conditions when the solid surface is positively charged. Further, infrared spectroscopy shows no evidence of chemical bond formation between sulfonate ions and the alumina surface. The adsorption process has been satisfactorily analyzed in terms of electrostatic interaction between the alkyl sulfonate ions and the positively charged alumina surface coupled with chain-chain (hemimicelle) interactions at high surfactant concentrations^{1,2}. The contact angle of alumina in water is found to be zero³ and thus the hydrophilic nature of the solid rules out the possibility of chain-solid interactions. In contrast to alumina, silver iodide is recognized to be partially hydrophobic⁴⁻⁶; Billett and Ottewill⁶ observed advancing contact angles as large as 47° on AgI in water. It will therefore be expected that chain-solid interactions should play a prominent role in this system. The potential-determining ions for AgI are Ag⁺ and I⁻ with the pzc occurring at pAg 5.5. In this system, pAg rather than pH is the most important variable. At pI 5 (pAg 11), Pravdić and Mirnik⁷ found that C₈ and C₆ amines reverse the zeta potential of negatively charged AgI. This can be interpreted in terms of hydrophobic bonding of the chains with the solid surface. The results of Ottewill and Watanabe⁸ clearly show that even at low concentrations, sodium dodecyl sulfate and sulfonate have a marked effect on the zeta potential of silver iodide. In addition, it now appears that the AgI surface may exhibit some chemisorption. Recent electron-micrographs indicate that a new chemical compound is created at the AgI surface when alkyl pyridinium bromides adsorb on silver iodide⁹. Thus, in the AgI system, adsorption may be affected by electrostatic, chemical, and hydrophobic bonding phenomena.

EXPERIMENTAL

Alumina-sulfonate system. — Details about the material characterization and experimental techniques of the alumina-alkyl sulfonate system are available in previous publications¹⁻³. The specific surface of the alpha alumina particles (Linde A alumina) is 14 m² per gram, giving an average diameter in the range of 10⁻⁵ cm. All measurements were conducted at 25° C and 2 × 10⁻³ M NaCl ionic strength, pH being adjusted with HCl or NaOH.

Silver iodide-sulfonate system. — Silver nitrate and potassium iodide of A. R. grade were used to prepare the AgI sol. For making AgI slides iodine was obtained as resublimed crystals from Mallinckrodt and silver wire of 99.5 to 99.8% purity was obtained from Sargent-Welch. The sodium salts of C₁₄, C₁₂, C₁₀ and C₈ sulfonic acids were supplied by Aldrich Chemical Co. while the C₅ salt was obtained from K & K Laboratories.

For the electrophoresis studies, a stock sol was prepared by adding 50 ml of 10⁻² M KI solution to an equal volume of 10⁻² M AgNO₃ solution with stirring. This was further aged in the dark for 12 to 18 hours. The final sol used for electro-

phoresis studies always contained 10^{-4} M AgI, with 10^{-3} M KNO_3 to control the ionic strength. The mobility measurements were conducted using the Riddick Zetameter¹⁰, a product of Zetameter Inc., New York.

The controlled ionic strength of 10^{-3} M KNO_3 gave a Debye-Huckel reciprocal length $1/\kappa$ of 95 Å. The average diameter of the particles, $2a$, was found by electron-microscopy to be 200 Å; consequently $\kappa a = 1$. Using the results of Wiersema *et al.*¹¹, for $\kappa a = 1$, (provided an error of 2.5 mV in the zeta potentials is tolerable), the conversion from mobilities to zeta potentials can be expressed as

$$U_e = 0.049 \zeta \quad (1)$$

where ζ is the zeta potential in millivolts and U_e is the electrophoretic mobility in micron/sec per volt/cm.

Following the method of Billett and Ottewill⁶, thin films of AgI were prepared by evaporating silver onto glass microscope slides under vacuum ($\sim 5 \times 10^{-6}$ torr). From the vacuum evaporator, the silver mirrors were quickly immersed in a 0.0025 N solution of iodine in 0.01 M KI solution for 20 to 30 seconds. The films were then aged in 10^{-4} M KI solution for 1.5 hours and kept under distilled water until used. The captive bubble technique⁶ was used to measure the contact angles. The AgI-plated slide was kept in the solution to be studied for about 15 minutes before taking measurements. An air bubble was placed on the film surface by a gentle increase in pressure, then after sitting on the film for about 15 seconds, it was given an additional increase in pressure. This yields the receding angle, θ_R . The pressure was then released until the contact boundary on the plate just moved, and the resulting angle was designated θ_A , the advancing angle.

All experiments were conducted at $20^\circ\text{C} \pm 2^\circ\text{C}$ and the water used for the solutions was triply distilled, the final distillate being kept under purified nitrogen until used.

RESULTS

Electrophoresis

Fig. 1 represents the zeta potential of alumina as a function of pH in the presence of different amounts of sodium dodecyl sulfonate and at an ionic strength of 2×10^{-3} M controlled with KNO_3 . These results show that the zeta potential of alumina is essentially independent of the presence of surfactant above pH 9 (the pzc of alumina). With decreases in the pH, the zeta

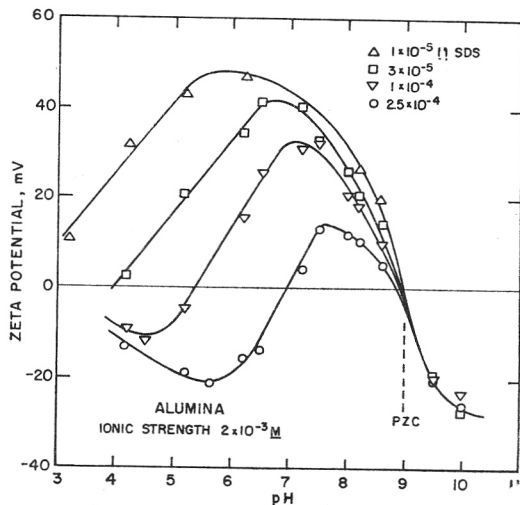


Fig. 1. The effect of pH on the zeta potential of alumina in the presence of sodium dodecyl sulfonate at 2×10^{-3} M ionic strength controlled with NaCl as the indifferent electrolyte¹⁵.

potential increases until a point is reached where the pH-zeta potential curve sharply reverses its slope. This point seems to be concentration dependent, occurring at lower pH values the lower the surfactant concentration. After the zeta potential has been reversed in sign upon further lowering of pH, there is another change in the slope of the curves. These same data are represented in a different way in Fig. 2 with the zeta potential plotted as a

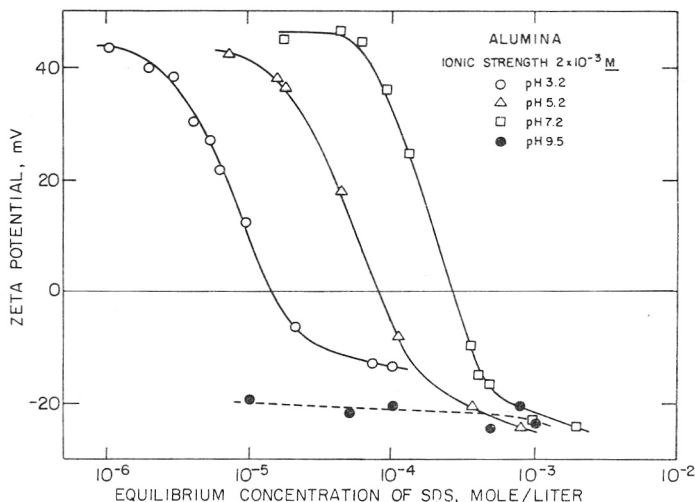


Fig. 2. The effect of the concentration of sodium dodecyl sulfonate on the zeta potential of alumina at various pH values¹⁵.

function of the concentration of dodecyl sulfonate at different pH values. At low pH's where the surface carries a high positive charge, alkyl sulfonate adsorption seems to have a marked effect on the zeta potential, and the higher the surface charge, *i. e.* lower pH, the lower the surfactant concentration required to reverse the zeta potential. However, when the pH exceeds the pzc, *e. g.* pH 9.5, increasing the surfactant concentration does not appear to affect the zeta potential significantly.

Fig. 3 shows the zeta potential of AgI as a function of pAg for various concentrations of tetradecyl sulfonate. On comparing these results with those given in Fig. 1, one finds a rather striking contrast to the alumina-dodecyl sulfonate system where the surfactant ions have little or no effect on the zeta potential once the pzc is reached. It can be seen in Fig. 3 that the pAg must be raised to about pAg 7, which is 1.5 units above the pzc, before the surfactant ions cease to have any effect on the zeta potential of AgI. It should be noted that all the curves appear to coincide in the neighborhood of pAg 7 independent of surfactant concentration. As the pAg is decreased below this point, the zeta potential increases and finally goes through a maximum, the higher the surfactant concentration, the higher the pAg at which this maximum occurs. Figs. 4 to 6 further show that the pAg at which the surfactant seems to lose its effect on the zeta potential of AgI is independent of chain length. These results show that even for a surfactant containing but 5 carbon atoms, an alkyl sulfonate is surface active on AgI. In contrast, alkyl sulfonates lose their surface activity on alumina² when the number of carbon atoms is less than

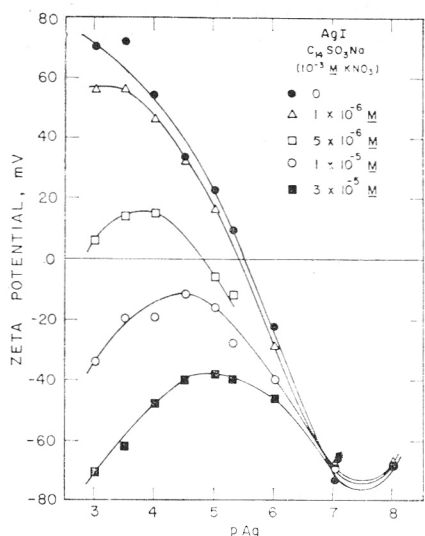


Fig. 3. The effect of pAg on the zeta potential of silver iodide in the presence of sodium tetradecyl sulfonate at 10^{-3} M ionic strength controlled with KNO_3 as the indifferent electrolyte.

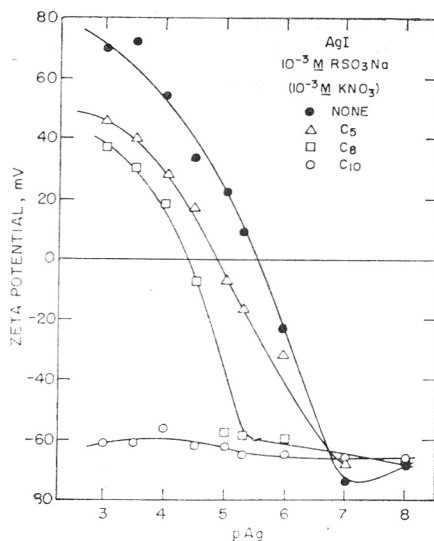


Fig. 4. The effect of pAg on the zeta potential of silver iodide in the presence of 10^{-3} M C_5 , C_8 and C_{10} sodium alkyl sulfonate.

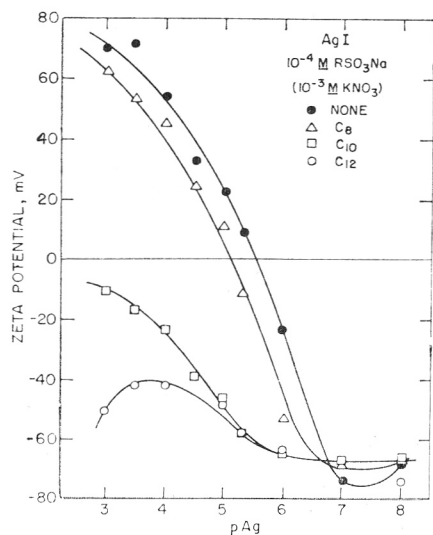


Fig. 5. The effect of pAg on the zeta potential of silver iodide in the presence of 10^{-4} M C_8 , C_{10} and C_{12} sodium alkyl sulfonate.

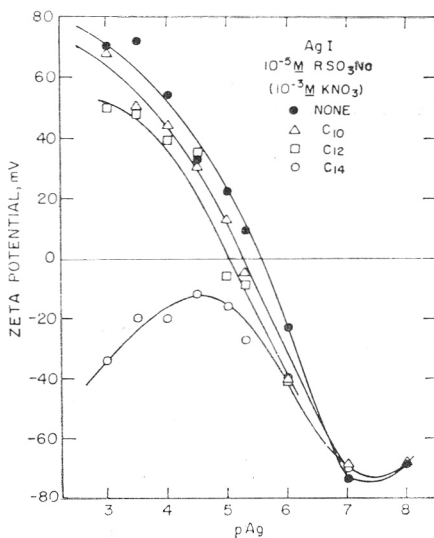


Fig. 6. The effect of pAg on the zeta potential of silver iodide in the presence of 10^{-5} M C_{10} , C_{12} and C_{14} sodium alkyl sulfonate.

10. The difference between the alumina and AgI systems is further illustrated by Fig. 7 where the zeta potential for AgI is plotted as a function of dodecyl sulfonate concentration at different pAg values. Contrary to what was observed

in the alumina system, it is seen here that the lower the pAg, *i. e.* the higher the surface charge, the higher the surfactant concentration required to reverse the zeta potential.

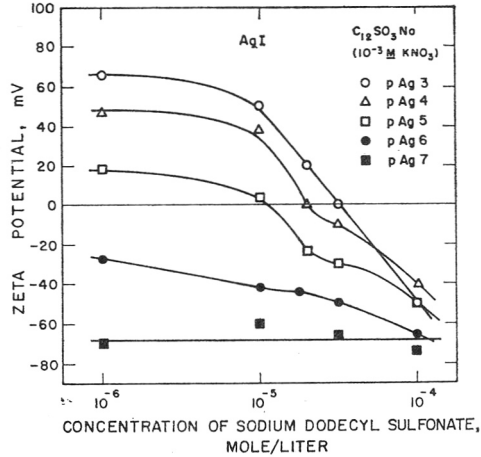


Fig. 7. The effect of the concentration of sodium dodecyl sulfonate on the zeta potential of silver iodide at various pAg values.

Wetting

The effect of dodecyl sulfonate on the »equilibrium« contact angles of alumina as a function of pH is illustrated in Fig. 8. (This angle is that of a free bubble on the surface and it approximates the receding angle on alumina³. At pH values above 9, the contact angle is zero, independent of surfactant concentration. Below pH 9, the contact angle increases steadily with pH, higher concentrations of surfactant resulting in larger angles, though at about pH 3 a leveling off of the contact angle at about 80 degrees is discernible.

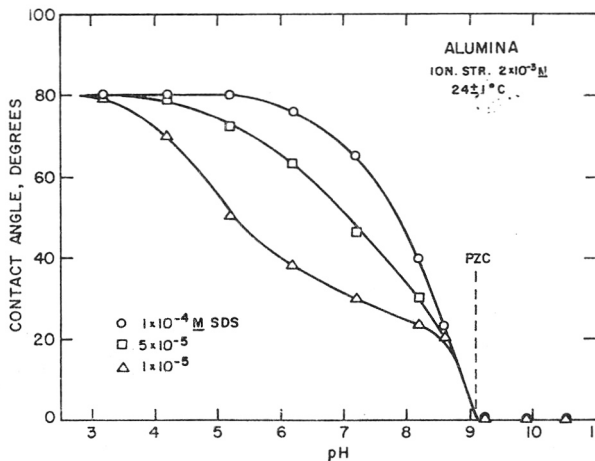


Fig. 8. The contact angle on alumina in the presence of sodium dodecyl sulfonate as a function of pH³.

The wetting behavior of AgI is presented in Figs. 9 and 10. In the absence of surfactant, *i. e.* Fig. 9, both receding and advancing contact angles go through a maximum at about pAg 5.4. These curves are drawn through the weighted

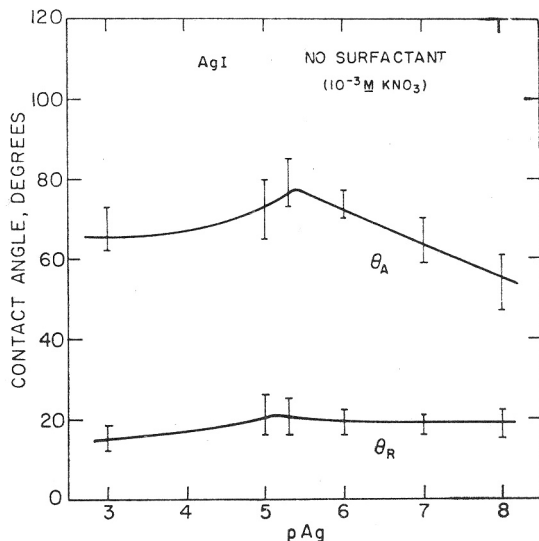


Fig. 9. The contact angle on silver iodide in the absence of surfactant as a function of pAg.

average of the experimentally determined contact angle values for each pAg. Ottewill¹² has also reported similar results including the maximum at about pAg 5.4 which is close to the pzc. The effect of tetradecyl sulfonate concentration on the wettability for different values of pAg are shown in Fig. 10. When the

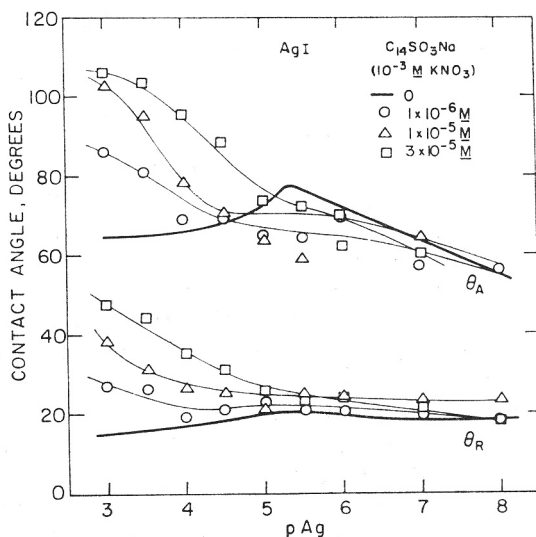


Fig. 10. The contact angle on silver iodide in the presence of sodium tetradecyl sulfonate as a function of pAg.

bulk concentration of the surfactant is low, the wetting behavior is very similar to that of the surfactant free system except at higher positive surface charge (low pAg) where a significant rise in contact angle is observed. As the concentration of surfactant increases, a corresponding increase in the contact angle is also observed.

DISCUSSION

In general, the electrochemical free energy of adsorption, $\Delta G_{\text{ads}}^{\circ}$ consists of many terms:

$$\Delta G_{\text{ads}}^{\circ} = \Delta G_{\text{el}} + \Delta G_{\text{sp}}^{\circ} \quad (2)$$

where ΔG_{el} is the free energy change due to electrostatic interactions experienced by the adsorbing species at the Stern plane ($= zF\psi_{\delta}$), $\Delta G_{\text{sp}}^{\circ}$ is the free energy change due to specific interactions at the surface and in this system may include the following terms: $\Delta G_{\text{CH}_2}^{**}$, $\Delta G_{\text{CH}_2}^*$, and $\Delta G_{\text{chem}}^{\circ}$. $\Delta G_{\text{CH}_2}^{**}$ represents the free energy change due to Van der Waals association of the hydrocarbon chains with each other forming hemimicelles, $\Delta G_{\text{CH}_2}^*$ is the free energy change associated with the Van der Waals interaction of the hydrocarbon chains with the solid surface, and $\Delta G_{\text{chem}}^{\circ}$ is the standard free energy change contributed by chemical bonding of the adsorbing species with the solid surface.

The hydrophobic bonding contributions to the specific free energy *i. e.* $\Delta G_{\text{CH}_2}^{**}$ and $\Delta G_{\text{CH}_2}^*$ depend on the chain length — the larger the number of CH_2 groups, the larger their negative value:

$$\Delta G_{\text{CH}_2}^{**} = N \Phi_{\text{CH}_2}^{**} \quad (3)$$

$$\Delta G_{\text{CH}_2}^* = N \Phi_{\text{CH}_2}^*$$

where $\Phi_{\text{CH}_2}^{**}$, $\Phi_{\text{CH}_2}^*$ represent the molar cohesive free energy associated with each CH_2 group for chain-chain and chain-solid surface interactions, respectively, and N is the number of CH_2 groups interacting per hydrocarbon chain of the surfactant. The process of adsorption is termed »physical« if the electrostatic and Van der Waals interactions constitute the driving force for adsorption. On the other hand, when the adsorbing species form chemical bonds with ions or atoms in the solid surface, the process is termed »chemisorption«.

Fig. 11 gives a schematic illustration of the effect of these various interactions on the zeta potential of any given solid. In systems in which the solid is hydrophilic, if the specific adsorption is due solely to hydrophobic chain-chain interactions, then at the pzc., *i. e.* point A, the mobility versus pPD curve (where PD is the activity of the appropriate potential-determining ion) should coincide with that obtained in the presence of only indifferent electrolyte. The alumina-dodecyl sulfonate system represents this condition. The fact that the zeta potential versus pH curves coincide above pH 9, the pzc, (see Fig. 1) indicates that the sulfonate ions are not adsorbed under these conditions. Further support for this conclusion is provided by Figure 8 which shows that above pH 9, alumina gives zero contact angle in the presence of dodecyl sulfonate. This latter result also confirms the hydrophilic nature of alumina, since the presence of chain-solid interaction should result in non zero contact angles above pH 9.

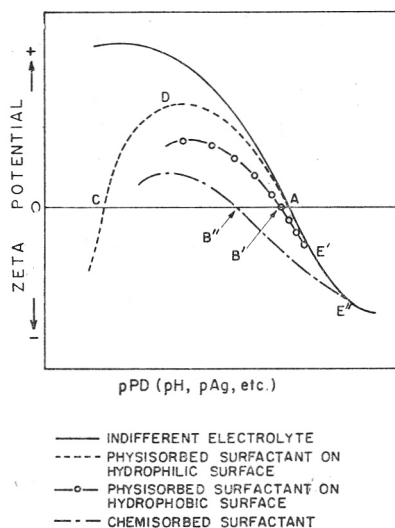


Fig. 11. Schematic representation of the effect of surface active agents on the zeta potential of various kinds of solids at different concentrations of potential determining ions.

As has already been developed elsewhere^{1,2}, at low concentrations of surfactants or at low surface potentials, the surfactant ions are adsorbed individually and adsorption results primarily from electrostatic forces between the surfactant ions and the charged solid surface. As the pH decreases, the surface charge increases; the consequent rise in surfactant adsorption encourages chain-chain interactions (hemimicelle formation) which in turn increases the adsorption energy so that at some point (say D of Fig. 11), the zeta potential reverses its slope and finally reverses its sign at C, which we have termed the point of zeta reversal, or the p_{zr}. With higher surfactant concentration, point D shifts to higher pH values. For example, at pH 7, the break in the slope occurs with about 10^{-4} M sulfonate while at pH 6, only 10^{-5} M is required, thus showing that to cause sufficient adsorption for hemimicelle formation in dilute surfactant solutions, the pH must be lowered in order to increase the surface charge density. This is exactly what is shown in Fig. 2 where for pH 3.2 about 10^{-5} M sulfonate seems adequate to reverse the zeta potential whereas at pH 7.2, the surfactant requirement exceeds 10^{-4} M. The second change in the slope of the ζ -pH curves of Fig. 1 must be attributed to the fact that at this stage, monolayer adsorption of surfactant ions has been attained and consequently, lowering the pH now affects the zeta potential primarily because of the resultant increase in surface charge. The potential in the Stern plane must be negative, therefore further adsorption would be discouraged since any new adsorbing sulfonate ions will be subjected to electrostatic repulsion. Thus, in Fig. 8, with 10^{-4} M dodecyl sulfonate the contact angle seems independent of pH at values less than pH 5 indicating that perhaps the increasing positive surface charge is able to induce only little additional surfactant adsorption, the fact that it is around pH 5 that the ζ -pH curve for 10^{-4} M dodecyl sulfonate (see Fig. 1) undergoes its secondary reversal of slope lends further support to this analysis.

In contrast to the alumina-sulfonate system, when the solid is hydrophobic, for sufficiently strong chain-solid interactions, it should be possible to reverse the zeta potential at some point B' before finally meeting the surfactant free curve at E'. Similarly, in systems in which chemisorption plays an important role, e. g. in the adsorption of sodium dodecyl sulfate on hematite¹³, the mobility versus pH curve crosses the pH axis at some point B'' and it is not until it reaches a pH value, say point E'', above the pzc that the curve finally coincides with that obtained for indifferent electrolytes.

The results for the AgI-sulfonate system shall now be analyzed in the light of the above discussion. Following the Stern-Grahame treatment of the electrical double layer, the concentration of ions adsorbed in the Stern layer, Γ_δ , is given by

$$\Gamma_\delta = 2rc \exp(-\Delta G_{\text{ads}}^\circ / RT) \quad (4)$$

where r is the effective radius of the ionic head, c is the bulk concentration of the adsorbed ion in mole/cm³, R is the gas constant and T the absolute temperature. In order to evaluate the magnitude of $\Delta G_{\text{ads}}^\circ$, two different approaches shall be used, based on the following:

(1) At the condition where the surfactant reverses the zeta potential (the pZR), e. g. B' and B'' of Fig. 11, the electrical contribution to the adsorption free energy is nil.

(2) At the condition where the ζ -pPD curve for the surfactant system meets the indifferent electrolyte curve, e. g. at E' and E'' of Fig. 11, the specific adsorption of the surfactant is nil. This means that the electrical and specific adsorption contributions to the free energy of adsorption are *oppositely equal*.

Evaluation of Adsorption Free Energy at the PZR

At the pZR, $\zeta = \psi_\delta = 0$, so that $\Delta G_{\text{el}} = 0$; therefore the double layer can be considered to be a molecular condenser with $\Delta G_{\text{ads}}^\circ = \Delta G_{\text{sp}}^\circ$. Under these conditions, the Stern-Grahame relation can be expressed as

$$\psi_0 C_m = \sigma_\delta = -2rc_0 zF \exp \frac{-\Delta G_{\text{sp}}^\circ}{RT} \quad (5)$$

where ψ_0 is the total double layer potential, C_m is the capacitance of the molecular condenser, σ_δ is the charge in the Stern plane, r is the effective radius of the ionic head of the adsorbed ion, c_0 is the concentration in mole per cm³ when $\zeta = 0$, z is the charge on the adsorbed ion, and F is Faraday's constant. For a given activity of potential determining ions, *viz* a_{I^-} and a_{Ag^+} , ψ_0 is obtained from the well known relation

$$\psi_0 = \frac{RT}{F} \ln \left(\frac{a_{\text{Ag}^+}^0}{a_{\text{Ag}^+}} \right) = - \frac{RT}{F} \ln \left(\frac{a_{\text{I}^-}}{a_{\text{I}^-}^0} \right) \quad (6)$$

where $a_{\text{Ag}^+}^0$ and $a_{\text{I}^-}^0$ are the activities of Ag^+ and I^- respectively at the pzc. For these calculations, C_m is assumed constant and equal to 15 $\mu\text{f}/\text{cm}^2$ with r being 2.9 \AA .

Table I summarizes the results obtained for $\Delta G_{\text{ads}}^\circ$ using Equation 5. In the case of the C_{12} sulfonate, the c_0 values used in these calculations can be read off the ζ versus $\log c$ curve shown in Fig. 7; the corresponding curves for

TABLE I

Calculation of ΔG_{sp}° Using the molecular condenser model with, $C_m = 15 \mu f/cm^2$; $r = 2.9 \text{ \AA}$

Alkyl Sulfonate	ΔG_{sp}° (in units of RT)		
	pAg 3	pAg 4	pAg 5
C5	4.7	4.7	4.6
C8	5.0	5.0	6.2
C10	8.0	8.0	8.1
C12	9.4	9.4	8.9
C14	10.9	10.6	10.0

the C_5 , C_8 , C_{10} , and C_{14} sulfonates are given elsewhere¹⁴, but the results are given here for the sake of completeness. There is a strong dependence on chain length, the values of ΔG_{sp}° increasing from 4.7 RT for C_5 to 10.9 RT for C_{14} ; the effect of pAg however does not seem as pronounced.

Evaluation of Adsorption Free Energy at the Point where ζ vs. pAg Curves Coincide

At point E (see Fig. 11) specific adsorption at the Stern plane must be nil and the specific adsorption potential is just counterbalanced by the electrostatic contribution:

$$\Delta G_{el} = \Delta G_{sp} = zF\Psi_{\delta} \quad (7)$$

Since the curves in Figs. 3 to 6 all meet the surfactant-free curve at about pAg 7, then for this condition,

$$\Psi_{\delta} = -70 \text{ mV and } \Delta G_{sp}^{\circ} \approx -2.8 RT \quad (8)$$

In addition, the fact that all the curves seem to coincide at pAg 7 independent of chain length, means that this adsorption phenomenon does not exhibit any chain length dependency, and it cannot therefore be attributed to chain-chain or chain-solid interactions. It is therefore suggested that this behavior is caused solely by the specificity of the *polar head* of the surfactant. In particular, the interaction of the sulfonate head with Ag^+ in the lattice gives rise to a chemisorption bond and this latter calculation estimates its magnitude, *i. e.*,

$$\Delta G_{chem}^{\circ} = -2.8 RT.$$

Therefore taking the ΔG_{sp}° value calculated with Equation 7 as $\Delta G_{chem}^{\circ} = -2.8 RT$, the hydrophobic contribution to the total specific adsorption free energy can be calculated by subtracting $\Delta G_{chem}^{\circ} = -2.8 RT$ from the ΔG_{sp}° values given by Equation 5. These have been tabulated in Table II.

There is a striking similarity between the values of $\Delta G_{sp}^{\circ} - 2.8 RT$ and the numbers obtained by dividing the respective chain lengths by 2, especially for the longer chain surfactants.

TABLE II

Calculation of ΔG_{sp}° for Hydrophobic Interaction

From calculations at point E, $\Delta G_{chem}^{\circ} = -2.8 RT$ independent of chain length.

Alkyl Sulfonate	ΔG_{sp}°	$(\Delta G_{s_1}^{\circ} - \Delta G_{chem}^{\circ})$	No. C atoms/2
C5	4.6 RT	1.8 RT	2.5
C8	6.2 RT	3.4 RT	4
C10	8.1 RT	5.3 RT	5
C12	8.9 RT	6.1 RT	6
C14	10.0 RT	7.2 RT	7

The free energy decrease accompanying the removal of a hydrocarbon chain from water is about $1 RT$ per mole. If on the other hand, the adsorbed surfactant consists of horizontally oriented chains, then the accompanying decrease in free energy might be $1/2 RT$ per mole of CH_2 groups (instead of $1 RT$) since even though half of the chain surface is next to the solid surface, the other half is still exposed to the water. On this basis therefore, the free energy associated with complete horizontal orientation of the chains will be $2.5 RT$, $4 RT$, $5 RT$, $6 RT$, and $7 RT$, respectively, for C_5 , C_8 , C_{10} , C_{12} , C_{14} . On comparing these values with the corresponding $(\Delta G_{sp}^{\circ} - 2.8 RT)$ values (Table II), viz. $1.8 RT$, $3.4 RT$, $5.3 RT$, $6.1 RT$, $7.2 RT$ respectively for C_5 , C_8 , C_{10} , C_{12} , and C_{14} , it seems reasonable to conclude that the adsorbed sulfonate ions orient their chains parallel to the solid surface indicating the presence of chain-solid hydrophobic interactions. This hydrophobic nature of the AgI surface has already been demonstrated in Fig. 9 which shows finite contact angles in surfactant-free solution which is as should be expected. The increase of the contact angles with decreasing pAg as shown in Fig. 10 is due to the fact that the amount of surfactant adsorbed increases with higher positive charge. The result that C_5 and C_8 have values of $(\Delta G_{sp}^{\circ} - 2.8 RT)$ which are below their respective $1/2 RT X$ (chain length) values shows that C_5 and C_8 are less surface active than their longer chain counterparts. It appears therefore that in the AgI-alkyl sulfonate system, electrostatic, chain-solid and chemical interactions may all contribute to the adsorption driving force.

Acknowledgements. The authors wish to thank the National Science Foundation for support of this research. Part of the work was carried out during the time that one of us (K.O.-A.) held a Jane Lewis Fellowship at the University of California. Extensive discussions with Prof. R. H. Ottewill are also acknowledged.

REFERENCES

1. P. Somasundaran and D. W. Fuerstenau, *J. Phys. Chem.* **70** (1966) 90.
2. T. Wakamatsu and D. W. Fuerstenau, *Advan. Chem Ser.* **79** (1968) 161.
3. T. Wakamatsu and D. W. Fuerstenau, *The Effect of Alkyl Sulfonates on the Wettability of Alumina*, accepted for publication in the *AIME Trans.*
4. N. Tcheurekdjian, A. C. Zettlemyer, and J. J. Chessick, *J. Phys. Chem.* **68** (1964) 773.
5. P. G. Hall and F. C. Tompkins, *Trans. Faraday Soc.* **58** (1962) 1734.
6. D. F. Billett and R. H. Ottewill, *Wetting*, S. C. I. Monograph No. 25, p. 253 (1967).
7. V. Pravdić and M. Mirnik, *Croat. Chem. Acta* **32** (1960) 1.

8. R. H. Ottewill and A. Watanabe, *Kolloid Z.* **170** (1960) 132.
9. R. H. Ottewill, private communication.
10. Zeta-Meter Manual, Zeta-Meter Inc. New York.
11. P. Wiersema, A. Loeb, and J. Th. G. Overbeek, *J. Colloid Interface Sci.* **22** (1966) 78.
12. D. F. Billett and R. H. Ottewill, *161st A.C.S., National Meeting*, Los Angeles, 1971.
13. H. L. Shergold and O. Mellgren, *Trans. Inst. Min. Met.*, London **78 C** (1969) 121.
14. K. Osseo-Asare, *The Effect of Alkyl Sulfonates on the Electrophoretic and Wetting Behavior of Silver Iodide*, M. S. Thesis, College of Engineering, University of California, Berkeley, 1972.
15. D. W. Fuerstenau, *Pure Appl. Chem.* **24** (1970) 135.

IZVOD

Adsorpcija sulfonata i pojave kvašenja na granici faza čvrsto-voda

K. Osseo-Asare i D. W. Fuerstenau

Mjerenje su elektroforetske pokretljivosti AgJ solova u prisutnosti alkil sulfonata i kutevi kvašenja za planarne površine AgJ, a rezultati su uspoređeni s onima za Al_2O_3 . Pokazano je, da kod Al_2O_3 dolazi samo do fizikalne interakcije između sulfonata i površine, dok kod AgJ ima indikacija i za fizikalnu i za kemijsku interakciju. Izračunate su standardne slobodne energije za specifičnu adsorpciju, kao i one za kemijsku interakciju koja se pokazuje neovisnom o duljini alifatskog lanca. Adsorpcija surfaktanata može se najbolje predstaviti modelom kod kojeg alifatski lanci leže duž površine AgJ, a kvantitativni termodinamički podaci su ujedno mjera za stupanj hidrofobnosti površine.

DEPARTMENT OF
MATERIALS SCIENCE AND ENGINEERING
UNIVERSITY OF CALIFORNIA
BERKELEY, CALIF., U. S. A.

Primljeno 20. studenoga 1972.