Surface Activity of Sodium Salts of *alpha*-Sulfo Fatty Esters. The Oil/Water Interface[1]

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Abstract

Adsorption studies at the heptane/water and the benzene/water interfaces have been conducted for four α-sulfo fatty esters: sodium hexyl α-sulfopelargonate, sodium heptyl α-sulfopelargonate, sodium methyl α-sulfomyristate, and sodium methyl α-sulfopalmitate. The results were compared with those at the air/water (A/W) interface (3). Surfactant solutions with constant counter-ion concentrations of 0.01 and 0.04 M Na^+ were used. Interfacial tensions were measured by using a drop-volume method and were found to be in the range 1 to 25 dynes/cm.

The critical micelle concentration (CMC) values of these esters were in the range 8.1 to 0.14 mM at the A/W interface (3); they were decreased by about 10% in the presence of heptane (7.2 to 0.11 mM) and by 30–40% in the presence of benzene (5.5 to 0.08 mM). This decrease in CMC was attributed to the water solubility of the hydrocarbon; the greater the solubility, the larger was the decrease in CMC.

The co-areas at the A/W interface were in the range 44 to 59 $Å^2$/molecule for all the esters (3). At the heptane/water interface they were in the range 49 to 66 $Å^2$/molecule and at the benzene/water interface in the range 59 to 75 $Å^2$/molecule, i.e., an increase of about 10% was obtained in the presence of heptane and about 30–40% in the presence of benzene. The surface films at the O/W interface were more expanded than at the A/W interface, as expected, owing to the lack of lateral cohesion between the hydrocarbon chains at the O/W interface.

Introduction

ANIONIC SURFACTANTS can be divided into two classes as determined by practical tests: wetting agents, for example, those which "wet-out" air from cotton (1,2) and detergents, those which remove oily dirt from such soiled surfaces as cotton. A good wetting agent is usually not a good detergent. The physical chemical reasons for the difference are obscure. Few detailed studies have been directed at an analysis of the pertinent properties that differentiate the two. The sodium salts of α-sulfo fatty esters [R CH (SO_3 Na) COO R′] are interesting compounds since they form an homologous series which displays greatly different properties, depending on the molecular configuration. If the acid chain R, on which the sulfo group resides, is long and the alcohol chain R′ is short, or vice versa, then the α-sulfo ester is a detergent. A long chain leads to a low critical micelle concentration (CMC) and presumably a greater tendency to solubilize oils.

But if R and R′ are about equal in length, then the α-sulfo ester is a wetting agent. Adsorption at the air/water (A/W) interface has been examined by Boucher et al. by using four of the α-sulfo esters, in turn, to seek differences between the two classes of surfactants (3). However at the A/W interface, cohesion (4) is possible between the carbon chains, hence the total surface pressure is made up of positive contributions from the kinetic effect and an electrical repulsive force and of a negative contribution from the cohesive force. At the oil/water (O/W) interface, the cohesive contribution is negligible because of the interpenetration of the hydrocarbon between the surfactant chains.

Further it is known that surfactants, such as sodium dodecyl sulfate (Na DS), behave ideally at the O/W interface whereas it shows nonideal behavior at the A/W interface (5). It was thought that studies at the O/W interface might yield results that differ markedly between the two varieties of surfactants. Hence a study of the adsorption of the same four α-sulfo esters was undertaken at the O/W interface, and the results were compared with those at the A/W interface (3).

Experimental Procedure

Materials. The four α-sulfo esters studied are listed in Table I under the two classes: wetting agents and detergents. These esters were prepared by Stirton, Weil, and their co-workers (6–9) and purified by repeated recrystallizations (3).

Baker-analyzed sodium chloride was heated in a platinum crucible at 750C for 3 hr to eliminate any surface-active impurities. Triply distilled water was used to make up the solutions. Spectro-analyzed n-heptane and benzene were supplied by the Fisher Scientific company and were used without any further purification.

Solutions containing several surfactant concentrations were prepared, and the sodium chloride solution was added so that all the solutions were at the same Na^+ concentration. Two different Na^+ concentrations, namely, 0.01 and 0.04 M, were employed.

The interfacial tensions (γ) at the *n*-heptane/water (H/W) and the benzene/water (B/W) interface were measured by using a drop-volume apparatus described previously (3,10). All the measurements were conducted at 25 ± 0.05C. About 5 to 6 min were allowed for each drop formation, and the average of about 10 drops was taken to calculate γ.

Results and Discussion

Interfacial tension versus log molar concentration plots are given in Fig. 1 for the two wetting agents, Na Hex αS Pelar and Na Hep αS Pelar, and in Fig. 2 for the two detergents, Na Me αS Myri and Na Me αS Palm. It was shown (3) that, in cases where the measurements are made at varying concentrations of the surfactant but at constant counter-ion concentration, the Gibbs equation takes the form

$$-d\,\gamma = RT\,\Gamma\,d\ln C \qquad [1]$$

where Γ is the amount of surfactant adsorbed, C is the molar concentration of the surfactant ions. From the

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[1] Presented at AOCS Meeting, October 1967, Chicago.

TABLE I

The α-Sulfo Fatty Esters Studied

Wetting Agent	No. of C's	Detergent
1) Sodium hexyl α-sulfopelargonate C_7H_{15} CH(SO_3Na) COO C_6H_{13} (abbr. Na Hex αS Pelar)	15	3) Sodium methyl α-sulfomyristate $C_{12}H_{25}$ CH(SO_3Na) COO CH_3 (abbr. Na Me αS Myri)
2) Sodium heptyl α-sulfopelargonate C_7H_{15} CH(SO_3Na) COO C_7H_{15} (abbr. Na Hep αS Pelar)	16	
	17	4) Sodium methyl α-sulfopalmitate $C_{14}H_{29}$ CH(SO_3Na) COO CH_3 (abbr. Na Me αS Palm)

plots of γ versus log C, the Γ values and the co-areas of the molecules at the interface were calculated. The CMC's, also obtained from the plots, Γ values, and co-areas are listed in Table II along with the corresponding values obtained at the A/W interface.

Fig. 1 and 2 and Table II indicate that the CMC values are lower at the O/W than at the A/W interface. There have been a number of reports (11–16) on the influence of the interface on the CMC values. All these reports indicate a similar decrease in CMC values at the O/W interface. The solubilization of the hydrocarbon in the micelle interior results in an increase in the micelle size and a slight change in the curvature of the micelle surface, as a result of which the electrical potential and hence the electrical work for micellization per micelle-forming ion will be decreased. Further, the surface free-energy decrease in the hydrocarbon chain of the surfactant on micellization may also increase. Both these factors tend to decrease the CMC (17). As expected, benzene lowered the CMC to a greater extent than *n*-heptane in accord with its greater water-solubility.

Standard free energies of micellization (ΔG) have been calculated by a number of investigators (18–21) by using the semi-empirical thermodynamic expression of the type:

$$\Delta G = 2\,RT \ln a_{\pm}\, b_{\pm} \qquad [2]$$

where $a_{\pm}$ = mole fraction

$b_{\pm}$ = activity coefficient of the monomer at the CMC

Herrmann (18) and Benjamin (19) and recently Rehfeld (16) represented the solubilization process diagrammatically. They have assumed that the activity of the hydrocarbon liquid in the micelle interior is equal to the activity of the excess hydrocarbon liquid at the O/W interface and that both the hydrocarbon dissolved in water and in the surface of the hydrated micelle are in the same state. The difference between ΔG in the presence and in the absence of the hydrocarbon should be a measure of the extent of solubilization and be in accordance with the CMC. The ΔG values for the four α-sulfo ester surfactants were calculated at the H/W and B/W, also at the A/W interfaces, by using Equation 2 and assuming that the ratio of the activity coefficients in the presence and in the absence of the hydrocarbon is unity since the concentration changes are small. The difference in the ΔG values between the O/W and the A/W interfaces are given in Table III. Again as expected, the ΔG difference at the B/W is much more than at the H/W interface.

A comparison of the co-areas obtained at the A/W interface (3) with those from the molecular models indicated that all four surfactants are oriented normally to the interface with the carbon chains outstretched and closely packed. Since the co-areas obtained at the O/W interface do not differ markedly from those at the A/W interface, it is believed that the orientation of the molecules at the O/W and A/W interfaces is the same. It is evident from Table II that the co-areas are about 10% higher at the H/W and about 30% higher at the B/W than at the A/W interface. This increase in the co-area indicates that the α-sulfo fatty ester films are more expanded at the O/W interface, depending on the solubility of the hydrocarbon. Similar results were reported by Hutchinson (22), Cockbain (23), Hayden and Phillips (24), Rehfeld (16), etc., for the adsorption of Na DS at several O/W interfaces.

Table II indicates that the co-areas of the wetting-agent type species are slightly higher than the deter-

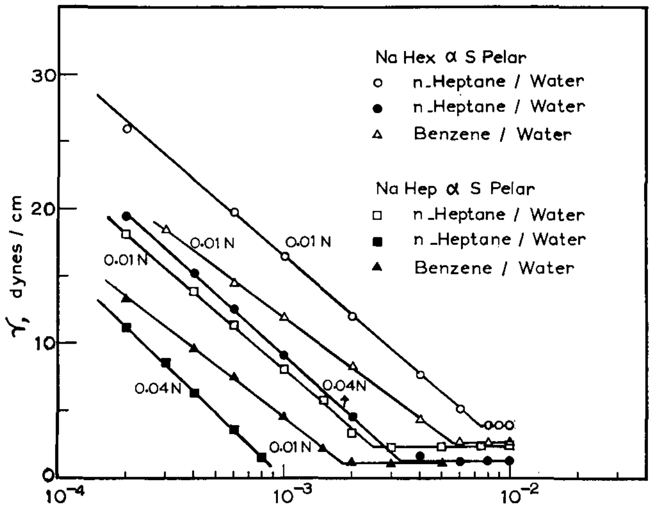

FIG. 1. Plots of γ against log C for solutions of Na Hex αS Pelar and Na Hep αS Pelar in 0.01 and 0.04 M Na^+ concentrations at H/W and B/W interfaces.

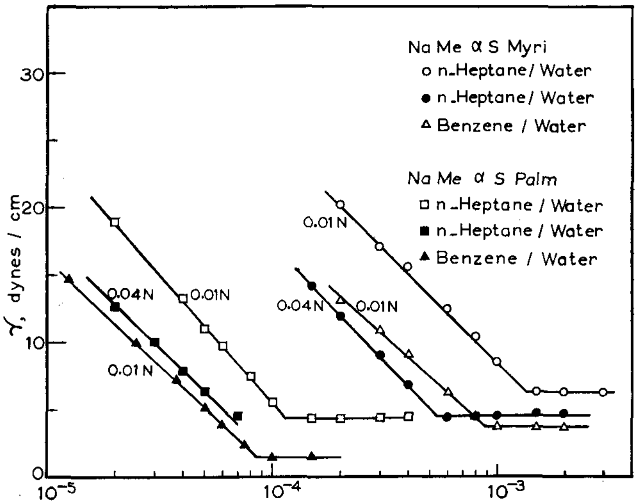

FIG. 2. Plots of γ against log C for solutions of Na Me αS Myri and Na Me αS Palm in 0.01 and 0.04 M Na^+ concentrations at H/W and B/W interfaces.

TABLE II

CMC, Γ, and Co-area of the α-Sulfo Fatty Esters at the O/W and A/W Interfaces

Compound	Na^+ Conc. M	CMC × 10^3 M			Γ × 10^{10} moles/cm^2			Co-area $Å^2$/molecule		
		H/W	B/W	A/W	H/W	B/W	A/W	H/W	B/W	A/W
Na Hex αS Pelar	0.01	7.2	5.5	8.1	2.53	2.20	2.80	66	75	59
	0.04	3.3		4.1	2.64		2.92	63		57
Na Hep αS Pelar[a]	0.01	2.5	1.8	2.7	2.54	2.28	2.93	65	73	57
	0.04				2.83		2.97	59		56
Na Me αS Myri	0.01	1.35	0.89	1.50	2.96	2.62	3.03	57	64	55
	0.04	0.54		0.70	3.09		3.27	54		51
Na Me αS Palm[a]	0.01	0.11	0.08	0.14	3.39	2.78	3.76	49	59	44
	0.04				2.87		3.52	58		47

[a] Na Hep αS Pelar and Na Me αS Palm "salted-out" before they reached the CMC in presence of 0.04 M Na^+.

TABLE III

Standard Free-Energy Difference Between the O/W and the A/W Interfaces

Compound	$\Delta G_{(H/W)}$ — $\Delta G_{(A/W)}$ cals/mole	$\Delta G_{(B/W)}$ — $\Delta G_{(A/W)}$ cals/mole
1) Na Hex αS Pelar	140	470
2) Na Hep αS Pelar	90	480
3) Na Me αS Myri	120	610
4) Na Me αS Palm	240	600

gents and that in both categories the molecules with the lesser number of carbon atoms yield somewhat larger co-areas. Increase in the ionic strength from 0.01 to 0.04 M causes a considerable decrease in the interfacial tension values. At a particular concentration below the CMC, a decrease in γ of about 5.5 to 8.5 dynes/cm was noted for the four α-sulfo esters.

At a given surfactant concentration the γ values are lowered by about 8.5 dynes/cm from Na Hex αS Pelar to Na Hep αS Pelar (one CH_2 difference) and by about 19.7 dynes/cm from Na Me αS Myri to Na Me αS Palm (two CH_2 difference). The fact that the addition of two CH_2 groups to the myristate has nearly twice the effect as the addition of one CH_2 group to the hexyl pelargonate indicates that the carbon chains of all these esters play similar roles at the interfaces.

By increasing the ionic strength from 0.01 to 0.04 M, the CMC values were lowered considerably as a result of decreased electrical energy per micelle-forming ion. Further, the co-areas of the molecules (at H/W interface) have decreased by about 5–10% as a result of lowering in the repulsion between the polar head groups. A remarkable feature of the results is that the co-area of Na Me αS Palm increases with increased Na^+ concentration contrary to the views presented by van Voorst Vader (25), who states that "if saturation adsorption occurs over a range of cation concentration, its values at all cation concentrations in this range must be equal, i.e., the plots of γ vs. log C must be parallel" or "if the surfactant ion adsorption increases with surfactant ion concentration, the plots on the γ against log C graph at various cation concentrations must lie on lines diverging at increasing surfactant concentration." The reason for such behavior is unknown.

The work of desorption per $-CH_2-$ group can be calculated by using the Langmuir interpretation of Traube's rule.[2] Langmuir (26) showed that

$$W = RT \ln \frac{C_1}{C_2} \qquad [3]$$

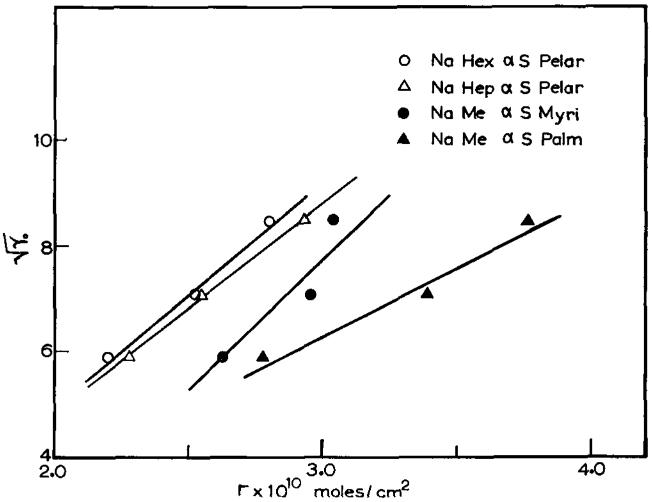

FIG. 3. Plots of Γ against $\sqrt{\gamma_o}$ for the four α-sulfo ester surfactants.

where W = work required to bring one $-CH_2-$ group from the interior to the interface and C_1 and C_2 are the bulk concentrations of two different surfactants which differ by one $-CH_2-$ group to give rise to the same γ value. If Traube's rule is obeyed, $C_1/C_2 = 3$. A check of Traube's rule was made by using Equation 3 for the four surfactants studied, and the results are presented in Table IV.

As is evident from Table IV, the values for C_1/C_2 are in the range 3.5 to 3.8 as against 3, a value if Traube's rule is applicable. The work of desorption per $-CH_2-$ group ranges from 760 to 790 cal/mole, close to the value of about 800 cals/mole for other systems (4,27). This suggests that the adsorbed films are free to move laterally in the oil phase; the latter penetrates freely between the carbon chains. The slightly low values represent the loss of entropy normal to the surface in the adsorbed film.

Van Voorst Vader (25) studied the adsorption of several surfactants at different O/W interfaces and observed that the Γ values generally increase with the interfacial tension (γ_o) between the pure liquids. For sodium undecyl sulfonate, the relation

$$\Gamma = K \sqrt{\gamma_o} \qquad [4]$$

TABLE IV

Traube's Rule and Work of Desorption of $-CH_2-$ Groups

Pairs of Surfactants	Difference in No. of $-CH_2-$ Groups	C_1/C_2 per $-CH_2-$		W per $-CH_2-$ cals/mole	
		H/W	B/W	H/W	B/W
1) Na Hex αS Pelar Na Hep αS Pelar	1	3.79	3.66	790	770
2) Na Me αS Myri Na Me αS Palm	2	3.58	3.68	760	790

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[2] Traube's rule is stated as "the concentration of the members of the homologous series required to achieve equal surface-tension lowering of the aqueous solution diminishes about three-fold for each $-CH_2-$ group added to the chain."

was found to be applicable. The validity of this equation was tested by using the data at three interfaces (including the A/W) for the α-sulfo ester surfactants. Plots of Γ against $\sqrt{\gamma_0}$ are presented in Fig. 3. They indicate that, for at least three esters, the same equation holds.

ACKNOWLEDGMENT

Work was done under contract with the U. S. Department of Agriculture and authorized by the Research and Marketing Act of 1946. It was supervised by A. J. Stirton and J. K. Weil of Eastern Utilization Research and Development Division, Agricultural Research Service, Philadelphia, Pa.

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[Received October 30, 1967]