ADSORPTION OF DETERGENTS AT THE LIQUID-LIQUID INTERFACE

PART 2

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Saturation adsorptions of surfactants containing several hydrophilic groups, and of surfactants simultaneously adsorbed, have been determined. The results may be interpreted as being due to the interaction between the hydrations of the various hydrophilic groups present at the interface.

In a previous article [1] it was shown that solutions of simple detergents can display saturation adsorption, the value of which is mainly governed by the nature and degree of hydration of their hydrophilic group and by the presence of other polar groups in the interface. This work has been extended to : (i) systems containing one surfactant having several different hydrophilic groups per molecule ; (ii) systems containing two different surfactants, each with a different hydrophilic group.

EXPERIMENTAL

MATERIALS

I. SODIUM UNDECYLSULPHONATE was synthesized and purified as described previously.[1]

II. SODIUM-5-OXAHEPTADECYL SULPHONATE was prepared by adding an equivalent amount of butane sultone at 200°C to a solution of sodium lauryl alcoholate in an equal amount of lauryl alcohol.[2] After 4 h the mixture was cooled, dissolved in a mixture of water and methanol (1 : 1), and extracted with light petroleum. The aqueous layer was neutralized and the water evaporated. The dry product obtained was extracted with n-pentane for 16 h after which its aqueous solutions displayed no minimum in the γ against log C curve.

III. SODIUM-5, 8-DIOXATETRADECYL SULPHONATE.—Synthesis and purification were carried out as described for (II), using hexanol monoethylene oxide as a starting material. The purity of this compound was checked by means of its hydroxyl content, which gives information regarding the average composition only.[3] Therefore, the formula of this detergent represents only the average composition.

IV. SODIUM 5,8-DIOXAOCTADECYL SULPHONATE.—The synthesis and purification are analogous to (III). Again, the formula represents only the average composition.

V. SODIUM-α-SULPHOLAURIC ACID BUTYL ESTER.—Monosodium-α-sulpholauric acid was suspended in absolute butanol and dry HCl was passed through. After the reaction, the mass was filtered, neutralized with Na_2CO_3 and filtered again. The ester was obtained by evaporation of the filtrate, and purified by extracting with n-pentane, until the γ against log C curve displayed no minimum.

VI. SODIUM-DI-ISO-OCTYLSULPHOSUCCINATE.—The commercial product Aerosol OT 100 % was used. It was purified by foam fractionation, and measurements were made within 30 min after completion of the fractionation.

VII. SODIUM LAUROYLTAURATE was prepared following the method of Desseigne.[4] The dried reaction product was extracted with ether and recrystallized first from absolute alcohol, then three times from 95 % alcohol. Then it was separated from the remaining fatty acid through specific adsorption on a Dowex 1×2 acetate column.[5] The laurate was recovered by shaking the resin with Na acetate solution. After conversion to the

acid, the acetic acid was separated off by means of ion exclusion, percolating the mixture through a Dowex 50×8 (H$^+$) column.

VIII. MONOSODIUM-α-SULPHOLAURIC ACID was obtained from (IX) by the addition of a calculated amount of acid and recrystallizing.

IX. DISODIUM-α-SULPHOLAURIC ACID.—Butyl laurate was sulphonated in SO$_2$ solution by means of an excess of SO$_3$.[6] The sulphur oxides were evaporated off and the residue was neutralized with aqueous NaOH, and again evaporated to dryness; the crystal mass was extracted by shaking with ether+ethanol mixture. The remaining crude disodium salt was recrystallized from a mixture of carbon tetrachloride+water+ethanol.

X. LAUROYLDIETHANOLAMIDE was synthesized according to Trowbridge et al.[7] The product was recrystallized from acetone until a m.p. 47-47·5° C was obtained.

Inorganic reagents were purified as described before.

RESULTS

SYSTEMS WITH ONE SURFACTANT

Solutions of various surfactant concentrations were prepared and NaCl added so that all solutions were at constant cation concentration. With disodium-α-sulpholaurate, both Na$_2$SO$_4$ and NaCl were added, and the concentration of cations and of bivalent ions ($Z^{2-}+SO_4^{2-}$) were both kept constant. Interfacial tensions were measured by the drop weight method and the adsorption was calculated using the appropriate form of the Gibbs' adsorption equation.[1]

When hydrolysis of the detergent could occur, the saturation adsorption value found by changing the detergent concentration was checked by calculation from measurements at constant detergent concentration and varying cation concentration. This procedure will reveal the presence of non-ionic surface-active products, that may be formed by hydrolysis of, e.g., Aerosol OT. The adsorption of such products will increase the change in interfacial tension on varying the concentration of a partly hydrolyzed detergent, but will not influence the change in interfacial tension on varying the cation concentration.

All the detergents investigated exhibited saturation adsorption at concentrations from about 30 % of the critical micelle concentration (c.m.c.) up to the c.m.c. The values obtained are given in table 1.

TABLE 1.—SATURATION ADSORPTIONS OF SULPHONATES HAVING ADDITIONAL HYDROPHILIC GROUPS

substance	hydrophilic group in addition to SO₃	[Na⁺] normality	adsorption at interfaces (Å²/detergent ion)			
			air	heptane	dibutyl ether	Me-caprinate
I	—	0·03	51·5	53·6	78·1	78·9
II	1 ether group	0·01	52·5	52	76	—
III	2 ether groups	0·03	72	—	—	—
		1·00	(31)	48	—	—
IV	2 ether groups	0·01	74	73	97	—
		0·03	59			
V	1 ester group	0·01	70	81	—	110
		0·02	(49)	81	—	110
VI	2 ester groups	0·003	115	111	—	139
VII	1 amide group	0·05	—	57	—	89
VIII	1 COOH group	0·05	—	109	—	
IX	1 COO⁻ group	0·08	—	55	—	

SIMULTANEOUS ADSORPTION OF DIFFERENT SURFACTANTS

The following systems have been investigated at pH 10·6:

K-laurate, lauroyldiethanolamide (KCl, polysoap AK 534)*/air

K-laurate, lauryl alcohol (KCl, polysoap AK 534)/air.

* Polysoap AK 534 is a copolymer of styrene and K-styryl undecanoate (1 : 1), with mol. wt. of ca. 300,000.

ADSORPTION OF DETERGENTS

The two non-ionics used do not dissolve readily in water and for rapid establishment of equilibrium during the measurements it was necessary to add a non-surface-active solubilizer (polysoap AK 534). The addition of a fixed amount of such a polysoap essentially provides a constant amount of permanent micelles [8] which solubilize the non-ionic.

Adsorptions may be calculated from surface tension measurements by Gibbs' law assuming that at constant polysoap concentration the ratio of free (C_F) and solubilized molecules (C_S) is constant.

Putting

$$K = C_F/C_S, \qquad (1)$$

since $C_S \gg C_F$, we obtain

$$C_F = KC_n, \qquad (2)$$

where C_n is the total concentration of the non-ionic. The Gibbs' adsorption equation at constant temperature can now be written,

$$d\gamma = -RT\Gamma_n d\ln C_F = -RT\Gamma_n d\ln C_n. \qquad (3)$$

where γ = surface tension in dynes/cm, R = gas constant, T = absolute temperature and Γ_n relative adsorption of the non-ionic. While the validity of eqn. (1) has not been verified, results of solubilization experiments on detergent solutions suggest that it is approximately valid over a wide concentration range.[9]

The sample of AK 534 used was slightly surface-active, presumably due to impurities. However, the saturation adsorption area of K-laurate in the presence of 0.139% polysoap was 40.5-41 Å^2 ($[K^+] = 0.04$ N), whereas in the absence of polysoap, this area was 43 Å^2. This difference is within the experimental error; consequently the adsorption areas are not seriously affected by the presence of the polysoap.

The surface tension of solutions was measured for three different laurate concentrations and three different concentrations of non-ionic in all possible combinations at constant K^+ concentration. From these data, the adsorption of laurate ion and of non-ionic were each determined by means of the Gibbs' equation, which assumes the form

$$d\gamma = -RT\Gamma_L d\ln C_L - RT\Gamma_n d\ln C_n, \qquad (4)$$

where Γ_L = relative adsorption of laurate ion, C_L = laurate ion concentration. In all experiments, a constant non-ionic adsorption was found in the concentration range investigated. The laurate adsorption was determined near the c.m.c. of the soap in the system and constant adsorption was found at a specific concentration of the non-ionic. The value[5] for the saturation adsorptions found are collected in table 2. Furthermore, measurements were made on the system water, sodium dodecylsulphonate + NaCl/benzene, lauryl alcohol at 30°C.

TABLE 2.—SATURATION ADSORPTIONS IN SYSTEMS CONTAINING 2 SURFACTANTS

conc. AK 534: 0.139%; temp. 20°C; pH = 10.6; $[K^+] = 0.04$ N

[K-laurate] (mmole/l.)	0	3	3·5	4·5
adsorption LEA (Å²/mol.)	98	98	98	98
[LEA] (g./l.)	0	0·1	0·2	0·4
adsorption KC₁₂ (Å²/mol.)	41	69	70	73
[K-laurate] (mmole/l.)	0	2	3	4·5
adsorption C₁₂OH (Å²/mol.)	59·5	59·5	61	62
[C₁₂OH] (mg/l.)	0	60	120	180
adsorption KC₁₂ (Å²/mol.)	40·5	50·5	49	53

The following values for the saturation adsorption of the sulphonate were found at different molar fractions X of the lauryl alcohol in benzene:

$X \cdot 100$	0	0·992	1·32	2·74	9·18
saturation adsorption sulphonate in Å^2/soap ion at $[\text{Na}^+] = 0.015$ M	57	69	69	69	69

The lauryl alcohol displays marked association; we did not succeed in calculating its adsorption.

DISCUSSION

DETERGENTS WITH MORE THAN ONE HYDROPHILIC GROUP

The detergents used all possess a sulphonate group.   Various regularities are revealed by calculation of the amounts by which surface areas per detergent ion increase as a result of different substituents.   These increments are recorded in table 3; differences of less than 5 % from the value of the pure sulphonate have been neglected, since they are within the accuracy of measurement.

TABLE 3.—INCREMENTS IN SURFACE AREA IN Å^2/DETERGENT ION
AS A RESULT OF ADDITIONAL HYDROPHILIC GROUPS

substance	hydrophilic group in addition to SO₃	interface			
		air	heptane	dibutyl ether	methyl caprinate
II	1 ether group	0	0	0	—
III	2 ether groups	20·5	(−5·6)	—	—
IV	2 ether groups	22·5	19·4	18·9	—
V	1 ester group	(18·5)	27·4	—	31·1
VI	2 ester groups	63·5	57·4	—	60·1
VIII	1 COOH group	—	55·4	—	—
VII	1 amide group	—	3·4	—	(10·1)
IX	1 COO⁻ group	—	0	—	—

INFLUENCE EXERTED BY THE NATURE OF THE INTERFACE ON THE ADSORPTION

The increase in surface area per detergent ion for sulphonates with additional ether or ester groups is generally independent of the nature of the interface. The interaction between the sulphonate group and the ether or ester groups, whose presence at the interface is caused by the second phase, is apparently not influenced by the presence of these hydrophilic groups in the soap itself.   The increments of VII with respect to heptane and methyl caprinate, however, display a relatively great difference, so that the above-mentioned rule will possibly not apply if hydrophilic groups other than those of the surfactant are present at the interface.

The anomalous increment of the adsorption of III with respect to heptane is probably caused by the high salt concentration (cf. table 1).   As mentioned already, this may lead to increased adsorption.[1]

INFLUENCE OF THE NATURE OF THE ADDITIONAL HYDROPHILIC GROUP

On arranging the hydrophilic groups from table 3 according to increasing increments, the following order is obtained: COO⁻, first ether group < acid amide < second ether group < ester group < COOH < second ester group.   Obviously the influence of the additional group becomes greater when it is a weaker base according to the Brønsted-Lowry terminology; i.e. when it adds protons less readily.[10]

The relation between the proton affinities of the groups and their effect on adsorption can be qualitatively explained as follows.   Hydrophilic groups which are more strongly basic than water will, on hydration, bind water by their protons; groups which are less basic than water will, on hydration, bind water on their oxygen side.   As is apparent from fig. 1, groups which are more strongly acid and

more strongly basic than water, will mutually stabilize their hydration.   The stabilizing effect will be greater if they differ more in basicity.   Stronger hydration, however, will result in a greater surface area per adsorbed ion, as we have found experimentally: in the presence of the strongly basic $-SO_3^-$-group the influence of additional hydrophilic groups increases at decreasing basicity.   The apparent exception formed by the first ether group is due to steric reasons: if this group is
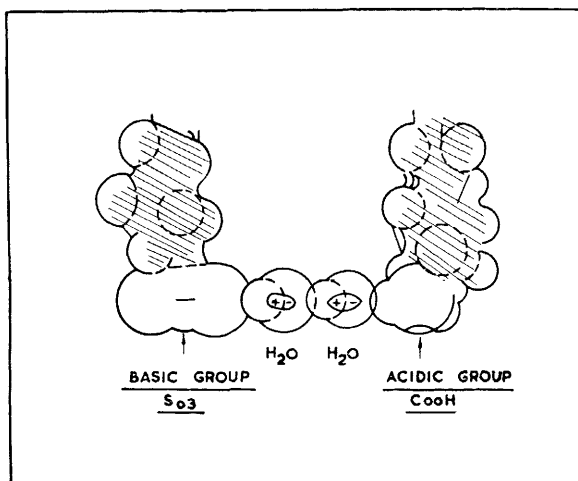
FIG. 1.—Orientation of water molecules by hydrophilic groups of different basicity.

to remain in contact with water, the α-δ CH_2 groups of the sodium-5-oxahepta-decylsulphonate will have to do the same.   However, the adsorption energy of 4 CH_2-groups from water at the air or heptane interface exceeds the adsorption energy of an ether group to water.[11]   Consequently the ether group of II will be lifted out of the water and it will no longer have any effect on the adsorption.

INFLUENCE OF STERIC FACTORS

For comparison of the influence exerted by various groups it was generally possible to use data relating to surfactants whose hydrophilic groups were in the α- or β-position.   It appears from our observations that slight differences in steric position do not have any appreciable effect on the value of the increments found. Comparison of the data relevant to V and VI in table 3 shows that the increments per ester group, irrespective of α- or β-position to the SO_3^--group, is practically constant at *ca.* 30 $Å^2$.   Presumably this implies that a constant volume of water of hydration is fairly strongly bound by the ester groups.

The relationship between the saturation adsorption of surface-active poly-ethylene oxide addition products and the chain-length of the polyethylene oxide group can likewise be explained on the assumption of a constant volume of water of hydration per ether group.   In this connection, table 4 gives data for the satur-ation adsorption of poly-ethoxy-alkylphenols.[12]

The relation between the value of the molecular area and n may be explained by assuming that, at saturation adsorption, the hydrated ether groups occur at random in closest packing at the interface.   Since the poly-ethoxy chains in the water assume the form which is statistically most probable, and the number of ethylene oxide groups is proportional to the number of statistical chain elements, the thickness of the interface (type Guggenheim) is proportional to the square root of the number of ethylene oxide groups, consequently proportional to $n^{\frac{1}{2}}$,

TABLE 4.—SATURATION ADSORPTION OF POLY-ETHOXY-ALKYLPHENOLS

phenol	molar ratio $C_2H_4O = n$	saturation adsorption (Å^2/per mole.)	saturation adsorption/$n^{\frac{1}{2}}$
octylphenol	8·5	53	18·2
nonylphenol	9·5	55	17·8
,,	10·5	60	18·5
,,	15	72	18·6
,,	20	82	18·3
,,	30	101	18·4
,,	100	173	17·3

n is the mean number of ethoxy-groups per molecule.

With increasing length of the polyethylene oxide chains, the number of ether groups in the interface, at constant detergent adsorption, would increase in proportion to n. If we assume that because of hydration, at saturation adsorption, the ether groups can only occur in specific maximal density, the surface area per non-ionic molecule must increase proportional to $n/n^{\frac{1}{2}} = n^{\frac{1}{2}}$, as found experimentally.

SIMULTANEOUS ADSORPTION OF DIFFERENT DETERGENTS

From the experimental data, again a table of increments in surface area due to the presence of the other surfactant was prepared.

TABLE 5.—MUTUAL EFFECT OF VARIOUS SURFACTANTS EXPRESSED AS INCREMENTS OF THEIR SURFACE AREAS PER MOLECULE

hydrophilic groups in the interface	nature of the interface	increment of soap (Å^2/ion)	increment of non-ionic, Å^2/mole
$COH + COO^-$	air/water	10	2·5
$SO_3^- + COH$	benzene/water	11	—
$CON(C_2H_4OH)_2 + COO^-$	air/water	30	0

The most striking result is that the adsorption of the non-ionic is virtually unchanged by the presence of soap, whereas the saturation adsorption of the soap is markedly affected by the presence of the non-ionic. If we assume again, that two hydrophilic groups of different basicity increase their energy of hydration mutually, this effect will be greatest if the two groups are present at the interface in approximately equal amounts. Since our experiments show that the saturation adsorptions of the non-ionics are lower than those of the soaps, an approximation of the 1 : 1 ratio can only be obtained by lowering the soap adsorption, and this is in conformity with what has been found experimentally. Comparison of the increment of the soap area caused by alcohol (10 Å^2) with the increments found for additional hydrophilic groups in one soap, reveals that it is intermediate between the increments of the amide group (3·4 Å^2) and those of the ether group (ca. 20 Å^2). This is what would be expected from the relative basicities. It seems that the influence of soaps with different hydrophilic groups on their mutual adsorption resembles that found in the case of additional hydrophilic groups in one soap. For example, the adsorption area of sodium undecylsulphonate at the methyl caprinate/water interface in the presence of free fatty acid increases from 70 Å^2/ion for the pure ester to ca. 110 Å^2/ion for the impure ester. This is in agreement with the marked drop in the adsorption that has been observed with soaps having more functional groups including COOH (table 3).

Analogous to our observation that the increment in surface area/ion increases with the number of hydrophilic groups in the detergent, it is found that the poly-functional di-ethanolamide group brings about a greater increase in the area/soap ion than a simple alcohol.

The hypothesis that the hydration of the hydrophilic groups sets a limit to the adsorption of detergents at interfaces, is seen to afford a satisfactory explanation of our observations. A quantitative development is hampered by lack of quantitative data about this hydration. However, the data collected may suffice in many cases to predict the adsorption behaviour of detergents on the basis of their chemical structure.

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