THE SURFACE ACTIVITY OF 1,16-HEXADECANE DISODIUM SULPHATE AT THE AIR:WATER INTERFACE

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The surface tensions of 1,16-hexadecane disodium sulphate in 0·001, 0·2 and 1·0M l.$^{-1}$ sodium chloride solutions have been determined by the Wilhelmy plate method. Considerable ageing effects were noted. The minimum molecular areas calculated were 95, 88 and 86 sq. Å respectively in the three salt solutions. The lowering of the surface tension was not as great as that caused by sodium dodecyl sulphate, and the hydrocarbon chain linking the two head groups in 1,16-hexadecane disodium sulphate appeared to prevent very close packing in the surface layer.

THE introduction of a second polar group, remote from the first, into the structure of normal soaps, has been found[1] to decrease the size of the aggregates formed. Studies with dipotassium 1,16-hexadecanedioate disclosed a concentration limit at 10 to 11 mM l.$^{-1}$, where the solute aggregated to give dimers.

It is of interest to study the surface tensions of solutions of this type of material; to ensure freedom from hydrolysis in dilute solution 1:16-hexadecane disodium sulphate (HDS) was chosen.

EXPERIMENTAL

Materials. 5 g. (0·019 mole) of 1,16-hexadecanediol was dissolved in 20 ml. glacial acetic acid, and 4·6 g. (0·038 mole) of chlorosulphonic acid added slowly to the solution, which was stirred and kept cool. After allowing to warm up to room temperature and stirring for a further thirty minutes, the mixture was neutralised with solid NaHCO$_3$. The crude HDS was extracted with two 50 ml. portions of boiling 90 per cent ethanol; on cooling the extract crude HDS crystallised. The solid was recrystallised three times from water, dried, extracted for 96 hours with ether to remove traces of glycol, and recrystallised three times from conductivity water. Analysis for sulphur gave 13·92 per cent (theoretical 13·89 per cent). Commercial methanol was fractionally distilled and the product had b.p. 64·7°, n$_D^{15}$ 1·3303. (Timmermans[2] gives b.p. 64·75°, n$_D^{15}$ 1·33057.) Ion exchanged water was distilled from a seasoned still. The sodium chloride used was Analar quality.

Surface tensions were measured by the Wilhelmy plate method[3,4]. A thin platinum plate was suspended from one arm of a chainomatic balance reading to 0·1 mg.; the balance rested on a platform movable in the vertical direction by a rack and pinion device. The exact point where

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the lower edge of the plate just touched the liquid surface could be determined by slowly lowering the balance platform. The weight required (G) to raise the plate from the interior of the liquid to this point in the surface was determined. To ensure zero contact angle, all measurements were made by lifting the plate from the interior of the liquid, also the liquid was placed in a tall flask which was almost submerged in a thermostat. This ensured a saturated atmosphere, which prevented evaporation from the line of contact between liquid and plate. All glassware and the plate were cleaned in chromic acid before use.

The surface tension, γ, was calculated from

$$\gamma = g \frac{(G - W)}{1}$$

where W was the weight of the dry plate in air, and 1 was its perimeter. All measurements were made at $25° \pm 0·05°$.

RESULTS

A check of the apparatus was made by measuring the surface tensions of water and methanol. Water at 25° gave $\gamma = 71·92$ dynes cm.$^{-1}$ (71·97); at 20°, $\gamma = 72·64$ dynes cm.$^{-1}$ (72·65). Methanol at 25°, $\gamma = 22·15$ dynes cm.$^{-1}$ (22·18)[2]. These results were in good agreement with literature figures, which are given in brackets.

Ageing effects were observed with all solutions of HDS. The Wilhelmy plate method proved to be particularly useful in studying these changing surface tensions. Some examples of surface ageing are given in Table I.

The surface tensions of the salt solutions alone were found to be constant, within experimental error, over the time-period studied. For HDS solutions, a constant value of the surface tension was generally obtained in 1 to 2 hours; equilibrium appeared to be reached faster in the more concentrated salt solutions.

FIG. 1. Plot of surface tension, γ, against log (normality HDS).

The results for the variation of surface tension with concentration are shown in Figure 1. All curves showed a break at the critical micelle concentration (CMC), the break becoming more pronounced as the salt concentration was increased. No minimum was observed in any of the
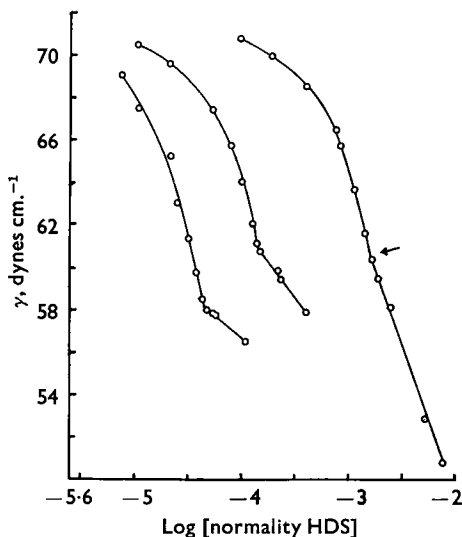
curves, demonstrating the purity of the HDS sample. The values of the CMC's were:

NaCl concentration, M l.$^{-1}$ ..   1·0   0·2   0·001

CMC, mM l.$^{-1}$ ..   ..   0·0215   0·0700   0·79

TABLE I

SURFACE TENSION AGEING EFFECTS WITH SOLUTIONS OF HDS

Surface tensions in:—

Time (mins.)	0·00M l.$^{-1}$ NaCl		0·2M l.$^{-1}$ NaCl		1·0M l.$^{-1}$ NaCl	
	Alone	+0·001386N HDS	Alone	+0·0001243N HDS	Alone	+0·00003156N HDS
0	71·9$_0$	67·2	71·9$_8$	65·2	73·2$_9$	63·0
5		66·4		64·7		62·5
10		65·8		64·2		62·2
20		64·5		63·8		61·8
30		63·5		63·4		61·6
40		62·8		63·2		61·4
50		—		63·1		61·3
60	71·8$_8$	62·2	72·0$_2$	62·8	73·3$_1$	61·3
80		61·9		62·4		—
100	71·9$_4$	61·7	72·0$_6$	61·1	73·3$_0$	61·4
120		61·6		61·0		—
140		61·7		61·1		—
180	71·9$_1$	61·6	72·0$_4$	61·1	73·2$_7$	61·3
240	71·9$_3$	61·6	72·0$_5$	61·1	73·2$_9$	61·3

DISCUSSION

The surface excess, τ_2, of a solute, at constant temperature and pressure, when the surface excess of the solvent is zero, has been shown to be related to the change in surface tension, $d\gamma$, and to the chemical potential, μ_2, of the solute by:

$$-d\gamma = \tau_2 d\mu_2 \qquad .. \qquad .. \qquad .. \qquad (1)$$

and as $d\mu_2 = RTd\ln a_2$, where a_2 is the activity of the solute,

$$-d\gamma = RT\tau_2 d\ln a_2 \qquad .. \qquad .. \qquad .. \qquad (1a)$$

For dilute solutions this equation approximates to

$$-d\gamma = RT\tau_2 d\ln c \qquad .. \qquad .. \qquad .. \qquad (2)$$

where c is the molar concentration.

For electrolytes the situation is more complicated. In the case of a 1:1 electrolyte (for example, sodium dodecyl sulphate Na^+DS^-) it has been suggested that the Gibb's equation should be written[5,6] as:

$$-d\gamma = 2RT\tau_2 d\ln a_{\pm} \qquad .. \qquad .. \qquad .. \qquad (3)$$

where $a_{\pm}$ is the mean activity, as for a completely dissociated univalent electrolyte

$$d\mu_2 = 2RTd\ln a_{\pm}$$

Results from radioactive isotope[7] and spread monolayer experiments[8] indicate that equation (3) does not always hold.

If the detergent is considered in the presence of an electrolyte with which it has one ion in common, certain simplifying assumptions[9] can be made, which lead to the use of equation (1a) for determining the surface excess. The results for τ_2 now agree with those from the radio-isotope and spread monolayer experiments.

In the present study, equation (2) is applied by considering each end of the molecule separately. The concentration term in (2) is taken as the normality, and from τ_2 the area of half the molecule can be obtained. The total area : molecule (A) is plotted against the surface pressure (π) in Figure 2 (1), (ii) and (iii).
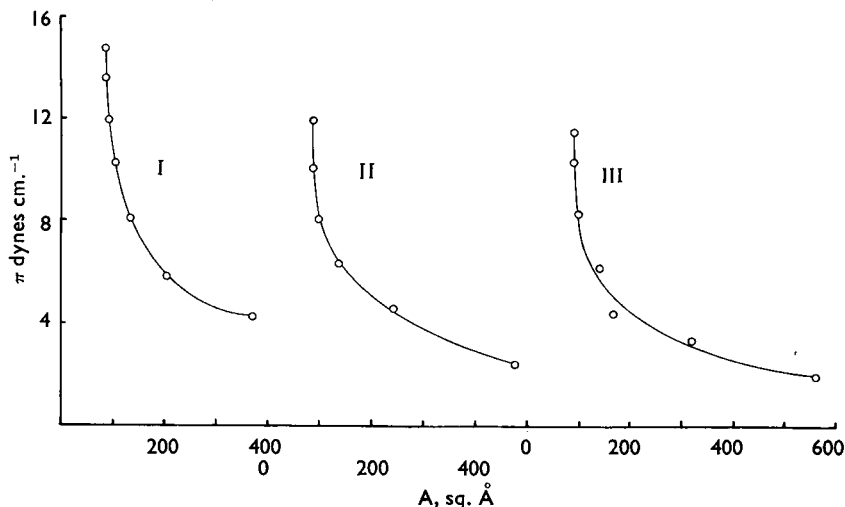

FIG. 2. Force (π)—area (A) curves for HDS in different sodium chloride concentrations. I, 1·0; II, 0·2; III, 0·001 M l.$^{-1}$ NaCl.

All π-A plots follow the same general pattern : there is a slow increase of π with decreasing area, till at about 120 to 150 Å, the surface pressure begins to increase sharply. This increase presumably corresponds to the point where the film begins to be close packed. The limiting areas at the highest surface pressures are given in Table II.

TABLE II

MOLECULAR AREAS AT HIGH SURFACE PRESSURES

NaCl concentration, M l.$^{-1}$		1·0	0·2	0·001
HDS at 25°, sq. Å		86	88	95
NaDS at 20°, sq. Å		27	33	59

Figures for sodium dodecyl sulphate are included for comparison.

Figures for sodium dodecyl sulphate are included for comparison.

The structure of the HDS film at the air : water interface is suggested to be the one in which both polar head groups are immersed in the water, and the hydrocarbon chain pressed up above the surface. In 1·0 and 0·2M l.$^{-1}$ sodium chloride solutions, the area : molecule for HDS is more than double that for NaDS. This indicates that the hydrocarbon chain prevents as close a packing as is given by NaDS. It would appear that the degree to which the hydrocarbon chain can be bent

effectively limits the area : molecule. Spread monolayers of NaDS on 75 per cent ammonium sulphate solutions gave a limiting area of approximately 20 sq. $Å^9$, and this value approaches the maximum amount to which NaDS can be compressed. It is obvious from these figures that the two head groups of HDS are not forced close together. It will be noted (Table II) that for NaDS a change of 22 sq. Å occurs on increasing the salt concentration from 0·001 to 1·0M $l.^{-1}$. For the same change in salt concentrations, HDS shows a change in the area : molecule of 9 sq. Å.

A crude idea of the shape of the HDS molecule at maximum compression can be gained by studying models. The fully extended molecule has an area of 120 sq. Å. A moderate amount of bending of the chain reduces the area : molecule to 80 to 90 sq. Å and a certain amount of strain will be imposed on the chain in a configuration of this type. Bending the chain until the two head groups touch imposes a great deal of strain, and gives an area : molecule of 60 to 70 sq. Å. The area : molecule obtained experimentally at the highest salt concentration (86 sq. Å) is compatible with a slightly bent chain.

The amount of surface tension lowering given by HDS is not as great as that given by NaDS. It is to be expected that fewer head groups per unit area can be forced into the surface by HDS than by NaDS. At 25° the CMC of NaDS is 0·785 mM $l.^{-1}$ in 0·2M $l.^{-1}$ sodium chloride, while in the same salt solution HDS has a CMC of 0·0700 mM $l.^{-1}$.

No ageing effects have been reported[10] for NaDS in salt solutions after the first few minutes. The ageing with HDS may be due to either the bending of the hydrocarbon chain, or difficulty in moving a molecule from the bulk to the surface.

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