SURFACE ACTIVITY OF A SERIES OF SYNTHETIC NON-IONIC DETERGENTS

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IN contrast to ionic detergents, the non-ionic type provides an opportunity to alter the hydrophilic portion of the molecule by varying the number of ethylene oxide units in the polyoxyethylene chain; lengthening this chain increases the hydrophilic properties of the molecules. A series of compounds based on hexadecyl alcohol, of general formula:

$$Me(CH_2)_{15}(OCH_2CH_2)_nOH$$

where n varied from six to twenty-one, has been synthesised (Elworthy and Macfarlane, 1962). A study of their micellar shape and hydration has been made. In the present communication the critical micelle concentrations (CMC) and areas/molecule at the air/water interface are reported.

APPARATUS AND METHOD

Surface tension measurements were made using the Wilhelmy plate method (Harkins and Anderson, 1937). A depolished platinum plate, perimeter, $1 = 6\cdot045$ cm., was suspended from the arm of a torsion balance, sensitivity $\pm 0\cdot2$ mg. The flask containing the solution was lifted by a rack and pinion device until the plate just touched the surface of the solution. The weight to lift 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 in this manner, and a saturated atmosphere was maintained above the solution. The difference between the weight of the plate in air and in the surface, W, is related to the surface tension, γ, by

$$\gamma = Wg/1$$

Measurements were made at $25° \pm 0\cdot01°$. All glassware and the plate were cleaned with chromic acid, followed by thorough rinsing in distilled water. All flasks containing solutions were set aside for 3 hr., the flasks thoroughly drained, and fresh solutions made up in the same flasks. This procedure compensates for adsorption of solute by the glassware.

RESULTS AND DISCUSSION

A check of the apparatus was made by measuring the surface tension of water, $\gamma = 72\cdot0$, $72\cdot1$ dynes/cm. (Harkins, 1959, gives $72\cdot0$ dynes/cm.), and of methanol, $\gamma = 22\cdot3$ (Timmermans, 1950, gives $22\cdot2$ dynes/cm.). Ageing effects were noted for all but the most concentrated solutions

studied; for a 9.59×10^{-7} mole/litre solution of hexaoxyethylene glycol monohexadecyl ether (Hn_6), the results were:

Time, hr. ..	0	1	2	3	4	5	7	9	10	26
γ, dynes/cm. ..	71·1	61·2	49·7	44·4	41·1	39·7	38·5	38·3	38·3	38·3

This effect may be due to a slow diffusion from the bulk to the surface, together with the possibility that considerable orientation of the molecules has to take place in the surface layer before equilibrium is reached.
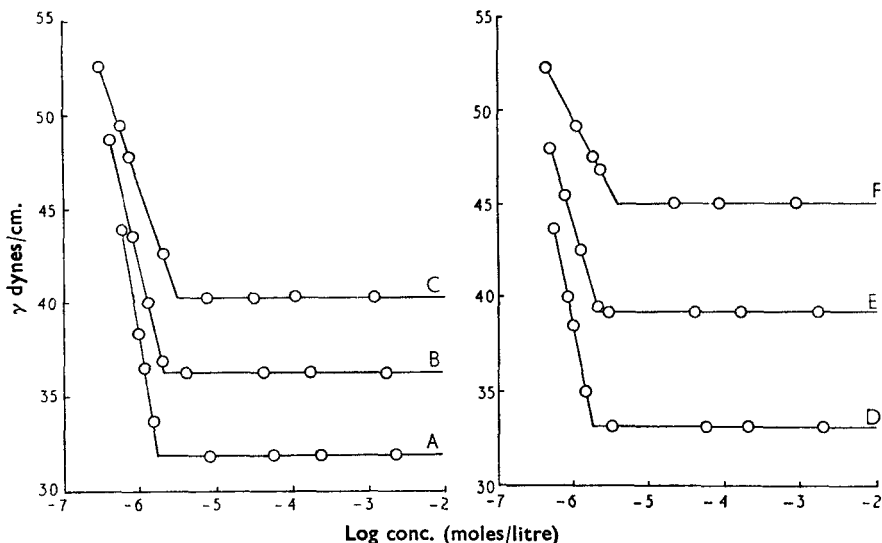

FIG. 1. Surface tension/log concentration plots for
$$Me(CH_2)_{15} (OCH_2CH_2)_n OH$$
A, $n = 6$, Hn_6; B, $n = 9$, Hn_9; C, $n = 15$, Hn_{15};
D, $n = 7$, Hn_7; E, $n = 12$, Hn_{12}; F, $n = 21$, Hn_{21}

In Figs. 1 and 2 the surface tensions of the detergents have been plotted against log concentration (moles/litre). From these graphs the CMCs were determined, and by using the simple form of the Gibbs' equation to calculate the surface excess, the areas/molecule were found.

Detergent	Hn_6	Hn_7	Hn_9	Hn_{12}	Hn_{15}	Hn_{21}
CMC, 10^6 moles/litre	1·6_6	1·7_4	2·0_9	2·3_4	3·0_9	3·8_9
Area/molecule (Å²) ..	38	44	53	72	81	120
Area/(CH_2CH_2O) (Å²) ..	6·3	6·3	5·9	6·0	5·4	5·7

It can be seen that a lengthening of the polyoxyethylene chain increases the CMC. This is a result of the increase in the hydrophilic properties of the molecule, which is in line with the fall in the micellar weight from 1.27×10^6 for Hn_6 to 8.2×10^4 for Hn_{21} (Elworthy and Macfarlane, 1962). The CMCs are represented by the equation:

$$\log CMC = -5.93 + 0.0245n$$

Hn_{21} falls in the range for cetomacrogol ($n = 20 - 24$), the CMC of which is higher than that of the synthetic material ($8 - 50 \times 10^{-6}$

moles/litre Hugo and Newton, 1960; Elworthy, 1960) which may be due to the polydisperse nature of cetomacrogol.

As the areas/molecule obtained are all larger than the cross sectional area of the hydrocarbon chain ($20 \cdot 5 \text{Å}^2$), it appears that the polyoxyethylene chain determines the area/molecule. Several workers have shown that the polyoxyethylene chain is considerably curled up in solution (Elworthy and Macfarlane, 1962; Rosch, 1961), and it seems likely that the chain is probably orientated in a position roughly parallel to the surface. The area/ethylene oxide unit *decreases* as the chain length *increases*. One end of the chain will be anchored to the surface by the hydrocarbon portion of the molecule, but the end remote from this point may be less strongly adsorbed at the surface, and may tend slightly away from it.

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