52. *Chemistry of Non-ionic Detergents. Part VI.*[1] *An Empirical Method for Estimating Micellar Hydration.*

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Measurements of vapour pressure over concentrated gels and solutions of non-ionic detergents have been used to obtain micellar hydration. These results agree with values for hydration deduced from viscosity measurements. The polyoxyethylene chain seems likely to take up a coiled configuration in the micelle; the trapping of water molecules in the micelles, and the variation of hydration with temperature, are discussed.

IN Part V,[1] light scattering and viscosity results were combined in calculating the micellar shapes and sizes of a series of synthetic non-ionic detergents $CH_3 \cdot [CH_2]_{15} \cdot [O \cdot CH_2 \cdot CH_2]_x \cdot OH$ (abbreviated to Hn_x), where x was 6—21. As the series was ascended the asymmetry of the micelles decreased, while the hydration increased. As no independent method of determining micellar hydration was available, certain assumptions about this quantity had to be made.

The solubility of non-ionic detergents in water is attributed to hydration of the polyoxyethylene chains. Oncley's[2] treatment enables both hydration and asymmetry to be related to the viscosity intercept, $(\eta_{sp}/\phi)_{\phi=0}$, but the problem in this analysis is to separate the two effects. Studies of hydration by means of polarimetry,[3] heats of solution,[4] and viscosity maxima[5] have been reported, but do not appear to be very satisfactory. In this paper, a tentative method for assessing hydration is proposed, in which the vapour pressure over gels and solutions of non-ionic detergents is measured, to determine the concentration at which the vapour pressure becomes equal to that of pure water. This estimate of hydration is compared with that obtained from viscosity results.[6] A similar procedure has been used to determine the hydration of phosphatide micelles in solution.[7]

EXPERIMENTAL AND RESULTS

Materials.—The preparation and properties of detergents with $x = 6, 7, 9$, and 12, have been reported.[1,8] A commercial sample of Hn_{24} was also used, being thoroughly dried before use and having a mean molecular weight (ethylene oxide assay) of 1295 (theor., 1300). The other compounds were synthetic materials.

Vapour-pressure Measurements.—These were made by the direct manometric method in an apparatus similar to that of Gibson and Adams.[9] The manometer liquid was a high-vacuum pump-oil (Edwards no. 18) for work at 20° and 25°, and mercury for work at 30°. Gels or solutions of detergent in water were introduced into the apparatus, and outgassed at 0·001 mm. The apparatus was transferred to a thermostat-bath controlled to 25° ± 0·01°, except for additional measurements on Hn_7 made at 20° and 30°, until the gel–water vapour phase had equilibrated (generally 1—3 hr.). Tests for equilibrium were carried out for 1—4 weeks. The vapour pressure of the gel, and of pure water contained in another part of the apparatus, were measured; a sample of gel was removed and analysed for water content by drying to constant weight. The vapour pressure of water at 20°, 25°, and 30° was found to be 17·50, 23·72, and 31·80 mm., respectively, is in reasonable agreement with recorded values[10] of 17·54, 23·76, and 31·82 mm.

[1] Part V, Elworthy and Macfarlane, *J.*, 1963, 907.
[2] Oncley, *Ann. New York Acad. Sci.*, 1940, **41**, 121.
[3] Karabinos, Hazdra, and Ballun, *Euclides*, 1955, **15**, 145.
[4] Karabinos and Metziger, *Trans. Illinois Acad. Sci.*, 1956, **48**, 118.
[5] Boehmke and Heusch, *Fette u. Seifen*, 1960, **62**, 87.
[6] Rosch, *Kolloid-Z.*, 1956, **147**, 78.
[7] Elworthy, *J.*, 1961, 5385.
[8] Elworthy and Macfarlane, *J.*, 1962, 537.
[9] Gibson and Adams, *J. Amer. Chem. Soc.*, 1933, **55**, 2679.
[10] Stokes and Robinson, " Electrolyte Solutions," Butterworths Scientific Publns., London, 2nd edn., 1959, p. 457.

Results.—In Figs. 1 and 2, plots of vapour pressure (p) against (a) g. of water per 100 g. of detergent are given. The concentration, w, at which the vapour pressure, within experimental error, becomes equal to that of pure water, increases steadily with polyoxyethylene chain length. Values of w were obtained by constructing isotherms of a/x against x, where x is the relative vapour pressure. The isotherms were linear above $x = 0.8$, enabling extrapolation to $x = 1$

TABLE 1.

Micellar hydration w (g. of water per g. of detergent) determined from the vapour pressure.

Detergent ...	Hn_6	Hn_7	Hn_9	Hn_{12}	Hn_{24}	Hn_7 (20°)	Hn_7 (30°)
w	0·39	0·44	0·65	0·96	2·18	0·28	0·52

to be made (Fig. 3). Values of w so obtained are given in Table 1.* When the results at 25° were plotted as g. of water (mole of detergent)$^{-1}$ × (No. of ethylene oxide units)$^{-1}$ = y, against the number of ethylene oxide units in each detergent = x, a good straight line was obtained, fitting the equation, $y = 4.3 + 4.73x$. Values of w for Hn_{15} and Hn_{21} were interpolated from this graph.

As water is progressively added to the solid detergent, break-down of the crystal structure occurs. Hydration of the polyoxyethylene chains leads to the formation of colloidal particles, having micellar weights in the region 10^5—10^7. Even in large concentrations, solutions of these particles will have a vapour pressure indistinguishable from that of water, within experimental error. The measured value of w is suggested as an estimate of micellar hydration.
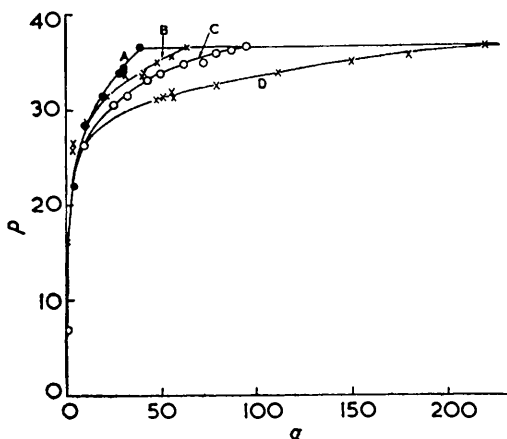

FIG. 1. Plots of p (cm. oil) against a at 25° for: A, Hn_6; B, Hn_9; C, Hn_{12}; D, Hn_{24}. See text for symbols.

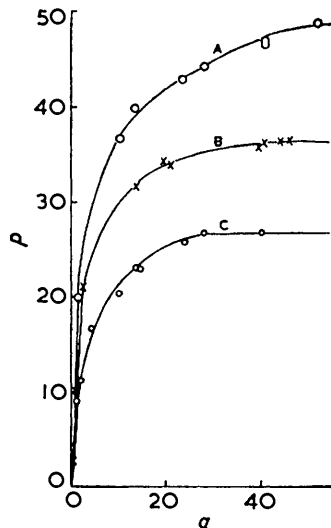(Horizontal lines show the vapour pressure of pure water.)

FIG. 2. Plots of p (cm. oil) against a for Hn_7 at: A, 30°; B, 25°; C, 20°.

It would be expected that the activity of the solvent would be given by an equation of the Flory–Huggins type for gels with a low water content. The activity would rise as water was added, until a point was reached where the micelles began to become detached from one another. The system at that stage would consist of very large particles mixed with water, and entropy effects (and hence their influence on the solvent activity) would be very small, so that the vapour pressure becomes, within experimental error, that of water. The extrapolation to $x = 1$ determines the ratio of water to detergent at the point of separation of micelles, and should give a measure of the amount of water required to hydrate the polyoxyethylene chains. At present this method of determining micellar hydration is empirical but it will be shown below that it yields results agreeing well with those obtained from viscosity measurements.

* No phase changes occurred at points on the isotherms where $x = 1$. We thank a Referee for raising this point.

There is no physical reason why detergents containing long polyoxyethylene chains should form other than spherical micelles at normal temperatures, enabling the Oncley equation to be used to calculate w, and a comparison to be made with the value obtained from vapour-pressure measurements. This is done in Table 2.

The agreement is good, except for Hn_7 at 20°. This system gives a viscosity intercept of 2·86, close to the Einstein value for unhydrated spheres of 2·5. The statistical method described [8] in Part III was used to calculate the limits of error of the viscosity intercept, and hence

TABLE 2.

Comparison of w from vapour pressure and viscosity methods.

Detergent	Hn_9	Hn_{12}	Hn_{15}	Hn_{21}	Hn_{22} *	Hn_7 (20°)
w (vapour pressure)	0·65	0·96	1·24	1·86	1·96	0·28
w (viscosity)	0·72	0·95	1·23	1·85	1·96	0·15

* Hn_{22} was a commercial sample studied in Part I.[11]

of w, giving $w = 0.15 \pm 0.16$ g. of water per g. of detergent. This lack of precision is due to the small differences in viscosity between solutions and solvent, and satisfactorily accounts for

Fig. 3. Plots of a/x against x for Hn_7 at three temperatures, and for the other detergents at 25°. See text for symbols.
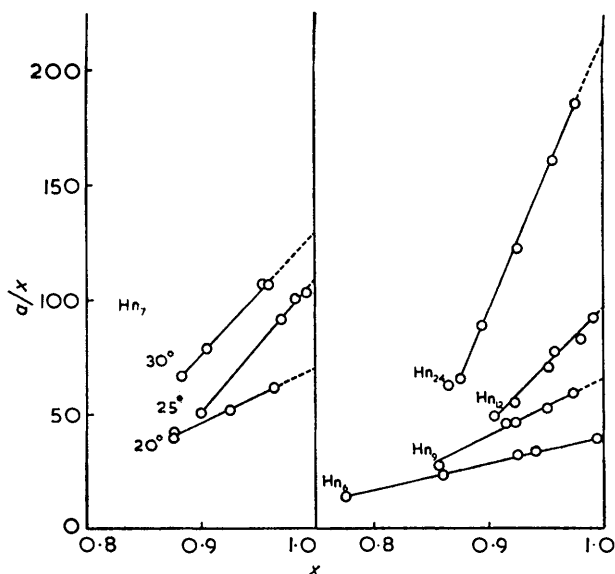
the differences between the results from the two methods. Compounds giving larger viscosity intercepts yielded more precise estimates of w, *e.g.*, for Hn_9, $w = 0.65 \pm 0.06$. The error in the vapour-pressure estimates of w is $\pm 10\%$. In spite of viscosities being measured on dilute solutions and vapour pressures on concentrated ones, the overall agreement between the two sets of results is sufficiently good to suggest that the vapour-pressure method can be tentatively used to determine the hydration of non-ionic detergents.

It appears that only Hn_6 and Hn_7 (at 25° or higher temperatures) gave asymmetric micelles, as shown by the viscosity intercepts. In Part V [1] assumptions concerning possible maximum and minimum micellar hydration had to be made, as no method for determining w was available. If the values of w from Table 1 are used, the number (n) of monomers in the micelle and the molecular volume of the monomer lead to the following values of the major (a) and minor (b) axes for a prolate ellipsoidal model of the micelles: Hn_6, $a = 442°$, $b = 40\text{Å}$; Hn_7, $a = 182°$, $b = 32$ Å.

The results for Hn_7 show that hydration increases with temperature. From plots of a against x (analogous to " sorption " isotherms), the differential heats of hydration ($\Delta \overline{H}$),

[11] Elworthy, *J. Pharm. Pharmacol.*, 1960, **12**, 260т.

assumed to be linear over the 20—30° temperature interval, and the differential entropies of hydration $(\Delta\overline{S})$ at 25°, were obtained by the the the use of conventional equations [12] (see Table 3).

TABLE 3.

Thermodynamic properties.

a	5	10	15	20	25	30
$\Delta\overline{H}$ (kcal. mole^{-1})	1·1	1·1	1·3	1·5	1·5	1·5
$\Delta\overline{S}$ (cal. mole^{-1} deg.$^{-1}$)	4·5	4·2	4·6	5·3	5·3	4·9

DISCUSSION

By using the mean value of w from Table 2, calculations of the total micellar volume, V, and radius, r_m, were made for the four largest synthetic detergents. The volume of micelle attributed to the hydrocarbon region depends on the arrangement of hydrocarbon chains in the micelle centre, *i.e.*, whether the radius of this region is taken as the length of the extended hexadecyl chain, which implies an arrangement similar to that of a solid, or whether the radius is calculated from the equation:

$$r_h = [3(\text{molecular volume hexadecane} \times n)/4\pi]^{\frac{1}{3}}.$$

The second method seems the more reasonable, as the hydrocarbon region is likely to be a liquid phase, and it was used in calculating r_h (see Table 4).

TABLE 4.

Micellar dimensions.

Detergent	$10^5 M$	$10^5 V$ (Å^3)	r_m (Å)	r_h (Å)	r_e * (Å)	r_e/x (Å)
Hn$_7$ (20°)	0·93	2·0$_1$	36·4	27·0	9·4	1·34
Hn$_9$	1·40	3·9$_2$	45·4	29·4	16·0	1·77
Hn$_{12}$	1·17	3·7$_5$	44·7	26·0	18·7	1·56
Hn$_{15}$	1·03	3·7$_2$	44·6	23·6	21·0	1·40
Hn$_{21}$	0·82	3·7$_2$	44·6	20·1	24·5	1·17

* r_e = Radius of micelle occupied by polyoxyethylene chain. r_e/x = Radius per ethylene oxide unit. M for Hn$_{15}$, interpolated from a graph of M against $1/x$.

The volumes of the hydrated micelles at 25° are remarkably constant, provided the detergents contain a sufficient number of ethylene oxide units to be spherical. If this behaviour is general for a series of non-ionic detergents based on a particular hydrocarbon, then, at a known temperature, the micellar weight can be obtained from viscosity measurements, once the volume (V) is known. While the radial length of the polyoxyethylene part of the micelle increases with chain length, the length occupied by each unit decreases.

Two principal types of arrangement of the polyoxyethylene chains in the micelles have been suggested: [13] a random arrangement, or an expanding spiral. Also, recent papers [14] have supported the idea of a curled chain in solution; examination of molecular models constructed to fit the dimensions given (Table 4) shows that the spiral arrangement is satisfactory, providing space for trapping of water molecules both inside and between the spirals.

The actual arrangement of water molecules relative to the polyoxyethylene chains is subject to conjecture. Oxonium derivatives, hydrogen bonding, and various types of orientation of water molecules have been suggested.[5,15,16] Kushner and Hubbard [16] found

[12] Barrer and Kelsey, *Trans. Faraday Soc.*, 1961, **57**, 452.
[13] Schick, Atlas, and Eirich, *J. Phys. Chem.*, 1962, **66**, 1326.
[14] Elworthy and Macfarlane, *J. Pharm. Pharmacol.*, 1962, **14**, 100т; Rosch, *Kolloid-Z.*, 1957, **150**, 153.
[15] Chwala and Martina, *Textile Rundschau*, 1947, 147; Wurzschmitt, *Z. analyt. Chem.*, 1950, **130**, 105.
[16] Kushner and Hubbard, *J. Phys. Chem.*, 1954, **58**, 1163.

43 water molecules associated with a ten-unit polyoxyethylene chain in Triton X100 micelles, and suggest that 20 of these were hydrogen-bonded to the ether-oxygen atoms, while the remainder were trapped. Another proposal, of 3—5 water molecules associated with each ether-oxygen atom, has been made.[5] A specific arrangement of water molecules around the ether-oxygen atoms is not in accord with experimental results. Near the surface of the hydrocarbon region, there is less space for the water molecules than further inside the micelle, so the proportion of water molecules for each unit of polyoxyethylene chain can increase as r_e increases. Endothermic $\Delta \bar{H}$ and positive $\Delta \bar{S}$ values were found, indicating that the interaction of water with the chains resembles mixing rather than any specific arrangement of water molecules around the ether-oxygen atoms; at any rate, the mixing process predominates over any orientation effects.

It has been suggested [1,17] that hydration decreases with increasing temperature; the results on Hn_7 show the opposite effect in the 20—30° temperature range. At 20°, the chains form a shorter, tighter spiral than at 25°(r_e; Table 4). Instability of these detergents in aqueous solution may be brought about either by increasing the temperature or by shortening the polyoxyethylene chain. The length of the short semi-axis of the ellipsoid representing the micelle is greater for Hn_6 than for Hn_7, and the former compound gives less stable solutions than the latter. Both increase of temperature and shortening of the chain lead to a more extended configuration for the chain.

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[17] Kuriyama, *Kolloid-Z.*, 1962, **181**, 144.