168. *Chemistry of Non-ionic Detergents. Part V.*[1] *Micellar Structures of a Series of Synthetic Non-ionic Detergents.*

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Light-scattering and viscosity techniques have been used in a study of the micellar properties in aqueous solution of synthetic non-ionic detergents, $C_{16}H_{33}\cdot[O\cdot CH_2\cdot CH_2]_x\cdot OH$, where x is 6—21. The largest detergent studied ($x = 21$) had a micellar weight of 82,000, the micelles being approximately spherical; as the series was descended the micellar size increased while the hydration decreased. Compounds where $x = 6$ or 7 had micellar weights of $1{\cdot}23 \times 10^6$ and $3{\cdot}2_7 \times 10^5$ respectively and were considerably asymmetric. Aggregation of these small micelles into larger ones took place as the concentration was increased. The aggregation was examined by using the mass-action law. The large micelles of the compound ($x = 6$) fitted a coil-like model, while those where $x = 7$ appeared to be rod-like. The micellar structure of the series has been examined in the light of asymmetry and hydration. Studies on the effect of temperature on solutions of compound ($x = 7$) showed that the micelle weight increased from $9{\cdot}3 \times 10^4$ at 20° to $3{\cdot}2_7 \times 10^5$ at 25°, and that the asymmetry of the micelles also increased sharply.

In Part III [2] the syntheses of nona- and dodeca-oxyethylene glycol monohexadecyl ether were reported. The micellar weights, determined by light scattering, were 140,000 and 117,000, respectively. The micellar size decreased with increasing oxyethylene chain length, owing to the increased affinity of the monomer for water; ultimate extension would give a polyoxyethylene material in which the hydrocarbon portion of the molecule would be insignificant, and which therefore would not form micelles. In order to study the decrease in molecular weight with increasing chain length, representative members of the series $CH_3\cdot[CH_2]_{15}\cdot[O\cdot CH_2\cdot CH_2]_x\cdot OH$ (abbreviated to Hn_x), from Hn_6 to Hn_{21} have been synthesised for physicochemical studies. At the low end of the series very large micelles would be expected.

The hydration of non-ionic detergents is an extremely complicated matter. It appears to be due to a trapping of water in the mesh of oxyethylene chains, and it also appears likely that the chains are coiled.[2,3] A commercial sample of Hn_{22} gave a micellar radius [4] of 48 Å, while the fully extended monomer is 101 Å long. Hydration of the micelles will obviously depend on the length of the polyoxyethylene chain, and on their degree of contraction. It will also depend on the geometry of the micelle: a rod-like structure is likely to be less hydrated between the polyoxyethylene chains along the long axis than along the short one. An attempt is made herein to work out some of the structural features of the micelles.

Experimental

Syntheses of Glycols and Detergents.—3,6,9,12,15-*Pentaoxaheptadecane*-1,17-*diol* (*hexaoxyethylene glycol*). This was prepared by the method of Fordyce *et al.*[5] from redistilled diethylene glycol (848 g.; b. p. 106°/0·1 mm., n_D^{20} 1·4509), sodium (46 g.), and 2,2′-dichlorodiethyl ether (143 g.; b. p. 76°/15 mm.). The glycol and dichlorodiethyl ether were redistilled immediately before use. After removal of the excess of glycol, the hexaoxyethylene glycol was distilled; it (140 g.) had b. p. 182°/0·01 mm., n_D^{38} 1·4589 (Found: C, 50·9; H, 9·1; $CH_2\cdot CH_2\cdot O$, 93·5. Calc. for $C_{12}H_{26}O_7$: C, 51·1; H, 9·3; $CH_2\cdot CH_2\cdot O$, 93·6%).

3,6,9,12,15,18-*Hexaoxaeicosane*-1,20-*diol* (*heptaoxyethylene glycol*). Sodium (46 g.) was slowly

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[1] Part IV, Elworthy and Macfarlane, *J. Pharm. Pharmacol.*, in the press.
[2] Elworthy and Macfarlane, *J.*, 1962, 537.
[3] Rosch, 3rd Internat. Congress on Surface Activity, section A, p. 163, Mainz Univ. Press, 1961.
[4] Elworthy, *J. Pharm. Pharmacol.*, 1960, **12**, 260T.
[5] Fordyce, Lovell, and Hibbert, *J. Amer. Chem. Soc.*, 1939, **61**, 1905.

dissolved in redistilled diethylene glycol (848 g.) by stirring under a layer of light petroleum (b. p. 100—120°) at $\not>$70°. Ethylene bis-(2-chloroethyl ether)[2] (187 g.) was added and the mixture stirred at 115° until neutral (4 hr.). Precipitated salt was filtered off and the excess of triethylene glycol removed by distillation. Vacuum-distillation of the residue gave *hepta-oxyethylene glycol* (103 g.), b. p. 201/0·01 mm., n_D^{38} 1·4600 (Found: C, 51·6; H, 9·3; $CH_2{\cdot}CH_2{\cdot}O$, 94·5. $C_{14}H_{30}O_8$ requires C, 51·5; H, 9·3; $CH_2{\cdot}CH_2{\cdot}O$, 94·5%).

1-*Chloro*-3,6,9,12,15,18,21,24,27-*nonaoxatritetracontane*. The monohexadecyl ether of nonaoxyethylene glycol was prepared as described previously.[2] This compound (10 g.) was heated under reflux with an excess of thionyl chloride (2·25 g.) for 4 hr. The volatile by-products of the reaction and excess of thionyl chloride were removed by heating the mixture under reduced pressure and then by distilling three 15 ml. portions of benzene from the residue. The final residue was dissolved in benzene (25 ml.) and washed with water (3 × 5 ml.). The washings were shaken with ether (10 ml.), and this ethereal layer was added to the benzene extract. After removal of the solvents, the residue (10 g.) was dried over phosphorus pentoxide. This material (5 g.) was adsorbed from benzene on to alumina (100 g.), and the column washed with 1 : 5 acetone–benzene until no further material was eluted (600 ml.). Evaporation of the eluate and recrystallisation of the residue from ether gave the *chloro-derivative* (4·55 g.), m. p. 39·5° (Found: C, 62·0; H, 10·7; Cl, 5·5. $C_{34}H_{69}ClO_9$ requires C, 62·1; H, 10·6; Cl, 5·4%).

3,6,9,12,15,18-*Hexaoxatetratriacontan*-1-*ol* (*hexaoxyethylene glycol monohexadecyl ether*, Hn_6). Sodium (2·3 g.), hexaoxyethylene glycol (112 g.), and hexadecyl bromide[2] (30·5 g.) gave, by the method described earlier for Hn_9, a *product* (18 g.) that, crystallised and chromatographed in the same way, had m. p. 37° (Found: C, 66·1; H, 11·5; $CH_2{\cdot}CH_2{\cdot}O$, 52·3. Calc. for $C_{28}H_{58}O_7$: C, 66·4; H, 11·5; $CH_2{\cdot}CH_2{\cdot}O$, 52·2%).

3,6,9,12,15,18,21-*Heptaoxaheptatriacontan*-1-*ol* (*heptaoxyethylene glycol monohexadecyl ether*, Hn_7). Sodium (1·55 g.), heptaoxyethylene glycol (88 g.), and hexadecyl bromide (20·6 g.) gave, by the method described[2] for Hn_9, a *product* (14 g.) that, crystallised and chromatographed in the same way, had m. p. 38·5° (Found: C, 65·4; H, 11·3; $CH_2{\cdot}CH_2{\cdot}O$, 56·0. $C_{30}H_{62}O_8$ requires C, 65·4; H, 11·3; $CH_2{\cdot}CH_2{\cdot}O$, 55·9%).

3,6,9,12,15,18,21,24,27,30,33,36,39,42,45-*Pentadecaoxaheneihexacontan*-1-*ol* (*pentadecaoxyethylene glycol monohexadecyl ether*, Hn_{15}). Sodium (0·46 g.) was dissolved in hexaoxyethylene glycol (22·6 g.) under a layer of light petroleum (b. p. 100—120°) at $\not>$90°, the above-mentioned chloride (13·1 g.) was added, and the mixture was stirred at 125° until neutral (3 hr.) and extracted with ether and light petroleum.[2] The residue from the extract was recrystallised twice from ether and twice fom acetone. The substance (2 g.) was adsorbed from 1 : 20 acetone–benzene on to alumina (50 g.) and the column washed with 1 : 1 acetone–benzene (600 ml.). This removed 1·3 g. of the initial load. Elution with 1 : 12 : 12 methanol–acetone–benzene (300 ml.) and recrystallisation of the eluted material from acetone gave the *ether*, Hn_{15} (0·45 g.), m. p. 45·5° (Found: C, 60·9; H, 10·7; $CH_2{\cdot}CH_2{\cdot}O$, 73·1. $C_{46}H_{94}O_{16}$ requires C, 61·2; H, 10·5; $CH_2{\cdot}CH_2{\cdot}O$, 73·2%).

3,6,9,12,15,18,21,24,27,30,33,36,39,42,45,48,51,54,57,60,63-*Heneicosanoxanonaheptacontan*-1-*ol* (*heneicosanoxyethylene glycol monohexadecyl ether*, Hn_{21}). Sodium (0·23 g.) was dissolved in dodecaoxyethylene glycol (22 g.), and the above-mentioned chloride (6·6 g.) was added. The mixture was heated, extracted, and chromatographed as for Hn_{15}. Here a better percentage of the initial column load was obtained as Hn_{21}, possibly because of better separation owing to the increased difference in chain length. The *product* had m. p. 48° (Found: C, 59·3; H, 10·2. $CH_2{\cdot}CH_2{\cdot}O$, 79·4. $C_{58}H_{128}O_{22}$ requires C, 59·6; H, 10·2; $CH_2{\cdot}CH_2{\cdot}O$, 79·2%).

Light-scattering Measurements.—The apparatus[6] and methods[2] used have been described. With Hn_6 and Hn_7 extreme care was taken in ageing solutions; they were kept in a thermostat-bath overnight at 25°, and filtered into the light-scattering cell at 25—26°. Turbidities were measured as a function of time until they were constant (generally 30—60 min.). No ageing effects were noted with Hn_{21} solutions. Concentrations were determined interferometrically after filtration.

Viscosities.—In addition to the capillary viscometer used before,[2] a Coutte apparatus[7] was used to check that Newtonian flow was obtained for Hn_6 solutions.

Densities.—Densities of the ethers Hn_{15} and Hn_{21} were determined by displacement in pure dry n-hexane, giving 1·078 and 1·142 g./ml., respectively. Neither of these compounds

[6] Elworthy and McIntosh, *J. Pharm. Pharmacol.*, 1961, **13**, 663.

[7] Ogston and Stanier, *Biochem. J.*, 1953, **53**, 4.

dissolved in the hexane. The short-chain compounds dissolve to a large extent, so the densities of the glycols were measured, giving: n_6, 1·124; n_7, 1·125; n_9, 1·128; and n_{12}, 1·133 g./ml., and the densities of the detergents were calculated from the molar volumes of the glycols, water, and cetyl alcohol (0·842 g./ml.). The density for Hn$_9$ previously given appears to be low, probably because of excessive dissolution in the displacement liquid.

Measurements were made at 25° ± 0·01°, except for light-scattering measurements for which the uncertainty was ±0·1°, and except for certain measurements on Hn$_7$. The precision of density measurements was ±0·001 g./ml.

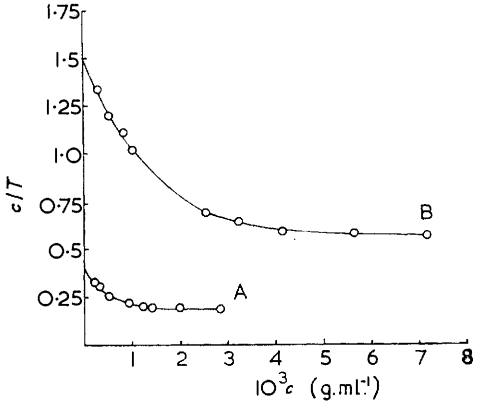

FIG. 1. Plot of c/T against c at 25°. For symbols see text.
A = Hn$_6$. B = Hn$_7$.

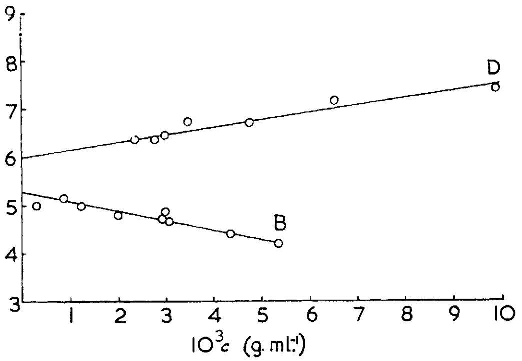

FIG. 2. Plot of c/T against c.
B = Hn$_7$ at 20°. D = Hn$_{21}$ at 25°.

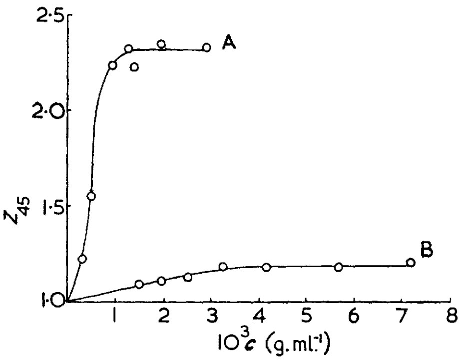

FIG. 3. Plot of Z_{45} against c at 25°.
A = Hn$_6$. B = Hn$_7$.

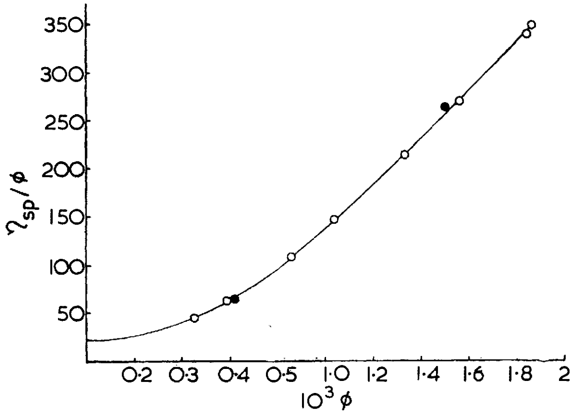

FIG. 4. Plot of η_{sp}/ϕ against ϕ for Hn$_6$ at 25°. For symbols see text. ○, By suspended level viscometer; ●, by Couette viscometer.

RESULTS

The light-scattering results are given in Figs. 1 and 2 as plots of c/T against c, where c is the concentration in g./ml., T is the turbidity in cm.$^{-1}$, and where the optical constant is given by $H = 32\pi^3 n_0^2(dn/dc)^2/3N\lambda^4$, n_0 being the refractive index of the solvent, dn/dc the specific refractive index increment, and λ the wavelength of the light used. Hn$_{21}$ behaves like Hn$_9$ and Hn$_{12}$ in that there is only a small slope on the plots. For the two smaller detergents there is a considerable up-swing of the line at low concentrations. The position of the intercept $(c/T)_{c=0}$ was fixed by making a large-scale c–T plot, interpolating values of the two quantities at very low concentrations, converting them into c/T, and plotting on the graph c/T against c; this procedure gave a reasonably accurate measure of the intercept.

All detergents containing nine or more ethylene oxide units gave Z_{45} values close to unity (Table 1) (where Z_{45} is 1·03), but Hn_6 and Hn_7 showed appreciable Z_{45} values at higher concentrations, indicating that some dimension of the micelle had become larger than $\lambda/20$ (Fig. 3). The Z values approached unity as the concentration tended to zero for these compounds, so there may be aggregation or growth of micelles in these systems.

The viscosity results are given in Figs. 4, 5, and 6, where η_{sp} is the specific viscosity, and ϕ is the volume fraction of solute. The behaviour of the longer chain detergents is again similar to that of Hn_9 and Hn_{12}, the intercept $(\eta_{sp}/\phi)_{\phi=0}$ increasing with chain length. However, solutions of Hn_6 and Hn_7 were very viscous, and while a straight-line plot resulted for Hn_7 (Fig. 5), extrapolation in Fig. 4 was uncertain, so the intercept for Hn_6 was obtained from a graph with $(\phi + \phi^2)$ as the ordinate, which was linear below $\phi = 0{\cdot}0010$. The high intercepts for Hn_6 and Hn_7 are probably due to micellar asymmetry.

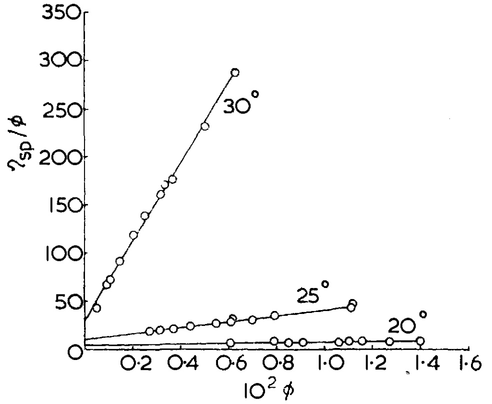

FIG. 5. Plot of η_{sp}/ϕ against ϕ for Hn_7 at the temperature marked.

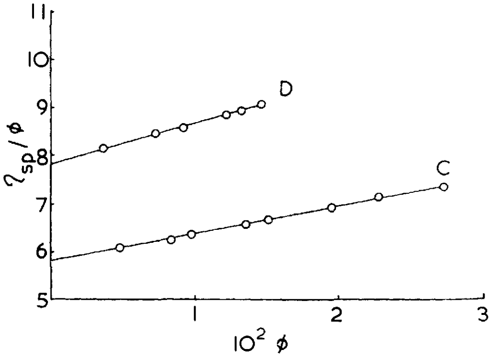

FIG. 6. Plot of η_{sp}/ϕ against ϕ at 25°. C = Hn_{15}; D = Hn_{21}.

Table 1 gives the critical micelle concentrations obtained [1] in Part IV by studying the surface tensions of solutions by the Wilhelmy plate method. These concentrations when previously reported [2] for Hn_9 and Hn_{12} were approximate, being obtained from light scattering in very dilute solutions. They are so small that no subtraction from the concentration term was made in calculating the molecular weights. There is a remarkable increase of both micellar weight and viscosity intercept as the oxyethylene chain is shortened.

TABLE 1.

Light-scattering and viscosity results.*

Detergent	dn/dc	$10^2\rho$	$10^{-5}M$	l	Z_{45}	$(\eta_{sp}/\phi)_{\phi=0}$	10^6cmc
Hn_6	0·135	1·3	12·3	2430	1·02	22·0	$1{\cdot}6_6$
Hn_7 (20°)	0·135	1·2	0·93	169	1·00	$2{\cdot}8_6$	—
(25°)	0·135	1·5	$3{\cdot}2_7$	594	1·02	$9{\cdot}5_3$	$1{\cdot}7_4$
(30°)	—	—	—	—	—	29·4	—
Hn_9	0·135	1·7	$1{\cdot}4_0$	219	1·03	$4{\cdot}3_1$	$2{\cdot}0_9$
Hn_{12}...............	0·134	0·9	$1{\cdot}1_7$	152	1·03	$4{\cdot}9_7$	$2{\cdot}3_4$
Hn_{15}...............	—	—	—	—	—	$5{\cdot}8_1$	$3{\cdot}0_9$
Hn_{21}...............	0·135	1·9	0·82	70	1·03	$7{\cdot}8_1$	$3{\cdot}8_9$

* dn/dc in ml./g.; ρ = depolarisation; M = molecular weight, corrected for depolarisation and dissymmetry; l = number of monomers in micelle; cmc = critical micelle concn. (moles/l.).

A few measurements were made on the effect of temperature on Hn_7 solutions. The micellar size triples over a 5° temperature range, and the viscosity intercept shows that a large asymmetry of the micelles develops.

DISCUSSION

The micellar weights given in Table 1 are those obtained by extrapolation of the light-scattering results to infinite dilution. For Hn_6 and Hn_7, the fall in the c/T figures and the development of Z values represent an aggregation of these units into larger ones as the concentration increases. An attempt to analyse the results in more detail for these detergents was made by assuming that the mass-action law, without activity coefficients, applies to the aggregation:

$$\log c_2 - m \log c_1 = K, \qquad (1)$$

where c_2 is the concentration of large micelles, c_1 is that of small micelles (both in g./ml.), m is the number of small micelles aggregating to give one large one, and K is a constant. The fraction, x, of small micelles aggregated will equal $c_2/(c_1 + c_2)$. The procedure used is illustrated for Hn_7 (cf. Table 2).

A solution of small micelles will have a turbidity, $T_1 = HM_1c_1$, while for a solution of the large micelles, $T_2 = HM_2c_2P(\theta)$, where $P(\theta)$ is the particle scattering factor. The Z_{45} values obtained for the small micelles are so close to unity that $P(\theta)$ has been neglected in the expression for T_1. The same optical constant, H, was used for both species, being that determined experimentally, as the concentrations where small micelles exist in solution are too minute for dn/dc to be measured accurately. M_1 is obtained from the intercepts in Fig. 1. The turbidity of a solution of concentration $c_t = (c_1 + c_2)$ is $T_t = (T_1 + T_2)$. For the larger micelles, $P(\theta)$ was obtained from the maximum Z_{45} values shown in Fig. 3 (1·18 for Hn_7). Two models were explored, a rod and a coil. A successive approximation procedure was used; a value of m being chosen, the molecular weight of the aggregated species $M_2 = mM_1$. Suitable values of c_1 were substituted in equation (1), K being chosen to give c_2 in the correct region. K and m were adjusted so that the total calculated turbidity for a solution agreed as closely as possible with the experimental value, when a c_t–T_t plot was used for the comparison. For Hn_7 we first obtained $\log c_2 - 3{\cdot}5 \log c_1 = 7{\cdot}45$, but when the Z_{45} values were calculated for the flat portion of Fig. 3, 1·15 instead of 1·18 was obtained. This error was due to the first approximation of taking all the light scattered at 45° and 135° to be due to the large micelles, while in fact some of it is due to the small micelles. The whole procedure was repeated with $Z_{45} = 1{\cdot}21$ for the large micelles. This gave a reasonable fit to the experimental curve, and as the $P(\theta)$ values for a rod and a coil were almost identical for this Z value, the fit applies to either model. The final equation was $\log c_2 - 3{\cdot}6 \log c_1 = 7{\cdot}80$.

TABLE 2.

Association of small into large micelles for Hn_7 at 25°.

10^3c_1	10^3c_2	10^3c_t	x	10^4T_t (obs.)	10^4T_t (calc.)	Z (obs.)	Z (calc.)
0·30	0·013	0·313	0·042	2·2	2·3	1·02	1·02
0·50	0·082	0·582	0·141	5·0	5·1	1·02	1·06
0·70	0·277	0·977	0·284	9·8	10·6	1·05	1·11
0·90	0·684	1·584	0·432	18·5	20·5	1·09	1·13
1·00	1·000	2·000	0·500	26·6	27·9	1·13	1·15
1·10	1·406	2·506	0·561	36·2	37·2	1·16	1·16
1·30	2·565	3·865	0·664	62·7	63·0	1·17	1·17
1·50	4·310	5·810	0·742	101·0	101·1	1·18	1·18
1·60	5·420	7·020	0·772	125·1	125·4	1·18	1·18
1·65	6·053	7·703	0·786	139·0	139·1	1·18	1·18

In view of the approximations of the treatment, *e.g.*, neglect of c^2 terms and virial coefficients in calculating the turbidities of the solutions, the agreement between calculated and observed values is good.

For Hn_6 the analysis was much more difficult for the rod-like model. A small change in Z_{45} causes a large change in $P(\theta)$, and, as the precision of determination of Z_{45} is about

1—2%, very large errors in $P(\theta)$ could be obtained. The best fit to the experimental results was by the equation: $\log c_2 - 18{\cdot}7 \log c_1 = 67{\cdot}5$. The length of the rod obtained from the true Z_{45} value for the larger micellar species was 12,000 Å, and the micellar weight 23×10^6. The extreme length of the rod makes this model seem unlikely. In order to decide which model was more realistic, a crude Zimm plot was made. There is a reasonably sharp break on a c–T plot, representing a critical micelle concentration between the large and the small micelles. Following Debye's method[8] of subtracting the turbidity at this critical micelle concentration from the total turbidity, and this concentration from the total concentration, and doing this at all angles, affords a Zimm plot for Hn_6. This procedure is a simplification, as the mass-action law governing the aggregation allows c_1 and T_1 to increase slightly above the critical micelle concentration. The micellar size was so large that the asymptote to the $(Hc/T)_{c=0}$ line was obtained, giving an intercept of $1/2M_n$. For an equilibrium system of this type, $M_n = M_w$. We obtained a micellar weight of $5{\cdot}2 \times 10^6$, which was much smaller than that found for the rod-like model. The results for Hn_6 were examined in much greater detail for the coil model, and a good mass-action-law fit was obtained by using the equation : $\log c_2 - 5{\cdot}1 \log c_1 = 14{\cdot}7$.

The agreement between T_t (obs.) and T_t (calc.) (see Table 3) was much better than could be obtained for the rod model. The micellar weight was $6{\cdot}2_8 \times 10^6$, in reasonable agreement with that from the crude Zimm plot, and the root-mean-square end-to-end length of the coil was 1970 Å.

TABLE 3.

Association of small into large micelles for Hn_6 at 25°.

10^4c_1	10^4c_2	10^4c_t	x	10^4T_t (obs.)	10^4T_t (calc.)	Z (obs.)	Z (calc.)
2·0	0·68	2·68	0·255	8·9	9·0	1·20	1·44
2·7	3·16	5·86	0·539	24·9	25·0	1·94	1·94
3·0	5·41	8·41	0·643	38·6	38·0	2·20	2·07
3·2	7·52	10·72	0·702	51·2	50·5	2·27	2·14
3·5	11·88	15·38	0·772	77·1	77·3	2·30	2·22
3·7	15·77	19·47	0·810	99·9	99·8	2·30	2·26
4·0	23·48	27·48	0·854	145·0	147·0	2·30	2·30
4·1	26·63	30·73	0·867	163·4	163·0	2·30	2·31

There is a large decrease in micellar weight (Table 1) as the detergent series is ascended, which is due to the increasing affinity of the polyoxyethylene chain for water. In solution, Hn_6 is probably in a metastable state; it is soluble only over an 8° temperature range, dissolving at 24° and having a cloud point at 32°. Hn_5 is insoluble in water.[9] Hn_{21} behaved normally, in that it gave no secondary aggregation into large micelles. The micellar weight of $8{\cdot}2 \times 10^4$ agreed approximately with that of the commercial Hn_{22} ($10{\cdot}1 \times 10^4$) studied in Part II.[4]

To disentangle the effects of hydration and asymmetry on the micelles is a complicated problem, as the hydration will depend, not only on the length of the polyoxyethylene chain, but also on the shape of the micelles. If the micelles are spherical, hydration would be expected to be a function of the polyoxyethylene chain length, as this part of the micelle provides space for the trapping of water. If the micelles are rod-shaped, the volume per monomer in which water can be trapped is smaller than in the spherical case, as the chains must be nearly parallel to one another along the long axis of the rod, and the main possibility for hydration lies around the cross section of the micelle, where the chains occupy a wedge-shaped sector of space.

The viscosity results will be examined in light of these considerations. If we assume that the deviation of the viscosity intercept from the value for unhydrated spheres (2·5)

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[8] Debye, *J. Phys. Chem.*, 1949, **53**, 1.

[9] Mulley, as ref. **3**, p. **31**.

is due solely to hydration, W (g. of water/g. of detergent), which can be calculated from Oncley's equation:[10]

$$(\eta_{sp}/\phi)_{\phi\,=\,0} = 2{\cdot}5\,(1 + W/\bar{v}d_s), \qquad (2)$$

where d_s is the density of solvent, and $\bar{v}$ is the specific volume of solute, then we can construct Fig. 7. From the very large value given by Hn_6 (not shown in Fig. 7) the hydration passes through a minimum, and then increases, as the polyoxyethylene chain becomes longer. As hydration should decrease with decreasing chain length, the very large values of the viscosity intercept for the small detergents are due to asymmetry of the micelles, which decreases as the series is ascended. The rise of W with chain length, shown by Hn_9 and larger compounds, arises, we suggest, because the effect of hydration outweighs that of asymmetry. There is no physical reason why the longer-chain detergents should give asymmetric micelles. If we assume that Hn_{21} is hydrated but not asymmetric, we can examine the effects of hydration and asymmetry by choosing two limiting cases for the hydration. A minimum level is chosen by letting Hn_6 be unhydrated and Hn_{21} fully hydrated. As an upper limit we let Hn_{15} and Hn_{21} be fully hydrated and draw an asymptote to the curve in Fig. 7. The results of this treatment are shown in Table 4.

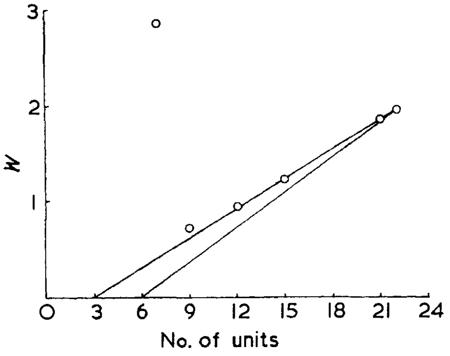

FIG. 7. Plots of W (g. of water per g. of detergent) against the number of ethylene oxide units in the detergents (see text).

TABLE 4.

Micellar dimensions.*

	Minimum hydration					Maximum hydration				
Detergent	$10^{-5}V$	a/b	a	b	W	$10^{-5}V$	a/b	a	b	W
Hn_6	21·1	13·8	458	33	0	27·0	11·8	448	38	0·29
Hn_7 (20°)	1·77	1·2	39	33	0·13	—	—	—	—	—
(25°)	6·24	7·0	193	28	0·13	7·71	5·7	182	32	0·40
(30°)	—	15·5	—	—	0·13	—	13·5	—	—	0·40
Hn_9	3·18	2·3	74	32	0·37	3·74	1·5	57	40	0·61
Hn_{12}	3·34	1·7	62	36	0·75	3·68	1·1	47	43	0·92
Hn_{15}	—	1·4	—	—	1·11	—	1·0	—	—	1·22
Hn_{21}	3·73	1·0	45	45	1·86	3·73	1·0	45	45	1·86

* V = micellar volume in Å^3; a and b are in Å, and are the long and short semi-axes, respectively.

The micelles have been treated as prolate ellipsoids, as a calculation for Hn_6 and Hn_7 shows, that, when reasonable values are taken for the cross sectional area per molecule and molecular lengths, and when the numbers of monomers in the micelle are those found by light scattering, the oblate model does not fit the viscosity results.

Whether Hn_6 is treated as hydrated or unhydrated, the cross-section of the micelle ($2b$) is greater than that of Hn_7 at 25°, indicating that the polyoxyethylene chain is more

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[10] Oncley, *Ann. New York Acad. Sci.*, 1940, **41**, 121.

extended in the former compound; and this may have a bearing on the stability of the micelles, in that less of a mesh structure exists to contain the hydrating water than in the other detergent micelles. It is generally acknowledged[11] that the stability of micelles of non-ionic detergents in aqueous solution is due to hydration, as any repulsive electrical forces which can exist between the micelles will be weak (and probably due to the adsorption of OH^- ions). The hydration decreases with increasing temperature, and at the cloud point the detergents separate, presumably because thermal agitation has broken up the hydrating barrier of the micelles. Although the difference between Hn_6 and Hn_7 is only one ethylene oxide unit, this has the most remarkable effect on the micelle size. From Table 4, and the values of b, the polyoxyethylene chain appears to have coiled in Hn_7 micelles, which fits in with ideas of increased hydration through the mesh effect, and this coiling has increased the stability in solution. The cloud point of Hn_7 is 53°.

The micellar size of Hn_7 decreases sharply with decreasing temperature. At 20° the viscosity intercept is $2{\cdot}8_6$, which is only slightly more than that required for unhydrated spheres; and, if the micelle is hydrated only, it contains 0·15 g. of water per g. of detergent. This order of hydration for Hn_7 makes the minimum-hydration assumption seem more likely. The viscosity results show that a large micellar asymmetry develops as the temperature is raised. This effect is being investigated, and it may be due to micellar dehydration causing the formation of a rod-like structure. Unfortunately, Hn_6 solutions could not be studied at temperatures lower than 25°, where the micellar asymmetry might be less.

Some idea of the structure of the large micelles formed by the two shortest detergents may be obtained from the results. The mass-action law shows that, for Hn_7, the large micelles are 3·6 times the size of the small ones and have a volume, on the minimum hydration assumption, of $1{\cdot}73 \times 10^6$ Å^3. From the light-scattering results the rod-like model has a length of 1065 Å. If this rod is allowed to approximate to a prolate ellipsoid, $a = 533$ Å, so $b = 28$ Å, in agreement with the value of b for the small micelles. Although this calculation is crude it implies that the small micelles grow in the direction of their long axes on aggregation. The light-scattering results also suggest that Hn_6 fits the coil model better than the rod one; however, the basic structural unit of the micelle may be rod-like. If Hn_6 is nearly unhydrated, the polyoxyethylene chains will be very flexible, and the basic rod structure could easily coil. By taking the b value from Table 4 for Hn_6, and the volume of the large micelles ($10{\cdot}8 \times 10^6$ Å^3) we obtain $2a = 4700$ Å. This length is great enough for the rod to coil. In contrast, the greater hydration of Hn_7 would tend to promote a rod-like micelle, owing, on a simple mechanical model, to the presence of water molecules driven like wedges between the flexible polyoxyethylene chains.

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[11] Kushner and Hubbard, *J. Phys. Chem.*, 1954, **58**, 1163.