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Authors' address:

Dr. Tsutomu Takamura, Hiromi Yoshida, and Kiyokatsu Inazuka; Central Research Laboratory, Tokyo Shibaura Electric Co., Ltd. 1 Komukai Toshiba-cho, Kawasaki (Japan).

From the School of Pharmacy, Royal College of Science and Technology, Glasgow, C. 1. (United Kingdom)

Chemistry of Non-Ionic Detergents

Part VII. Variations of the Micellar Structure of Some Synthetic Non-Ionic Detergents with Temperature

By P. H. Elworthy and C. McDonald

With 5 figures and 7 tables

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Introduction

A number of authors (1-7) have studied the effects of temperature on the micellar structure of non-ionic detergents. According to *Balmbra* et al. (7), using the synthetic compound $CH_3(CH_2)_{11}(OCH_2CH_2)_6OH$, there was an exponential rise of micellar weight with temperature; *Kuriyama*(5) has reported a much slighter increase using fractionated compounds, and there appears to be a certain discrepancy between these results. It has often been stated that micellar dehydration increases with temperature, although recent results of *Elworthy* and *Macfarlane* (8) indicate otherwise; at the cloud point there is a separation into detergent rich and detergent poor phases.

Probably the use of commercial detergents having a distribution of ethylene oxide chain lengths can confuse the picture of temperature effects; for this reason we have studied synthetic compounds of the hexadecyl series, $CH_3(CH_2)_{15}(OCH_2CH_2)_xOH$ where x = 7.8, and 9. (Abbreviated to Hn_7 , Hn_8 , and Hn_9 .) Also, this sequence of compounds allows a study of the alteration of hydrophobic/hydrophilic balance on the temperature effects to be made.

Experimental

Materials

3, 6, 9, 12, 15, 18, 21, heptaoxatricosane-1:23 diol (octaoxyethylene glycol n_9). This was prepared by the method previously described for nonaoxyethylene glycol (9) from sodium (57.5 g.), triethylene glycol (1500 g.), and β_{β} dichlorodiethyl ether (179 g.). The product (160 g.) had b. p. 216 °C (0.01 mm), n_D^{30} = 1.4661. Found, C, 51.8%; H, 9.2; ethylene oxide, 95.0%. Calculated for $C_{16}H_{34}O_{9}$, C, 51.9%; H, 9.3%; ethylene oxide, 95.1%.

ethylene oxide, 95.1%. 3, 6, 9, 12, 15, 18, 21, 24 octaoxatetracontane-1-01 (octaoxyethylene glycol monohexadecyl ether, Hn_8). Prepared from sodium (1.18 g.), octaoxyethylene glycol (75 g.), and hexadecyl bromide (16.3) g.. After working up the reaction mixture as described by Elworthy and Macfarlane (9), the product was chromatographed, then crystallised from ether and from acetone. It had m. p. 41.5 °C. Found, C, 64.2%; H, 11.1; ethylene oxide, 59.2%. Calculated for $C_{32}H_{45}O_{9}$, C, 64.6%; H, 11,1; ethylene oxide, 59.2%. The starting materials for the syntheses were all redistilled twice before use and had physical constants agreeing with the best literature figures. The preparation and properties of septaoxyethylene glycol monohexadecyl ether (Hn_7) (10) and of nonaoxyethylene glycol monohexadecyl ether (Hn_9) (9) have been reported.

Water for light-scattering measurements was twice distilled from permanganate.

Light-Scattering Measurements

The apparatus described by Elworthy and McIntosh (11) was used. Immediately after an extensive calibration with Ludox solutions, the turbidity of A.R. benzene was found to be 27.2 \pm 0.4 \times 10⁻⁵ cm⁻¹. A check on the calibration at the time of this work gave 27.3 \pm 0.3 \times 10⁻⁵ cm⁻¹, indicating that there was no change in calibration constant with time. Solutions were made dustfree by filtering through Millipore disks (mean pore size 0.45 μ).

Concentrations were checked interferometrically after filtration. Temperature control in light-scattering measurements was to $\pm 0.1^{\circ}$, using a thermometer calibrated by the N.P.L.

Specific Refractive Index Increments (dn/dc), Viscosities, and Vapour Pressures

Were measured as described previously (9, 10).

Temperature control of these measurements was to \pm 0.01°.

Densities

As displacement experiments are difficult due to the lack of a liquid in which the detergents are insoluble, the densities were calculated from the molar volumes of the glycols and of hexadecane, neglecting the molar volume of hydrogen. As a check on this method the densities of Hn_8 at 45° and Hn_9 at 45° and $53.5~^\circ\text{C}$ were measured directly in a 1 ml. pycnometer, giving 0.950 for Hn_8 , and 0.968 and 0.954 g./ml. respectively for Hn_9 . The densities calculated from molar volumes were 0.952, 0.968, and 0.954 g./ml. respectively. The densities found for the glycols were:

Temperature	15	20	25	3 0	35	45
$dt_4, n_7 g./ml.$ $dt_4, n_8 g./ml.$	$\begin{array}{c} 1.13\\ 1.170\end{array}$	1.127	$\begin{array}{c} 1.123 \\ 1.168 \end{array}$	1.119	1.153	1.137
Temperature	45	50	53.5	57.5		
dt ₄ , n ₉ g./ml.	1.148	1.135	1.132	1.131		

The densities determined for hexadecane agreed to 0.0002 g./ml. with literature values (12).



Fig. 1. Variation of $(c - c_1) (T - T_1)$ with concentration. A, Hn_7 , 15°. B, Hn_7 , 17.5°, C, Hn_9 , 45°. D, Hn_9 , 50°. E, Hn_9 , 53.5°. F, Hn_9 , 57.5°. G, Hn_8 , 15°. H, Hn_8 , 25°. I, Hn_8 , 35°. J, Hn_8 , 37.4°. K, Hn_8 , 39.3°. L, Hn_8 , 44.3°

Results

The light-scattering results are shown in Fig. 1 as plots of $(c-c_1)/(T-T_1)$ against $(c-c_1)$ where c is concentration in g./ml., and T is turbidity. Balmbra et al. (7) obtained breaks in c vs. T plots having the appearance of critical micelle concentrations (cmc), but occurring at concentrations much greater than the

Table 1Results from Light-Scattering

	Temp.	$M imes 10^{-5}$	m	Z	Q	dn/dc	$B imes 10^4$	$c_{1} imes 10^{3}$
Hn_{π}								
	15	0.90	164	1.03	0.002	0.136.	0.42	0.20
	17.5	1.14	207	1.03	0.002	0.135	1.46	0.20
	20	1.37*	249	1.00	0.012	0.135	0.84	0.36
	25	3.27	594	1.07	0.015	0.135	0.02	0.30
Hn_{s}				-				
5	15	1.31	220	1.04	0.010	0.133.	2.42	0.20
	25	1.43	240	1.01	0.008	0.131	2.43	0.20
	35	1.61	271	1.04	0.019	0.130_{r}	1.56	0.25
	37.4	3.98	668	1.11	0.002	0.130	0.04	0.40
	39.3	6.02	1010	1.12	0.022	0.130^{-1}_{0}	-0.09	0.45
	44.3	16.7	2800	1.17	0.007	0.129_{4}°	0.11	0.50
Hn_{9}								
-	25	1.40	219	1.03	0.016	0.135.	3.28	0.20
	45	1.76	243	1.03	0	0.132	1.95	0.20
	50	3.50	549	1.09	0.010	0.132^{*}_{2}	-0.14	0.40
	53.5	6.41	1000	1.11	0.008	0.132_{0}^{2}	-0.17	0.52
	57.5	8.80	1380	1.14	0.013	0.131_{0}	-0.50	0.60

m = number of monomers in micelles, Z = dissymmetry at 45°, $\rho =$ depolarisation, B = second virial coefficient. *) Data recalculated from reference (10), using $c_l = 0.36 \times 10^{-3}$ g./ml. cmc. This concentration, c_1 , probably represents a second association limit. c_1 , and the turbidity at this concentration, T_1 , were determined from large scale graphs of cagainst T at low concentrations. The lightscattering results are summarised in Table 1, along with relevant data on Hn_7 and Hn_9 .

The micellar weights were calculated from (13)

$$H(c - c_1)/(T - T_1) = 1/MP(\Theta) + 2Bc \qquad (1)$$

where $P(\theta)$ is the particle scattering factor, and H is the optical constant, $H = 32 \pi^3 n_0^2 (dn/dc)^2/3 N \lambda^4$, the symbols having their usual significance.

Micellar weights given in Table 1 have been corrected for depolarisation and dissymmetry; they increase with increase of temperature. For Hn_8 and Hn_9 the increase is small at low temperatures, but rapid at higher ones. A plot of log M vs. temperature shows this effect clearly (Fig. 5). At the higher temperatures small dissymmetries are present; there is a decrease of second virial coefficients as temperature increases.

The viscosity results are given in Fig. 2, as plots of η_{SP}/c against c where η_{SP} is the specific viscosity. The change of the intercepts of these plots, (7), with temperature is similar to the change of log. M with temperature (Fig. 3); both sets of results show that there appears to be a threshold temperature, T_h ,



Fig. 2. Reduced viscosity against concentration for: Top graph: A, Hn_9 , 45°. B, Hn_9 , 35°. C, Hn_7 , 15°. Main graph: D, Hn_9 , 65°. E, Hn_9 , 59.8°. F, Hn_8 , 45°. G, Hn_9 , 55°. H, Hn_8 , 40°. I, Hn_8 , 38°. J, Hn_9 , 50k. K, Hn_8 , 35°. L, Hn_8 , 25°. M, Hn_8 , 15°

above which viscosity intercepts and molecular weights rise exponentially.



Fig. 3. Changes in log (intrinsic viscosity) with temperature for Hn_7 , Hn_8 , and Hn_9

The vapour pressure results are given in Fig. 4 as plots of vapour pressure (cm. Hg.) against concentration, a, (g. water/g. detergent). As previously reported(8), it is easy to



Fig. 4. Vapour pressures against concentration, a, (g. water/g. detergent) for: A, Hn_8 , 45° . B, Hn_9 , 45° . C, Hn_8 , 35° . D, Hn_8 , 25° . E, Hn_7 , 15° . F, Hn_8 , 15°

extrapolate graphs of a/x against x to x = 1, where x is the relative vapour pressure. At the point the vapour pressure is indistinguishable from that of pure water, within experimental error, and here sufficient water is present to fully hydrate the polyoxyethylene chains, giving micelles. The concentration at x = 1 has been shown (8) to give a measure of micellar hydration, agreeing well with values calculated from viscosity results. The hydration calculated from the vapour pressure results is given in Table 2 as $W_{v,p}$. Below the threshold temperature, there is no physical reason for the micelles being asymmetric, and we calculated $W_{\text{vis.}}$ from the viscosity results, using

$$[\eta] = \nu \left(V_2 + W_1 \, V_1^0 \right) \tag{2}$$

where ν is Simha's (14) shape factor, V_2 = specific volume of solute, and V_1 = specific volume of solvent.

 Table 2

 Hydrations from Viscosity and Vapour Pressure Results

Hn, Temperature	15	20	25	į	80		
$[\eta] \\ W_{v.p.}(g./g.) \\ W_{vis.}(g./g.)$	3.2_0 0.29 0.24	2.9_1 0.28 0.18	9.7 ₀ 0.44	29 0.	.9 52		
Hn_8 Temperature	15	25	35		38	40	45
$[\eta] \\ W_{v.p.}(g./g.) \\ W_{vis.}(g./g.)$	3.6_0 0.50 0.42	3.8 ₈ 0.58 0.52	4.2 ₀ 0.66 0.64	5	.96	8.50	$\begin{array}{c} 22.0 \\ 0.75 \end{array}$
Hn, Temperature	25	35	45	50	55	59.8	65
$[\eta] \\ W_{v.p.}(g./g.) \\ W_{vis.} (g./g.)$	4.2 ₉ 0.65 0.72	4.5 ₀ 0.77	4.6 ₉ 0.83 0.83	6.0 ₃	10.1	18.7	34.9

Results for Hn_7 at 20, 25, and 30 and for Hn_9 at 25 are taken from *Elworthy* and *Macfarlane* (8).

Macfarlane (15a) has calculated the limits of error in the determination of $W_{\rm vis.}$ to be ± 5 -15%, and $\pm 10\%$ for the determination of $W_{\rm v.p.}$. Considering these limits of error, there is reasonable agreement between the values of W found by the two methods. Plots of the average value of W were linear against temperature, with equations

$$\begin{array}{l} Hn_{7} \ W = 0.100 \, + \, 0.014 \ \ \mathrm{T} \\ Hn_{8} \ W = 0.315 \, + \, 0.0097 \ \mathrm{T} \\ Hn_{9} \ W = 0.500 \, + \, 0.0075 \ \mathrm{T} \end{array}$$

where T is in °C.

Cloud points were constant in the region 1×10^{-3} to 4×10^{-2} g/ml., being 55° for Hn_7 , and 75° for Hn_9 .

Discussion

Structure of Micelles below T_h .

From Fig. 3, the threshold temperature for Hn_7 , Hn_8 , and Hn_9 are 22.0, 36.3, and 47.9 °C respectively.

There is a slow increase of micellar weight with temperature in this region. The viscosity intercepts are small, close to the Einstein value 2.5 for unhydrated spheres. Both viscosity and vapour pressure results indicate that hydration increases with temperature. This somewhat surprising result will be discussed later. We can gain some insight into what occurs in this low temperature region by calculating the micellar dimensions, from m, W, M, and the densities of detergent and water. Letting the micelle have a fluid interior, with liquid hexadecane in the centre, the results are given Table 3, where $r_m =$ micellar radius, $r_h =$ radius of hydrocarbon region, and $r_e =$ radius of polyoxythelene region.

 Table 3

 Dimensions of Various Micellar Regions

Deter- gent	Tempe- rature	V×10−5 (Å) ³ r _m (Å)	r_h (Å)	r_e (Å)
Hn_7	15	2.03	36.4	26.7	9.7
	17.5	2.61	39.6	28.9	10.7
	20	3.25	42.7	30.7	12.0
Hn_{B}	15	3.23	42.6	29.4	13.1
0	25	3.76	44.8	30.4	14.4
	35	4.52	47.6	31.7	15.9
Hn_{\circ}	25	3.93	45.4	29.5	15.9
3	45	5.48	50.8	31.9	18.9

The radial length of the micelle occupied by the polyoxyethylene chain increases with temperature. At normal temperatures, it is considered that this chain may have the form of an expanding spiral, or a similar arrangement in which the length occupied is considerably less than the extended length. Table 3 shows that the chain becomes more extended as the temperature is raised. This increased radius of the micelle would give a means for trapping more water in the mesh of polyoxyethylene chains.

Structure of Micelles at T_h

From the linear parts of Fig. 5 below T_h , values of M at T_h were determined, and the properties of the micelles at this temperature calculated.



Fig. 5. Variation in log (micellar weight) with temperature for Hn_7 , Hn_8 , and Hn_9

	Hn ₇	Hn_{8}	Hn_9
$M \times 10^{-5}$	1.61	1.63	1.81
m	292	274	284
W(g./g.)	0.40	0.67	0.86
$V \times 10^{-5}$ (Å) ³	3.90	4.62	5.74
r_m (Å)	45.3	48.0	51.6
$r_h(\mathbf{A})$	32.4	31.8	32.3
$r_{a}(\overline{A})$	12.9	16.2	19.3
r_e/no et. o.	1.85	2.02	2.14

Table 4 Properties of Micelles at T_h

It is extremely interesting to note that within the limits of experimental error, at the threshold temperature, the number of monomers in the micelle is the same for each detergent. The micellar volume, λ , is greatest for Hn_9 , as this is the most heavily hydrated detergent.

In calculating the volume of the hydrocarbon core of the micelles we have assumed that this interior is fluid. r_e can be seen to be greater at T_h than at lower temperatures, but the polyoxyethylene chain is still not fully extended. (Extended lengths 26, 30, and 34 Å from molecular models). The radial length per ethylene oxide unit increases with detergent chain length.

We may investigate a second model of the micelles. Taylor (17) gives for calculation the end to end length of hydrocarbon chains, L,

$$L^{2} = \sigma^{2} n \left(\frac{1 + \cos \theta}{1 - \cos \theta} \right) \left(\frac{1 + a}{1 - a} \right)$$
[3]

where $\sigma = C - C$ bond length, n = number of links in the chain, θ = supplement of valency angle, and a is the average value of the cosine of the angle of rotation for one rotation. For hexadecane we obtain L = 13.8 Å. The ends of the hydrocarbon chains cannot all be in the micelle centre, so we assume a space must be present there, its surface being covered by the ends of 283 monomers (mean value) each with cross-sectional area 16 $Å^2$ [crystallographic area of hydrocarbon chain (22)]. The radius of this space is thus 19 Å, and the radius of the hydrocarbon region 19 + 13.8 =32.8 Å. Both models give roughly the same radii for the hydrocarbon portion, in spite of the crudity of the models.

Unfortunately we cannot calculate the lengths of the polyoxyethylene chains from equation (3), due to the lack of knowledge of rotational energy barriers. However, we can obtain an approximation by calculating for a hydrocarbon chain of the same number of linkages as the polyoxyethylene chain (the ether bond angle is close to the C-C angle,

and the bond distance is 1.42 Å (18). The results are given below:

Temperature	22°	36.3°	47.9°
L (Å)	17.2	17.8	18.4
L (a = 0) (Å)	10.2	10.9	11.5
r_e (Å)	12.9	16.2	19.3

The lengths of the polyoxyethylene chains are too small when calculated for freely rotating bonds. Bunn (19) and Holmes state that the presence of ether linkages in hydrocarbon chains greatly increases the flexibility. For Hn_7 , the value of r_e falls between the two cases investigated, while for Hn_8 and Hn_9 , r_e is close to the value of L for an equivalent hydrocarbon chain in the presence of restricted rotation. It seems possible that the progressively increasing hydration as the series is ascended may increase the interactions between chain and solvent, and increase the extension of the chain.

As the temperature is raised above T_h the micellar growth becomes extremely rapid, and asymmetry develops. The state of the micelles at T_h may represent a critical condition. Geometrical factors may be present, the number of monomers present in the micelles being the maximum number which can be packed into a spherical shape. Addition of further monomers would tend to upset the sphericity. *Macfarlane* (15b) has shown that the parts of the polyoxyethylene chain closest to the surface of the hydrocarbon regions are very closely packed (at normal temperatures) and that they may effectively prevent water from coming into contact with that region. However, there is a general extension of the chains as temperature rises, together with an increase of the area of the hydrocarbon region (m increases). Both these effects may lessen the protecting effect of the innermost parts of the polyoxyethylene chains. It is possible to visualise a state of affairs where water may come into contact with the surface of the hydrocarbon region, giving a sudden increase of interfacial tension at some points on the hydrocarbon/polyoxyethylene boundary, which would have a contracting effect, and cause the micelle to elongate. This situation is a speculative one, but does provide a basis for understanding the sudden growth of molecular weight at a particular temperature.

Structure of Micelles above T_h

From Fig. 5, there is a sharp increase of M above T_h , followed by a slower rise; for Hn_8 and $Hn_9 \log M$ is linear with temperature in

this second region. $(37.4-44.3^{\circ} \text{ for } Hn_8, \text{ and } 50-57.5^{\circ} \text{ for } Hn_8)$. From a plot of log (7) against log M, which was linear, the slopes of the graphs are 0.90 and 1.07 for Hn_8 and Hn_9 respectively. Simha's shape factors can be generalised, in the region of ν of interest to:

Oblate ellipsoids; v = 1.45 + 0.661 b/a [4a]

Prolate ellipsoids; $\nu = \text{const.} + \text{const.'} a/b^{1,2-1,5}$ [4b]

Tanford 20_0 gives for flexibly coiled molecules.

$$[\eta] = \text{const.''} M^{1/2}$$
 . [4 c]

For the ellipsoidal models the axial ratio is proportional to molecular weight, so we should obtain from $\log [\mu] - \log M$ plots a slope of *l* for oblate ellipsoids, 1.2-1.5 for prolate ellipsoids, and 0.5 for flexible coils in poor solvents, where B = O or is negative. The slopes found here indicate that the micelles resemble oblate ellipsoids more than any other model shape. We have assumed that W has a constant value in the above treatment (see equation [2]) and this is roughly correct over the small temperature range studied, but if we calculate v using the W values in Table 2, the slopes of $\log \nu$ against \log M plots are 0.85 and 0.88 for Hn_8 and Hn_9 respectively, still indicating that the oblate model fits the particle best. Calculations of the micellar dimensions in this region of temperature are given in Table 5, using the oblate model.

 Table 5

 Micellar Dimensions at Higher Temperatures

<u> </u>	T	v	b/a	$V \times 10_{6}$	a	b
Hn ₈	37.4	3.12	2.5	1.14	48	120
	39.3	4.37	4.5	1.74	45	203
	44.3	10.9	14.2	4.98	44	620
Hn_9	50.0	3.13	2.5	1.12	47	118
	53.5	4.62	4.8	1.71	43	209
	57.5	7.22	8.7	3.93	47	414

The length of the short semi axis is reasonably constant, considering that three sets of experimental data are combined in these calculations, and is only a few Å shorter than the fully extended monomer lengths, giving the idea the extension of the peg chain may proceed rapidly above T_h . There is thus a very rapid growth of disk shaped particles, which, with further increase in temperature, presumably continues until the micelles become of giant size and are macroscopically visible. Presumably at the cloud point the micelles have grown so large that a second phase is formed. This second phase should contain the majority of the detergent, which has been found experimentally (24).

It is interesting to examine the steeply rising part of the curve in Fig. 5, up to 37.4° for Hn_8 and 50° for Hn_9 . Using points interpolated from Figs. 3 and 5, the slope of the $\log[7] - \log M$ graph are 0.45 and 0.50 for Hn_8 and Hn_9 respectively. These calculations are tentative, but they do suggest that the micelles resemble coils in this region, rather than other models. In this region the micelles have not yet become very asymmetric, and consist of a hydrocarbon core surrounded by reasonably flexible polyoxyethylene chains. Provided that this type of structure remains spherical it somewhat resembles a coiled molecule. An increase in the molecular weight, of, say, a polystyrene molecule in solution, means that the total volume of solution pervaded by the molecule increases spherically about the centre of mass. However an increase in micellar weight is subject to the condition that all the hydrocarbon chains must remain in the micellar centre, and so we expect molecular expansion to occur only in two dimensions. The results show that this appears to be the case, in that the micelles take the oblate shape.

Other Considerations

By treating the vapour pressure results as sorption isotherms from plots of a against x, using the standard relationships (21) the differential partial molar enthalpies $(\Delta \overline{H})$ and entropies $(\Delta \overline{S})$ of hydration were determined for Hn_8 . $(\Delta \overline{H}$ in kcal. mole⁻¹, $\Delta \overline{S}$ in cal. mole⁻¹ deg.⁻¹).

Table 6 Thermodynamic Properties for Hn_8

a	$arDelta \widetilde{H}_{20}^\circ$	$\Delta \overline{H}_{30}^{\circ}$	$arDelta \overline{H}_{40}^{\circ}$	$arDelta \overline{S}_{20}^{\circ}$	$\Delta \overline{S}_{40^{\circ}}$
0.4	1.5	1.8	2.8	5.7	10.2
0.45	1.2	1.4	2.3	4.6	7.6
0.50	1.3	1.3	2.3	4.5	7.8

The positive values of $\Delta \overline{S}$ found indicate that a mixing process is predominating over any specific arrangement of water molecules around the polyoxyethylene chains, and the increase of $\Delta \overline{S}$ with temperature shows that the mixing is greater at higher temperatures, which fits in with the increase of hydration with temperature found earlier. Examination of other papers describing micellar hydration of non-ionic detergents reveals no direct experimental evidence that a decrease of hydration with increasing temperature occurs. The present work indicates that the reverse is consistent with the extension of the polyoxyethylene chains with temperature recorded here.

Second virial coefficients for spherical particles are calculated on the basis of the excluded volume (20b) (Table 7). The agreement between these values and the experimental ones (Table 1) is not good ¹).

 $\label{eq:Table 7} Table \ 7$ Calculated Second Virial Coefficients, $B imes 10^4$

Temperature	15°	20°	25°	35°	40°
Hn ₇	0.56	0.43			
Hn_8	0.45		0.44	0.42	
Hn_9			0.48		0.43

The contribution to the chemical potential of the solvent, μ_1 , given by the excluded volume should remain approximately constant. At low temperatures *B* (experimental) is greater than *B* (calculated), and hence other factors must contribute to the non-ideality.

The derivation of the relationship between B and excluded volume assumes that $\Delta Hmix$ is constant as concentration is changed, making a constant contribution to μ_1 , and this assumption may not be correct. The decrease in B with increasing temperature must also be accounted for; it has been shown that the polyoxyethylene chains straighten with increasing temperature.

Longuet-Higgins (23) states that an extended chain is in a more ordered state than a coiled one. The process of extension may provide a lowering of the entropy of the system which opposes the effects of excluded volume and $\Delta Hmix$, and which predominates at higher temperatures to give a negative second virial coefficient. The micellar structure with its hydrocarbon region, and its region of mixing between water and polyoxyethylene chains, is a complex one, and only a qualitative discussion of the thermodynamic properties has been attempted.

The temperature at which B = 0 corresponds roughly to T_h eg. Hn_8 , B = 0 at

37°, $T_h = 36.3°$; Hn_9 , B = 0 at 49°, $T_h = 48.9°$. It is considered that a balance of factors makes B = 0 at this temperature. It should also be noted that the cloud points are about 30° above T_h for all detergents, so phase separation does not occur at B = 0, but at a considerably higher temperature.

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Summary

Three synthetic non-ionic detergents,

$CH_3(CH_2)_{15}(OCH_2CH_2)_xOH$,

where x = 7, 8, and 9. ie. Hn_7 , Hn_8 and Hn_9 have been studied in aqueous solution by light-scattering, viscosity, and vapour pressure techniques. The micellar weights and intrinsic viscosities increased as temperature increased, the rise becoming very rapid above threshold temperatures (T_h) of 22°, 36.3°, and 47.9° for the three detergents respectively. Micellar hydrations determined by the vapour pressure method agreed with those calculated from viscosity intercepts in the region below T_h , where the micelles appeared to be spherical, and hydration was found to increase with temperature. At T_h , micelles of the different detergents contained the same number of monomers. Above T_h the micelles became asymmetric, fitting the oblate ellipsoidal model best. The structure of the micelles was discussed, as was the decrease of second virial coefficient with temperature.

Zusammenfassung

Drei synthetische nichtionische Detergentien,

$CH_3(CH_2)_{15}(OCH_2CH_2)_xOH$

mit x = 7, 8, 9 (Hn_7, Hn_8 und Hn_9) wurden in wäßriger Lösung durch Bestimmung von Lichtstreuung, Viskosität und Dampfdrucktechnik untersucht. Die Micellgewichte und die Intrinsic-Viskositäten wurden mit steigender Temperatur größer Der Anstieg wird sehr rasch oberhalb der Temperaturschwellen (T_h) von 22° , 36,3° und 47,9° für diese drei Detergentien. Micellare Hydratation aus Dampfdruckmessungen stimmt mit den aus den Viskositätsabschnitten im Bereich unter T_h , wo die Micellen kugelig zu sein scheinen, überein, und die Hydratation steigt mit der Temperatur. Bei T_h enthalten die Micellen der verschiedenen Detergentien die gleiche Zahl an Monomeren. Oberhalb T_h werden sie asymmetrisch, wobei ein abgeflachtes Ellipsoid am besten paßt. Die Strukturen der Micellen wurden diskutiert ebenso wie die Abnahme des zweiten Virialkoeffizienten mit der Temperatur.

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Author's address:

Dr. P. H. Elworthy, School of Pharmacy, Royal College of Science & Technology, Glasgow, C. 1.

From the School of Pharmacy, Royal College of Science and Technology, Glasgow, C. 1 (United Kingdom)

Chemistry of Non-Ionic Detergents

Part VIII. Critical Micelle Concentrations and Thermodynamics of Micellisation of Synthetic Detergents containing Branched Hydrocarbon Chains

By P. H. Elworthy and A. T. Florence

With 1 figure and 3 tables

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Introduction

Although some surface tension data have been reported for ethylene oxide condensates of tridecanol (1, 2), few studies have been made of non-ionic detergents containing branched hydrocarbon chains. The tridecanol condensates gave higher critical micelle concentrations than their straight chain analogues (2). Surface chemical studies on synthetic compounds with straight hydrocarbon chains are also limited (3, 4, 5). The present paper reports some properties of synthetic detergents with branched hydrocarbon chains, and also of compounds with short, straight chains. As the cmc's of most non-ionic detergents are very small, it has been impossible to obtain data on the monomers; the short chain length compounds reported here provide a starting point for their study.

Experimental

Materials

Alkyl Bromides: n-propyl-, n-butyl-, n-hexyl- and β , β' dimethyl ethyl bromides were twice fractionated before use. β , β' diethyl ethyl bromide was prepared from the parent alcohol by the HBr/H₂SO₄ method (6), the product being twice fractionated. β , β' dipropyl and β , β' dibutyl ethyl bromides were prepared from the disubstituted malonic ester, by decarboxylation, esterification, reduction with lithium aluminium hydride, bromination, and fractionation. All bromides had analysis figures and physical constants in agreement with calculated or literature values.

Glycols: hexa-, and nona-oxyethylene glycols were prepared as described before (7, 8), having physical constants in agreement with those already determined (7, 8).

Detergents: Following the general method (7, 8), sodium (1 mole) was dissolved in the required glycol (4 moles) at $70-80^{\circ}$ with stirring, and the relevant bromide (1 mole) added. The mixture was kept stirred, and heated to a temperature just below the boiling point of the bromide (in the case of the shorter chain compounds), or at 130-140° until neutral (2-12 hours). The mixture was cooled to 50°, an equal volume of water added, and the detergent extracted with 3 to 4 portions of hot petroleum ether (b. pt. 60-80°). After removal of this solvent, the residue was distilled under high vacuum, the low boiling fractions being discarded.

Distillation alone did not produce sufficiently pure compounds, as it appeared that some oxidation products were formed during this process. 2 g. of distilled detergent was therefore chromatographed on 30 g. Mallinckrodt silica gel, containing 20% of celite. After adsorption on to the column from benzene solution, elution with acetone – benzene mixtures containing up to 30% acetone removed about 0.7 g. of the initial column load. Careful elution with a 24:25:1 acetone: benzene: methanol mixture gave 1 g. pure detergent. Examination of the initial fraction by I. R. spectroscopy showed the presence of carbonyl containing (3) and unsaturated impurities, which were absent from the purified detergent. Any unreacted glycol was heldfirmly on the column. Reaction of hexaoxyethylene