

Partial molal volumes of some non-ionic detergents in monomeric and micellar form

A. T. FLORENCE

Partial molal volumes of five synthetic non-ionic detergents have been measured above and below their critical micellar concentrations. The increases in volume on micellisation are discussed in terms of changes in hydration and hydrophobic bonding. The change in partial molal volume at the critical micellar concentration decreased with temperature. At 20° increases of 5, 9 and 17 ml mole⁻¹ were obtained for the n-butyl, n-hexyl and n-octyl hexaoxyethylene glycol ethers respectively. For comparison with the alkyl ethers, the partial molal volume of hexaoxyethylene glycol was determined at four temperatures. The utility of density measurements for the determination of the critical micelle concentration of these non-ionic detergents depended on the temperature of the system; at higher temperatures the change in slope of density-concentration plots at the critical micelle concentration decreases and sometimes is not detectable.

THE partial molal volumes of ionic surface-active agents increase on micelle formation (Wright & Tartar, 1939; Paquette, Lingafelter & Tartar, 1943; Harkins, Mattoon & Corrin, 1946; Shinoda & Soda, 1963) to the extent of 10 to 22 ml mole⁻¹ of detergent. No similar data have been obtained for polyoxyethylene glycol alkyl ethers and this communication sets out to provide information on the partial molal volumes of some members of this class of non-ionic detergents above and below their critical micellar concentrations (CMC). This information is important because changes in partial molal volume in aqueous solution must be related to changes in the state of the monomer, particularly to changes in hydrophobe-water interactions (Némethy & Scheraga, 1962).

Density measurements have been used to determine the CMC of ionic detergents (Harkins & others, 1946). How far this method is useful for obtaining the CMC of non-ionic surfactants has been assessed.

Experimental

The compounds examined have been described previously (Elworthy & Florence, 1964, 1965). The straight chain detergents have a general formula Me·[CH₂]_x·[OCH₂CH₂]₆·OH with x = 3, 5 and 7 (designated C₄n₆, C₆n₆ etc.) and the two branched chain detergents R₂·CH·CH₂·[OCH₂·CH₂]₆·OH with R = Me or Et designated Me₂n₆ and Et₂n₆. Cetomacrogol 1000 (Evans Medical) was recrystallised from an acetone-ether mixture. Hexaoxyethylene glycol (n₆) was prepared as before and purified by repeated fractional distillation.

A Lipkin pycnometer of approximately 11 ml capacity was used to measure the density of the solutions, according to the procedure of Bauer & Lewin (1960). A smaller pycnometer (0.5 ml capacity) was used for pure liquids. Each density was the mean of at least two determinations. The precision obtained on repeat measurements at 20° was ±0.00003 g ml⁻¹ with a temperature control of ±0.01°.

From the Department of Pharmacy, University of Strathclyde, Glasgow, C.1.

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Water for calibration of the pycnometers and preparation of the solutions was once distilled from potassium permanganate solution.

Results

Density measurements on solutions of Me_2n_6 were made over the whole range of concentrations and the results are recorded in Fig. 1. The deviation from linearity at the CMC can clearly be seen. Measurements on the other systems were confined to a maximum of 8% w/w concentration.

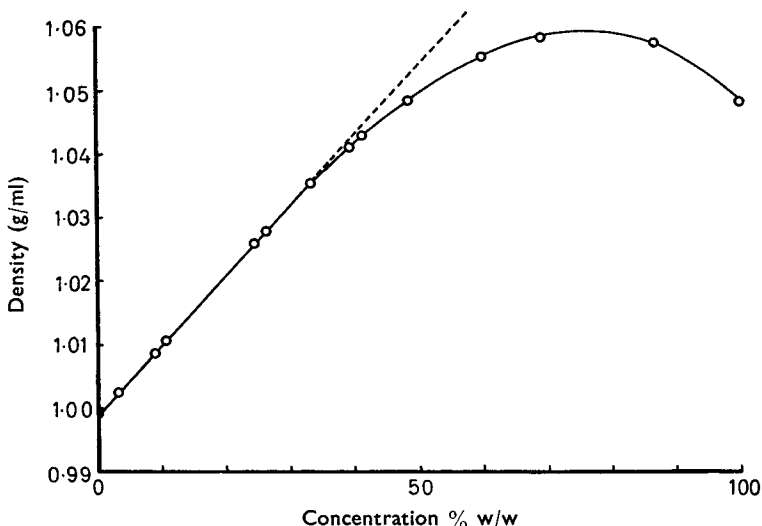


FIG. 1. The variation of the density of solutions of Me_2n_6 at 20° with concentration. The deviation from linearity begins at the CMC (34% w/w) and the density passes through a maximum at 74% w/w, the latter probably being due to a change in structure of the solution.

Density-concentration plots are given in Fig. 2 for C_6n_6 and C_8n_6 . The effect of temperature on the density plots of the two detergents is shown in this figure. The change of slope in the plots at the CMC of C_8n_6 is significant at 20° , indicating a CMC of 0.38% w/v compared with a value of 0.42% w/v extrapolated from the results of Corkill, Goodman & Ottewill (1961); at 30° the break is much less pronounced and at 40° is hardly detectable using the present technique. Bury & Parry (1935) found the change of slope in density plots for potassium laurate at the CMC to be smaller at 35° than at 25° and forecast that at higher temperatures the change would become too small to be detected. Lal (1953) confirmed this trend with lauryl sulphonic acid.

The changes in slope of the density-concentration plots are reflected in the changes in the partial molal volumes (PMV) of the detergents at the CMC. Calculated values of PMV of pure liquid detergent, monomeric detergent and micellar detergent are listed in Table 1.

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It will be seen that there is a decrease in molal volume as the liquid detergent or glycol is placed in solution. Such decreases on solution have been ascribed to the high internal pressure of water (Masterton, 1954). On micellisation the alkyl chains of the monomers are removed from their aqueous environment and they expand causing increases in partial molal volume. These are recorded in the last column of Table 1.

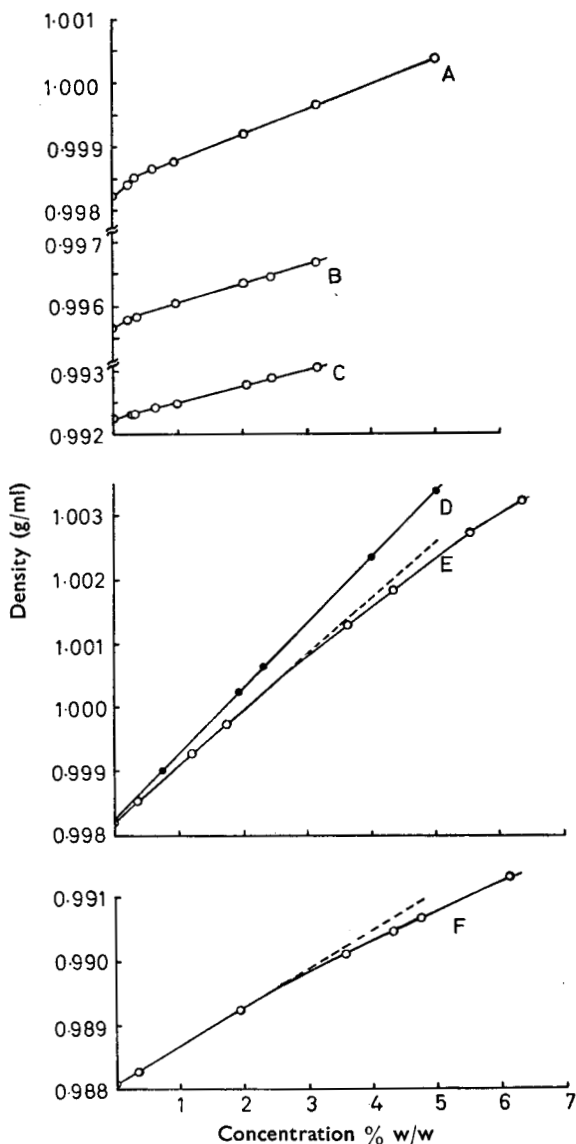


FIG. 2. Density-concentration plots of: A, C_8n_6 at 20°; B, C_8n_6 at 30°; C, C_8n_6 at 40°; D, cetomacrogol 1000 at 20°; E, C_6n_6 at 20°; F, C_6n_6 at 50°C.

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 TABLE 1. PARTIAL MOLAL VOLUMES OF PURE LIQUID, MONOMERIC AND MICELLAR DETERGENTS (ml mole⁻¹)

Compound	Temperature °C	V ₀ pure liquid state (molal volume)	\bar{V} monomeric state	\bar{V}_m micellar state	Change on micellisation ml mole ⁻¹ $\bar{V}_m - \bar{V}$
Me ₂ n ₈	20°	323	302	308*	6
	20°	360	336	341	5
	20°	324	302	307*	5
C ₄ n ₈	30°	327	305	—	—
	40°	331	—	—	—
	20°	362	333	342	9
C ₆ n ₈	30°	364.7	341	345	4
	40°	367.3	345	347	2
	50°	369.6	347.3	352.7	5.4
	20°	397.2	363	380	17
	30°	399.2	377	383	6
Cetomacrogol 1000	40°	400.9	384	387	3
	20°	—	†	1085	—
	30°	—	†	1099	—
Hexagol	20°	250.6	238	—	—
	30°	252.1	244	—	—
	40°	253.6	246	—	—
	50°	255.0	247	—	—

* Measured in the region up to 6% w/w above the CMC as PMV of these two compounds increases slowly with concentration.

† The CMC of cetomacrogol 1000 is too low to measure the PMV below this concentration. The results on micellar solutions are included to verify the trend of volume increases with short chain-length compounds.

The increase in volume is greater the longer the alkyl chain and in general becomes smaller with increase in temperature.

The partial molal volumes of the monomers (\bar{V}), which do not vary with concentration within the limits of experimental error, are much smaller than those of the pure liquids (V_0) and $\bar{V} - V_0$ becomes more negative, as might be expected, as the alkyl chain length increases. The contraction of hexagol on solution at 20° amounts to 12.6 ml mole⁻¹. Breuer (1964) has estimated that the formation of a hydrogen bond in aqueous solution is accompanied by a contraction of 1.05 ml mole⁻¹. This would suggest that, in the present instance, there were twelve hydrogen bonds involved. As six water molecules have been found to hydrate the hexaoxyethylene glycol chain (Elworthy & Florence, unpublished results), an arrangement of the water molecules involving these twelve hydrogen bonds may be envisaged. While, at this stage, it is not possible to be unequivocal about the arrangement of the hydrating water and the hydrogen bonds, as there is the possibility of some intramolecular bonding involving the terminal hydroxyl group, we may relate $\bar{V} - V_0$ to hydration. On this basis, $\bar{V} - V_0$ for this glycol at 30° (−8.1 ml mole⁻¹) corresponds to 4 water molecules of hydration, a figure which compares favourably with the viscosity estimate of 4.5 molecules.

The contribution of the glycol chain in each of the synthetic detergents may be assumed to be identical and the remainder of the contraction in solution may be assumed to be due to the hydrocarbon chain. A mechanism for the volume reduction of non-polar solutes in aqueous solution has been given by Némethy & Scheraga (1962), who computed that the formation of a hydrophobic bond—a partial reversal of the solution process—was accompanied by a volume increase ΔV_H which is a function of the number of water molecules ΔY hydrating the hydrocarbon chain.

At 20°, $\Delta V_H = 0.78 \Delta Y$ ml mole⁻¹. Using this equation it is possible to find ΔY knowing ΔV_H from Table 1. The values of ΔY so found should be of use in attempts to quantify the thermodynamics of the micellisation process.

Discussion

Except for the C₄n₆ and Me₂n₆* compounds the partial molal volumes of the compounds examined were constant in micellar solutions. Very slight increases were evident with Et₂n₆ and C₆n₆. According to Shinoda & Soda (1963) constancy of the PMV above the CMC coincides with a pseudophase separation model of micelle formation. Activity measurements on C₄n₆, Me₂n₆ and Et₂n₆ indicate that the pseudophase model does not hold for these compounds (Elworthy & Florence, unpublished results). The present behaviour agrees with this view.

It might be expected that the volume of the monomer would increase on micellisation by the same amount as the contraction attributed to the alkyl chain on solution (Table 2) because micellisation is a reversal

TABLE 2. ESTIMATES OF THE NUMBER OF WATER MOLECULES HYDRATING THE ALKYL CHAINS OF THE DETERGENT MONOMERS (20°)

Detergent	Contraction on solution due to alkyl chain, ml	Number of water molecules ($\Delta V_H/0.78$)
Me ₂ n ₆	9	12
Et ₂ n ₆	11.5	15
C ₄ n ₆	10	13
C ₄ n ₆	17	23
C ₆ n ₆	22	29

of the solution process as far as the alkyl chain is concerned. But the changes are much less. For example, with C₆n₆, the increase in volume on micellisation is only 9 ml mole⁻¹ whereas the decrease in volume due to the hydrocarbon chain-water interaction is 17 ml mole⁻¹. This may be the result of incomplete removal of the alkyl chains from contact with water or an increase in the solvation of the polyoxyethylene chains.

The results for the effect of temperature on the change of PMV at the CMC (Table 1) show clearly that the change on micelle formation diminishes with increasing temperature. This is to be expected as the water structure breaks down. The non-linear increase in PMV of the monomers may be explained after Masterton (1954) on the basis of two competing processes affecting the alkyl chain: (i) the normal linear expansion of the molecules and (ii) the breakdown of the cage-like water structure around the alkyl chains. The result for C₆n₆ at 50° is anomalous and at this stage it is impossible to say whether this is due to a change in micellar state or not. The trend of results shown here may be related to enthalpy and entropy changes in similar systems. Crook, Fordyce & Trebbi (1963) have observed that the entropies of micellisation of a series of *p*-*t*-octyl phenol polyoxyethylene ethers decrease with temperature and were all negative above 65°, implying changes in water structure.

* PMV of Me₂n₆ at 50% w/w = 313 ml mole⁻¹, at 70% = 318.5 ml mole⁻¹

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As a means of determining CMC's, density measurements provide a bulk property which is a valuable alternative to surface measurements. However, difficulties are caused by the low CMC's of most non-ionic detergents and by the fact that the alteration in slope of the density plots at the CMC is subject to the temperature of the system. Often the change in slope is almost impossible to detect (e.g. C_8n_6 at 40°) rendering the method of little use, unless more precise determinations of density are made in dilute solutions by a more accurate technique such as the magnetic float method. This technique would extend the scope of density measurements to a wider range of detergents than those quoted here.

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