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Partial Molar Volumes of Some 1-Alcohols in Micellar Solutions

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The volumetric behaviour of 1-pentanol, 1-hexanol and 1-heptanol were investigated by means of density measurements in micellar solutions of sodium decanoate, disodium 2-carboxytetradecanoate, sodium dodecylsulfate and hexadecyltrimethylammonium bromide at 298.15, 303.15 and 313.15 K. The partial molar volumes of the alcohols in the different micellar solutions have been compared with the molar volumes of the pure alcohols and the partial molar volumes at infinite dilution in water and in heptane. The results show a greater tendency for the higher alcohols to be solubilized in the micelles. The degree of solubilization seems to be a function of the surfactant molality.

The partial molar volume has proved to be a useful quantity in obtaining information about surfactant solutions.[1–13] The surfactant molar volumes increase on passing from the aqueous environment below the c.m.c. to the nonpolar one above the c.m.c.[2,7,11,12] It has been concluded that the micellar interior is liquid-like and that the hydrocarbon chains acquire a slightly looser structure than in liquid hydrocarbon.[1,4] Corkill *et al.*[4] also suggest that the hydration of the methylene groups adjacent to the hydrophilic group is retained in the micellar state.

The partial molar volume of the surfactant has also been studied under the influence of various additives.[1,14–25] Added neutral salts [1,18,19] and higher alcohols [1] had very little effect on the partial molar volumes of the surfactants. As lower alcohols were added, it was observed that the partial molar volumes of the surfactant molecules in the singly dispersed state first decreased and then increased.[17,21,25] Adddition of these alcohols apparently affected the solvent structure and solute–solvent interactions by changing the composition and dielectric constant of the environment.[25] On the other hand, the partial molar volumes of the surfactants in the micellar state increase gradually upon addition of lower alcohols.[17,21,24,25]

There have, however, been rather few investigations [1,21,26–29] of the volumetric behaviour of the additives. Vikingstad *et al.*[21,28,29] report that the partial molar volumes of *n*-alkanes and *n*-alcohols in sodium alkanoate micelles are higher than those in water but close to those of pure alkanes and alcohols, respectively. For alcohols the volumes descrease with increasing chain length of the surfactant [1,29] and with increasing surfactant concentration.[29]

When an alcohol is added to an aqueous micellar solution, it will be partitioned between the aqueous and micellar phases. The measured partial molar volume will be affected by this partitioning, and it is thus possible to obtain information about the degree of solubilization. Manabe *et al.*[26] have even calculated distribution coefficients of some alcohols in sodium dodecylsulfate from partial molar volume data.

It thus seems worth while to carry out systematic studies of the partial molar volumes of solubilizates in surfactant solutions. In this work we present data for pentanol, hexanol and heptanol in various surfactants.

EXPERIMENTAL

Chemicals. Sodium decanoate (NaC_{10}) was prepared by neutralization of decanoic acid with NaOH. Disodium 2-carboxytetradecanoate (Na_2Cl_{15}) was made from malonic ester synthesis

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using dodecylbromid and diethyl malonate. The details have been described elsewhere.[10,12] Hexadecyltrimethylammonium bromide (HTAB) was from Sigma and sodium dodecylsulfate (NaDDS) was BDH-"specially pure". The surfactants were dried in an evacuated desiccator at about 340 K for 48 h before they were used. 1-Pentanol (C_5OH), 1-hexanol (C_6OH) and 1-heptanol (C_7OH) were *puriss* quality from Fluka and were used without further purification.

Measurements. All solutions were made by weight. The densities of the solutions were measured with a Paar DMA 601 density meter. The temperature was controlled to better than ±0.005 K as measured by a Hewlett-Packard quartz thermometer.

RESULTS AND DISCUSSION

All measurements were made in homogeneous solutions in the water-rich region of the different water–surfactant–alcohol systems.

The apparent molar volumes of the alcohols, V_{ϕ,C_nOH}, were calculated by eqn. (1).

$$V_{\phi,C_nOH} = \frac{\rho^* - \rho}{m_{C_nOH}\rho^*\rho} + \frac{M_{C_nOH}}{\rho} \qquad (1)$$

Here M_{C_nOH} is the molar mass and m_{C_nOH} the molality of the alcohol, calculated as mol kg^{-1} solvent (water+surfactant). In eqn. (1) ρ and ρ^* are the densities of the solution and solvent, respectively.

Fig. 1 shows typical plots of V_{ϕ,C_nOH} *versus* m_{C_nOH} in different surfactant solutions. The partial molar volumes of the alcohols at infinite dilution, $V^\infty_{C_nOH}$, were obtained from linear extrapolations. The concentration dependence of the apparent molar volume is generally considered to reflect solute–solute interactions other than the long-range Debye-Hückel type.[30] From Fig. 1 it can be seen that the slope of V_{ϕ,C_nOH} *versus* m_{C_nOH} is larger in the NaDDS and HTAB solutions than in NaC_{10} solutions. In the latter case, the concentration ratio between alcohol and surfactant never exceeds 1:1. However, for the NaDDS and HTAB systems this ratio may become as large as 5:1. It is therefore possible that the larger slope observed for these systems reflects interactions between alcohol molecules in the micellar phase.

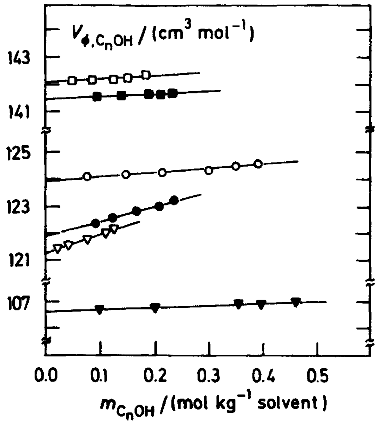

Fig. 1. Apparent molar volumes of 1-alcohols plotted *versus* the alcohol molality in different surfactant solutions at 303.15 K: 1-Heptanol in 0.15 m Na_2C_{15} (□), in 0.45 m NaC_{10} (■); 1-hexanol in 0.45 m NaC_{10} (○); in 0.1 m NaDDS (●), in 0.02 m HTAB (▽); 1-pentanol in 0.45 m NaC_{10} (▼).

Table 1. Partial molar volumes of some 1-alcohols, $V^\infty_{C_nOH}$, in micellar solutions of sodium decanoate at 303.15 and 313.15 K. The errors in measured $V^\infty_{C_nOH}$ were within ∓ 0.4 cm^3 mol^{-1}.

Alcohol	*T* K	$V^\infty_{C_nOH}$, cm$_3$ mol^{-1} 0.30 m	0.45 m	0.60 m	0.90 m
C_7OH	303.15	142.0	141.5	141.2	140.7
	313.15	143.5	142.9	142.5	142.1
C_6OH	303.15	124.6	124.1	123.9	123.7
	313.15	125.5	125.1	125.0	124.8
C_5OH	303.15	106.6	106.6	106.6	106.6
	313.15	107.7	107.6	107.6	107.6

The partial molar volumes of 1-heptanol, 1-hexanol and 1-pentanol in micellar solutions are given in Table 1 as a function of $m_{NaC_{10}}$ at 303,15 and 313,15 K. Vikingstad [29] has measured the corresponding values in 1 m NaC_{10} at 298.15 K. By extrapolation of our data, we find good agreement with his values. It can be seen from Table 1 that for C_7OH and C_6OH there is a small decrease in the volumes as $m_{NaC_{10}}$ increases.

$V^{\infty}_{C_nOH}$ apparently varies with the surfactant molality. In order to compare data for various alcohols in various surfactants a common reference point, with regard to surfactant concentration, must be found. The natural choice seems to be an extrapolation of $V^{\infty}_{C_nOH}$ to the c.m.c. of the surfactant concerned. One thus obtains the partial molar volume of the alcohol infinitely diluted in a surfactant at its c.m.c., $V^{\infty}_{C_nOH\,(cmc)}$. An example of such an extrapolation is given in Fig. 2.

Since the alcohol is distributed between the micellar and aqueous phases, the following expression can be set up for the measured partial molar volume

$$V_{C_nOH} = \alpha V^{mic}_{C_nOH} + (1-\alpha) V^{aq}_{C_nOH} \qquad (2)$$

Here α is the fraction of alcohol molecules solubilized in the micelles. $V^{mic}_{C_nOH}$ and $V^{aq}_{C_nOH}$ are the partial molar volumes of alcohol in the micellar and aqueous phases, respectively. Manabe *et al.*[26] have measured partial molar volumes of alcohols in NaDDS solutions below the c.m.c., obtaining a partial molar volume equal to the one in pure water. $V^{aq}_{C_nOH}$ in eqn. (2) may therefore be taken as equal to the partial molar volume of the alcohol in water. $V^{mic}_{C_nOH}$ cannot be measured. However, Manabe *et al.*[26] have calculated distribution coefficients from eqn. (2) by assuming that $V^{mic}_{C_nOH}$ is equal to the molar volume of the pure alcohol, $V^{*}_{C_nOH}$. This appeared to be a reasonable assumption since the partial molar volumes of nonanol and decanol were almost equal to $V^{*}_{C_9OH}$ and $V^{*}_{C_{10}OH}$, respectively, and very little nonanol or decanol are believed to be dissolved in the aqueous phase. Our results, however, show that even $V^{\infty}_{C_7OH(cmc)}$ in NaC_{10} at 303.15 K is almost equal to $V^{*}_{C_7OH}$. Using the argument of Manabe *et al.*[26] this equality indicates that practically all heptanol is solubilized in the micelles. In our opinion this is not reasonable. Vikingstad [29] has measured $V^{\infty}_{C_{10}OH}$ in 2 m sodium octanoate and obtained a value of 193.6 cm^3 mol^{-1} which exceeds the value of $V^{*}_{C_{10}OH}$ by 2 cm^3 mol^{-1}. Accordingly, we think that it is not correct to identify $V^{mic}_{C_nOH}$ with $V^{*}_{C_nOH}$. The correct value of the partial molar volume of an alcohol in the micellar phase, $V^{mic}_{C_nOH}$, probably lies between the value in pure alcohol and the value in liquid alkane. The partial molar volumes of alcohols in liquid heptane are given in Table 2, and they are seen to be larger than $V^{*}_{C_nOH}$.

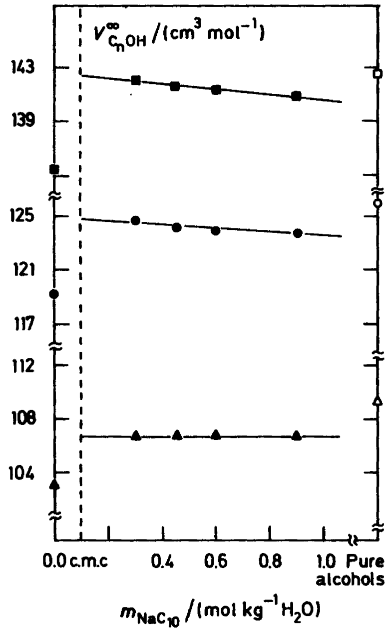

Fig. 2. Partial molar volumes of 1-heptanol (■), 1-hexanol (●) and 1-pentanol (▲) in micellar solutions of sodium decanoate at 303.15 K plotted *versus* the surfactant molality. The partial molar volumes of the alcohols infinitely diluted in water are also plotted in the figure together with the molar volumes of the pure alcohols (open symbols).

Because $V^{mic}_{C_nOH}$ in eqn. (2) is unknown, the volumetric results presented in this work cannot at present be used in any quantitative calculations of the distribution of the alcohols in micellar solutions. From the results, it is, however, possible to give a qualitative description of the distribution process. From Fig. 2 and Table 2 it turns out that $V^{aq}_{C_nOH} < V^{\infty}_{C_nOH(cmc)} < V^{*}_{C_nOH}$. The difference between $V^{aq}_{C_nOH}$ and $V^{\infty}_{C_nOH(cmc)}$ is smallest for pentanol increasing with the chain

Table 2. Partial molar volumes of some 1-alcohols in different solvents at 303.15 K and the molar volumes of the same alcohols and at the same temperature.

Alcohol	Volume, $cm^3\ mol^{-1}$ H_2O [a]	NaC_{10} [b] at c.m.c.	Na_2C_{15} [c] at c.m.c.	Nadds [b] at c.m.c.	HTAB [b] at c.m.c.	Pure [d] alcohol	Heptane [b]
C_7OH	135.10	142.4	143	–	–	142.51	147.5
C_6OH	119.02	124.7	125	121.9	121.3	125.89	131.4
C_5OH	102.94	106.6	106	–	–	109.17	115.1

[a] The values are estimated from Refs. 31 and 34 and are assumed to be better than ±0.10 $cm^3\ mol^{-1}$. [b] The errors are within ±0.4 $cm^3\ mol^{-1}$. [c] The values have been calculated from a few experimental data. [d] The error margin is less than ±0.10 $cm^3\ mol^{-1}$.

length of the alcohol. It means that the higher the alcohol, the larger is the fraction of alcohols solubilized in the micellar state. If $V^{aq}_{C_nOH}$ and $V^{mic}_{C_nOH}$ are constants in eqn. (2), the variation in $V^{\infty}_{C_nOH}$ with surfactant molality in Figs. 2 and 3 means that both a and the distribution coefficient depend on the surfactant molality. Thermodynamic and emf measurements also indicate such a dependence upon surfactant molality.[32,33]

From Table 2 it can be seen that $V^{\infty}_{C_nOH}$ depends on the surfactant. First it appears that the various polar groups of the surfactants could be a significant factor for this difference in $V^{\infty}_{C_nOH}$. However, Vikingstad [29] has observed similar differences in $V^{\infty}_{C_nOH}$ for homologous series of surfactants. It was suggested that this was caused by differences in the packing of the alcohol molecules in the interior of the micelle. Consequently, a second explanation is that $V^{\infty}_{C_nOH}$ depends on the micellar size. Thirdly, differences in the solubilization equilibria may also lead to different values of $V^{\infty}_{C_nOH}$ in different surfactant solutions. The latter effect can be estimated since distribution coefficients have been determined for alcohol–surfactant systems saturated with respect to the alcohol.[32] This contribution turns out to be quite small and works in the opposite direction of the observed differences. The effects of various polar groups or micellar size cannot be separated at this stage, but Vikingstad's argument on the size effects [29] still seems the most plausible.

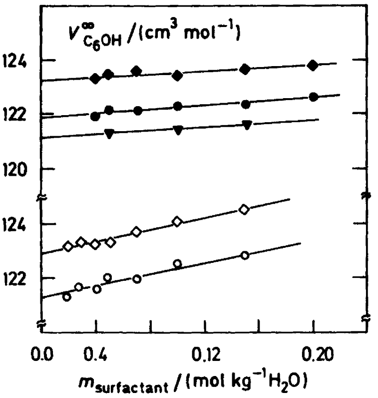

Fig. 3. Partial molar volumes of 1-hexanol in micellar surfactant solutions at 313.15 K (◆), 303.15 (●) and 298.15 K (▼) plotted *versus* the surfactant molality. Filled symbols NaDDS and open symbols HTAB.

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