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The Partial Molar Volume of 1-Alkanols in a Sodium Dodecylsulfate Solution around Its Critical Micelle Concentration

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Synopsis. The partial molar volume (V_a) of 1-alkanols (C_6–C_8) was determined at 25 °C in a solution of sodium dodecylsulfate up to its critical micelle concentration in water. The V_a in micellar solutions is higher than that in non-micellar ones. This increase in V_a has been explained in terms of the promotion of micellization by the addition of alkanol.

The partial molar volume of 1-alkanols[1,2] and alkanes[3,4] in a micellar solution of surfactants has been reported to be higher than that in water. The higher value has been attributed to the incorpotation of the solubilizate in micelles, their inside having an oil-like character.

On the other hand, the higher value can possibly be explained in terms of the transformation of the monomer surfactant species into a micellar one on the addition of the solubilizate, judging from the following well-known facts. One is the lowering of the critical micelle concentration (cmc) of the surfactants in the presence of alkanols.[5] Another is the higher partial molar volume of the micellar surfactant species than that of the monomer one in water.[6] No quantitative explanation derived from the viewpoint of micellization has, however, been proposed until now.

In order to confirm the validity of this explanation, the partial molar volume of 1-alkanols (C_6–C_8) was determined in solutions of sodium dodecylsulfate (SDS), up to 8 mmol kg^{-1}, just around cmc$_0$ (cmc in water) at 25 °C. The method of determination was the same dilatometric one as was used in previous studies[1,7]: a small amount of alkanol was successively injected into a dilatometer filled with a SDS solution.

The dependence of the experimentally determined partial molar volume (V_a) on the concentration of alkanol (C_a) for heptanol is illustrated in Fig. 1. In SDS solutions with very low concentrations as well as in water, V_a continues to be constant up to the solubility of the alkanol, followed by higher constant V_a values obtained in a turbid solution. When the SDS concentration (C_s) exceeds a certain value (C_s=2 mmol kg^{-1} for heptanol), an abrupt increase in V_a from a lower constant value to a higher one appears, without turbidity, at an alkanol concentration (C_a^*). Thereafter, the solution is saturated with the alkanol. The trend is obvious that C_a^* decreases and the solubility increases as C_s increases. As may be seen in Fig. 1, the respective concentrations, C_a^*, and the solubility coincide reasonably well with the alkanol concentration at the cmc of SDS, as determined by a surface-tension method.[8] The consistency shows that the abrupt increase in V_a at C_a^* is due to the beginning of micelle formation upon the addition of alkanol.

As for each SDS solution, the values of V_a below C_a^*, between C_a^* and the solubility, and above the solubility are averaged to give the respective mean values, V_a^f, V_a^m, and V_a^s, which are then plotted in Fig. 2 against C_s, together with the literature data.[1] It may be seen that each value has little dependence on C_s. V_a^f is close to the V_a in water: V_a^f corresponds to the partial molar volume of monomerically dissolving alkanol. V_a^m reflects the partial molar volume of alkanol in the presence of micelles, and V_a^s corresponds to that of alkanol in the separated phase. The values for each state of alkanol are averaged again, denoted by $\bar{V}_a^f$, $\bar{V}_a^m$, and $\bar{V}_a^s$, and listed in Table 1. It may be noticed that $\bar{V}_a^m$ is in agreement with the partial molar volume of each alkanol determined above the cmc$_0$ of SDS (Fig. 1). This fact suggests that the partial molar volume of alkanol at just cmc$_0$ must be equal to $\bar{V}_a^m$. $\bar{V}_a^s$ is close to the molar volume of pure liquid alkanol[1] (see Table 1), although the alkanol in the separated phase is not pure, but saturated with water.

In order to simplify the discussion, we will consider the volumetric behavior under the particular condition that the concentrations of both the micelle and the added alkanol are extremely low. If a small amount of alkanol (ΔC_a mol) is added to such a SDS solution (1 dm^3) with a very low concentration of the micelle (at cmc$_0$), it is probable that almost the entire amount of the added alkanol will dissolve monomerically in the aqueous bulk phase and cause the volume-increase by

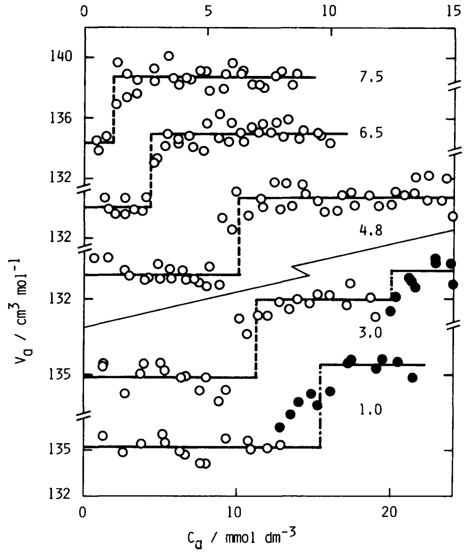

Fig. 1. The dependence of partial molar volume of 1-heptanol on its concentration in SDS solution at 25 °C. Closed circle indicates appearance of turbidity. Broken line and chain one indicate the concentration of the alkanol at cmc of SDS and solubility of the alkanol, respectively, taken from Ref. (1). Number represents C_s (mmol kg^{-1}).

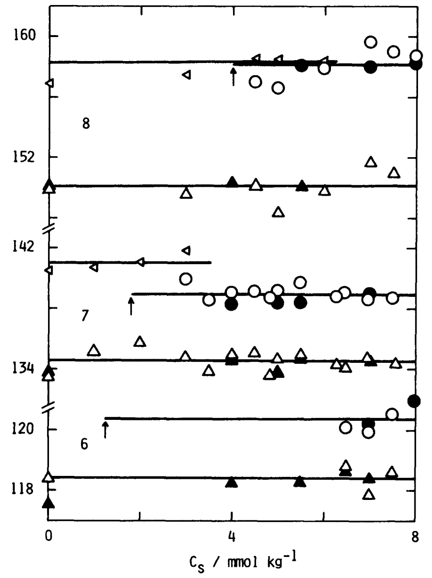

Fig. 2. The dependence of partial molar volume of 1-alkanols on the concentration of SDS at 25 °C. Large triangle, circle, and small triangle represent $\bar{V}^{\mathrm{f}}_{\mathrm{a}}$, $\bar{V}^{\mathrm{m}}_{\mathrm{a}}$, and $\bar{V}^{\mathrm{s}}_{\mathrm{a}}$, respectively. Closed mark is from Ref.(1). Number indicated the number of carbon atoms in the alkanol molecule. Arrow indicates C_s below which micelle formation is impposible, described in Ref. (8).

Table 1. Partial molar volume of 1-alkanols in an SDS solution at 25 °C

	Partial molar volume/cm^3 mol^{-1}				
	$\bar{V}^{\mathrm{f}}_{\mathrm{a}}$	$\bar{V}^{\mathrm{m}}_{\mathrm{a}}$		$\bar{V}^{\mathrm{s}}_{\mathrm{a}}$	Molar volume$^{\mathrm{b)}}$
		Below cmc$_0$	Above cmc$_0$$^{\mathrm{b)}}$		
N$^{\mathrm{a)}}$	—	—	—	—	—
6	118.36	120.38	120.93		124.70
7	134.50	138.87	139.04	141.02	141.59
8	150.12	158.11	157.53	158.21	157.91

a) Number of carbon atoms in an alkanol molecule.
b) Taken from Ref. (1).

$\Delta\bar{V}_s$ ($-\Delta$cmc) resulting from the micellization of Δcmc mol of SDS, since the increase in the concentration of alkanol (ΔC_a mol dm^{-3}) leads to the decrease in cmc (Δcmc mol dm^{-3}), where $\Delta\bar{V}_s$ indicates the partial molar volume increment of SDS on its micellization. Therefore, the total volume increment of the whole solution is $\bar{V}^{\mathrm{f}}_{\mathrm{a}}\ \Delta C_a + \Delta\bar{V}_s$ ($-\Delta$cmc). On the basis of the general definition of the partial molar volume, the volume increment per mole of alkanol added to the micellar solution, $\bar{V}^{\mathrm{m}}_{\mathrm{a}}$, corresponds to $\bar{V}^{\mathrm{f}}_{\mathrm{a}}$ $+\Delta\bar{V}_s$ ($-\Delta$cmc/ΔC_a) *i.e.* $\bar{V}^{\mathrm{m}}_{\mathrm{a}}-\bar{V}^{\mathrm{f}}_{\mathrm{a}}=\Delta\bar{V}_s$ ($-\Delta$cmc/ΔC_a). The validity of the equation can be checked in Fig. 3, by using the literature data of the rate of cmc-lowering, Δcmc/ΔC_a, of 1-alkanols in an SDS solution⁵⁾ and of the $\Delta\bar{V}_s$ for SDS in water (11 cm^3 mol^{-1}).⁶⁾ It can be recoginzed that the point ($\bar{V}^{\mathrm{m}}_{\mathrm{a}}-\bar{V}^{\mathrm{f}}_{\mathrm{a}}$, $-\Delta$cmc/ΔC_a) for each alkanol falls on a straight curve with a slope of unity and passing through 11 cm^3 mol^{-1} ($\Delta\bar{V}_a$) at the unity of $-\Delta$cmc/ΔC_a, taking the experimental errors of each term into account. The result gives the conclusion that the gain in the partial molar volume, $\bar{V}^{\mathrm{m}}_{\mathrm{a}}-\bar{V}^{\mathrm{f}}_{\mathrm{a}}$, is essentially to be attributed, no to the solubilization of the added alkanol,¹·²⁾ but to the promotion of the micellization of SDS alone.

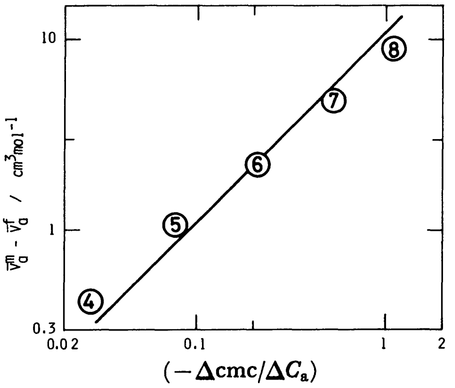

Fig. 3. The relation between log ($\bar{V}^{\mathrm{m}}_{\mathrm{a}}-\bar{V}^{\mathrm{f}}_{\mathrm{a}}$) and log ($-\Delta$cmc/$\Delta C_a$) in 1-alkanol —SDS system at 25 °C. Number indicates the number of carbon atoms in alkanol molecule. For the straight curve, see in text. $\bar{V}^{\mathrm{m}}_{\mathrm{a}}$ and $\bar{V}^{\mathrm{f}}_{\mathrm{a}}$ of 1-butanol and 1-pentanol are taken from Ref.(1).

Above cmc$_0$, $\bar{V}^{\mathrm{m}}_{\mathrm{a}}$ must be correlated in a complicated manner with the amount of solubilized alkanol. If we can estimate the quantity corresponding to Δcmc/ΔC_a at any concentration of the surfactant, the further analysis of $\bar{V}^{\mathrm{m}}_{\mathrm{a}}$ will be possible.

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