# The Partial Molar Volumes of Normal Alkanols in Aqueous Sodium Dodecyl Sulfate Solutions

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(Received May 1, 1976)

The partial molar volumes of normal alkanols ($C_mH_{2m+1}OH$, $m=1$—10) in aqueous sodium dodecyl sulfate solutions were measured by a dilatometric method at 25 °C. For the alkanols ($m=4$—8), different constant partial molar volumes appeared below and above the CMC value, whereas no such difference was observed for lower alkanols ($m=1$—3), and for higher alkanols ($m=8$—10) the partial molar volumes above the CMC value are nearly identical with their own molar volumes. The partition coefficient of the alkanols between the bulk and micellar phases is estimated on the basis of the volumetric results.

It is known that the addition of small amounts of alkanol depresses the critical micelle concentration (CMC) of surfactants,[1-4] and some factors have been considered in order to explain the phenomenon from the viewpoint that the added alkanol is partitioned between the bulk and micellar phases. Few determinations, excepting a single work,[5] have ever been made of the amount of alkanol solubilized in micelles, in spite of the necessity of the quantity for estimating the factors contributing to solubilization phenomena. It is known that the partial molar volumes of alkyl derivatives[6-9] including surfactants[10-14] increase on passing from an aqueous environment to a nonpolar one. There have been, however, restricted investigations[15,16] of the volumetric behavior of solubilizates.

In the present study, the partial molar volumes of a series of normal alkanols were determined in sodium dodecyl sulfate solutions below and above CMC. On the basis of these results, a partition coefficient of alkanol between the bulk and micellar phases is estimated.

## Experimental

The sodium dodecyl sulfate (SDS) were prepared as follows. Esterized dodecyl alcohol with sulfuric acid in absolute acetone was neutralized with a concentrated aqueous sodium hydroxide solution. The crude SDS crystal obtained from the acetone phase of the reaction mixture was recrystallized five times from acetone containing a small amount of water and then refluxed with petroleum ether. The CMC of the SDS in water was 8.30 mmol/kg[17] as determined by the conductivity method at 25 °C.

The methods of purification of water and normal alkanols used were the same as those described in an earlier paper.[9] Among the alkanols, nonyl alcohol was a commercially purified material (Tokyo Kasei Kogyo Co., Ltd., G. R. grade) and was used without further purification.

Partial molar volumes of alkanols in SDS solutions were measured using the same dilatometric method as shown in a previous paper,[9] in the alkanol-concentration range up to about 1 g/l. For higher alkanols, the solution in the dilatometer was stirred with each addition of alkanol for about one hour in order to insure sufficient dissolution. The dilatometer used in the measurements of the molar volumes of pure alkanols consits of only a glass capillary and injection parts.

## Results and Discussion

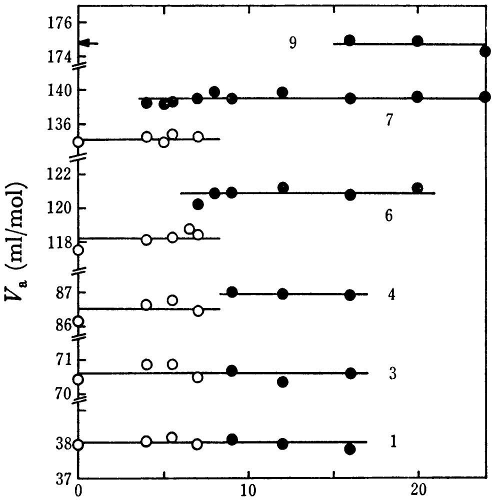

Fig. 1. Dependence of $V_a$ on SDS concentration; ○: $V_a$ below CMC, ●: $V_a$ above CMC, and —: averaged $V_a$ ($V_a^D$ or $V_a^M$). The number indicates chain length of alcohol, and the arrow molar volume of nonyl alcohol.

*Partial Molar Volumes of Normal Alkanols.* The partial molar volume, $V_a$, of normal alkanols ($m=1$—10) was determined at different specific SDS concentrations, where $m$ refers to the number of carbon atoms in the alkanol molecule. The results are plotted in Fig. 1 against the SDS concentration. It was found for alkanols with $m=4$—8 that a pair of almost constant $V_a$ values appears: one below the CMC of SDS, expressed as $V_a{}^D$, and the other above CMC, $V_a{}^M$, where the CMC values are the ones in the presence of the added alkanols. This figure is coincident with the volumetric results of surfactants in water,[10] that is, in line with a pseudo-phase separation model of micelle formation.[18] Accordingly, the $V_a{}^D$ value can be regarded as a partial molar volume of alkanol dissolved in a singly dispersed state, since the $V_a$ in water cannot be distinguished from $V_a{}^D$, and $V_a{}^M$ is probably contributed form the alkanol molecule dissolved in both the singly dispersed and solubilized states.

For lower alkanols ($m=1$—3), however, all $V_a$ values obtained here do not correspond to $V_a{}^M$ but only to $V_a{}^D$ even at SDS concentrations above the CMC value. During some determinations of the $V_a{}^M$ of higher alkanols ($m=8$—10), the concentration of alkanol eventually attained a maximum additive concentration (MAC),[19] at which turbidity appeared. The $V_a^M$ in the absence of turbidity is little different from the partial molar volume determined in the presence of turbidity, and also from the molar volume of alkanol in the normal liquid state. The $V_a^D$ value of alkanols ($m$=9, 10) could not be determined because of their very slight miscibility in water[20] and in SDS solutions below the CMC value. The almost constant $V_a^D$ values as well as $V_a^M$ values were averaged, respectively, and the mean values are shown in Table 1.

Table 1. THE MOLAR VOLUMES AND PARTIAL MOLAR VOLUMES OF NORMAL ALKANOLS IN SDS SOLUTIONS, AND THE VALUES OF $j$ AND $j/(1-j)$

| $m$ | $V_a^D$ (ml/mol) | $V_a^M$ (ml/mol) | molar volume (ml/mol) | $j$ | $j/(1-j)$ |
|---|---|---|---|---|---|
| 1 | 38.05 | | 40.72[a)] | | |
| 2 | 55.05 | | 58.68[a)] | | |
| 3 | 70.61 | | 75.13 | | |
| 4 | 86.48 | 86.90 | 91.85 | 0.077 | 0.084 |
| 5 | $102.3_4$ | $103.5_4$ | $109.0_3$ | 0.196 | 0.244 |
| 6 | $118.1_9$ | $120.9_3$ | $124.7_0$ | 0.402 | 0.672 |
| 7 | $134.1_5$ | $139.0_4$ | $141.5_9$ | 0.660 | 1.94 |
| 8 | $149.9_0$ | $157.5_3$ | $157.9_1$ | 0.93 | 13 |
| 9 | | $174.7_0$ | $174.7_1$ | | |
| 10 | | $191.6_8$ | $191.1_2$ | | |

a) Taken from Rcf. 29.

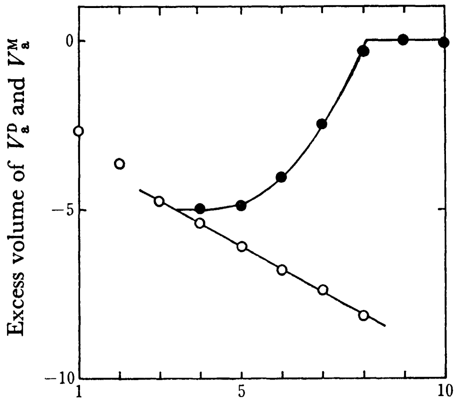

Fig. 2. Correlation of excess volumes with chain length of alcohol; ○: excess volume of $V_a^D$, ●: excess volume of $V_a^M$.

Figure 2 shows the dependence of both $V_a^D$ and $V_a^M$ on the chain length, $m$, in terms of the excess partial molar volume, the increment in the partial molar volume with respect to the molar volume, $V_a^\circ$, which is calculated from the equation:

$$V_a^\circ = 16.55m + 25.71 \quad (m=3\text{—}10). \tag{1}$$

This equation is obtained by the least-squares method from the measured molar volumes given in Table 1. The excess volume of $V_a^D$ is negative and decreases linearly with an increase in the chain length ($m$=3—8) except for lower alkanols ($m$=1, 2). Such a finding has also been made on the partial molar volumes of normal alkanols in water.[9] Hence the relation between $V_a^D$ and the chain length is expressed by the least-squares method as

$$V_a^D = 15.87m + 23.02 \quad (m=3\text{—}8). \tag{2}$$

The excess volume of $V_a^M$ is negative and increases with an increase in the chain length for $m$=4—7 and then becomes zero at about $m$=8 or above. From the viewpoint of a pseudo-phase separation model of micelle formation, it is supposed that the added alkanol in the micellar solution is partitionally dissolved between the bulk and micellar phases. The solubilized fraction of added alkanol probably increases with the chain length of the alkanol molecule, and almost the entire amounts of these higher alkanols would be solubilized; the partial molar volume of the alkanol in the solubilized state should be identical with the molar volume in their normal liquid states.[16]

The curve for $V_a^M$, in Fig. 2, can be extrapolated to intersect with the one for $V_a^D$ at about $m$=3.5. This critical chain length is comparable with that ($C_3$—$C_5$) estimated from the partial molar volume change of the surfactants on micellization as the shortest one needed for micellization according to Corkill *et al.*[12] It is likely that a solubilizate as well as surfactant with a normal alkyl chain shorter than four carbon atoms can hardly participate in the solubilization or micellization.

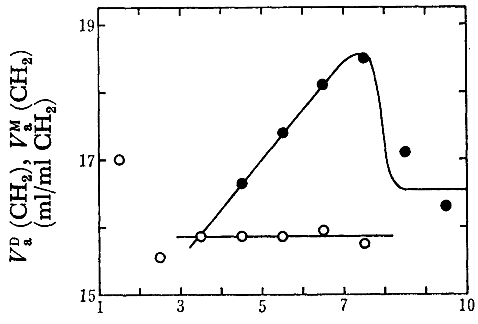

Fig. 3. Dependence of volume increment per methylene group on chain length of alcohol; ○: $V_a^D$ (CH$_2$), ●: $V_a^M$ (CH$_2$).

*Volume Increment per Methylene Group.* It is interesting and useful to discuss the increment in the partial molar volume per methylene group for normal alkanols with successive numbers of carbon atoms since the increment gives information about the environment of the group. As is shown in Fig. 3, the increment for $V_a^D$, denoted by $V_a^D(CH_2)$, except for lower alkanols ($m$=1, 2), has an almost constant value (15.87 ml/mol $CH_2$, *cf.* Eq. 2) which is in good agreement with the corresponding values of various normal alkyl chain derivatives in water (≈16 ml/mol $CH_2$).[21,22] The increment for $V_a^M$, $V_a^M(CH_2)$, indicates a nearly linear increase with an increase in the chain length ($m$=4—7) and then sharply decreases passing through a maximum to a probably constant value (16.55 ml/mol $CH_2$, *cf.* Eq. 1) above $m$=8, taking into account the identity of $V_a^M$ and the molar volume. The $V_a^M(CH_2)$ attains the constant $V_a^D(CH_2)$ at about $m=3.5$. These results for $V_a^M(CH_2)$ may be consistent with the interpretation on Fig. 2. The linear increase in the increment means that the $V_a^M$ value is a quadratic function of the chain length:

$$V_a^M = 0.3675m^2 + 13.34m + 27.66 \quad (m=4—7), \qquad (3)$$

where the coefficients were determined by the method of least squares.

Corkill *et al.*[12] supposed that the interior of the micelles is in a more expanded state than that in the normal liquid form of normal alkanes because the volume increment per methylene group of some homologous series of surfactants above CMC was 17.3 ml/mol $CH_2$, where the corresponding value of normal alkanes[12] and normal alkanols in their liquid states is identically 16.6 ml/mol $CH_2$ (*cf.* Eq. 1). However, the present results indicate that the $V_a^M(CH_2)$ of the higher alkanols ($m=8—10$) is rather comparable to the latter value. The apparent expansion of micelles formed with surfactant molecules alone may be caused, in addition to the volume increment per methylene group itself, by some other additional factors characteristic of micellization, which also depend linearly on the chain length of the surfactant. Because the volume increment per methylene group appears to be variable, as in the present case, $V_a^M(CH_2)$ increases even up to about 18.5 ml/mol $CH_2$, as is seen in Fig. 3.

*Estimation of the Partition Coefficient.* It is possible to estimate a partition coefficient for the alkanol in a solution with any composition, between the bulk and micellar phases, from the difference between $V_a^D$ and $V_a^M$. The fraction of alkanol solubilized in one mol of added alkanol, $j$, may be related with the volumetric values, as follows:

$$V_a^M = \bar{V}_a^D(1-j) + \bar{V}_a^M j \qquad (4)$$

where $\bar{V}_a^D$ and $\bar{V}_a^M$ are the partial molar volumes of alkanol in the singly dispersed and solubilized states, respectively, and the former is regarded as same as the $V_a^D$ shown in Table 1. If the $\bar{V}_a^M$ value is identical with the molar volume for all alkanols, as in the case of higher alkanols ($m=8—10$), the equation can be calculated for $j$. The values obtained of $j$ and $j/(1-j)$ which is the ratio of the fraction of alkanol solubilized to that dissolved monomerically are shown in Table 1.

The logarithmic values of $j$, $1-j$, and $j/(1-j)$ are plotted against chain length in Fig. 4. The curve of $\log j$ increases with an increase of $m$ and attains zero at about $m=8$, whereas $\log(1-j)$ increases with decreasing $m$ and attains zero at about $m=3.5$. These results are also consistent with the explanation given above. The $\log\{j/(1-j)\}$ *vs.* $m$ plot is a straight line with a positive slope given by

$$\log\{j/(1-j)\} = 0.453m - 2.89 \quad (m=4—7), \qquad (5)$$

which was obtained from a least-squares fit of the plots. If the decrease in the CMC value for the addition of alkanol is neglegible, a partition coefficient, $K$, for alkanol between the bulk and micellar phases is defined in molar fraction units as

$$K = \{j/(C_s-C_s^\circ)\}/\{(1-j)/n_w\}, \qquad (6)$$

where $C_s$ is the total SDS concentration, $C_s^\circ$ is the CMC value in water, 8.30 mmol/kg, and $n_w$ is molar number of water, 55.5 mole. It is noted that the $K$ of a given alkanol depends on $C_s$ although $j/(1-j)$ does not. Hayano and Hayase[5] have determined the partition coefficients of alkanols ($m=4—6$) by vapor pressure measurements in a 30 mmol/l SDS solution at 25 °C. The present calculated values of $K$ for the respective alkanols at the same SDS concentrations are in fairly good agreement with their values, *e.g.*, for amyl alcohol, $6.24\times10^2$ was obtained here in comparison with their value of $7.29\times10^2$.

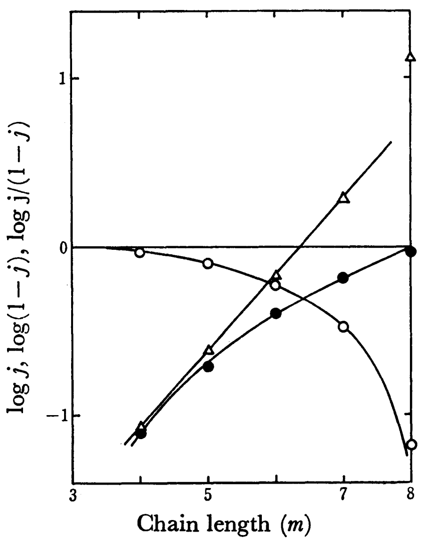

Fig. 4. Dependence of log $j$, log $(1-j)$, and log $\{j/(1-j)\}$ on chain length of alcohol; ●: log $j$, ○: log$(1-j)$, △: log $\{j/(1-j)\}$.

The standard free energy change of transfer for the methylene group of an alkanol molecule from the bulk to micellar phases can be calculated from the $K$ values and was found to be −619 cal/mol $CH_2$. This value is independent of the SDS concentration, and is in good agreement with the corresponding values of various surfactants on their micellizations.[23–25]

The authors would like to acknowledge the continuing guidance and encouragement of Professor Ryohei Matuura and Assistant Professor Shoji Kaneshina of Kyushu University.

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