Partial Molal Volumes of Surfactants in Methanol–Water Mixtures

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The partial molal volumes of surfactants in the micellar state ($\bar{V}_m$) and in the singly dispersed state ($\bar{V}_s$) have been determined at 25 °C in methanol–water mixtures up to the composition of 25 mol% methanol. The $\bar{V}_m$ of sodium dodecyl sulfate (SDS) increases gradually with the addition of methanol across the plateau region (3—15 mol% methanol). On the other hand, the $\bar{V}_s$ values of SDS and its homologous salts containing the alkyl chain of carbon numbers from 6 to 10 decrease initially with the addition of methanol and then increase up to 25 mol% methanol *via* the minimum at 3 mol% methanol. The value of $\bar{V}_m$—$\bar{V}_s$ reaches its maximum at 3 mol% methanol and then approaches zero at about 30 mol% methanol. The latter behavior is an indication of the lack of any micelle formation. In order to elucidate the solute-solvent interactions, the split of $\bar{V}_s$ into the contributions of the ionic and the hydrophobic part was attempted. Consequently, the variation in $\bar{V}_s$ with the solvent composition can primarily be attributed to the behavior of the hydrophobic group in solutions. On the basis of these results, the interactions between the hydrophobic part of the solute and the binary solvent were discussed.

The micelle formation of surfactants in solutions has been known to be affected by the temperature, the pressure, and various kinds of additives. Studies of the effect of organic additives on the critical micelle concentration (CMC) have led to an understanding of the part played by the solvent in the micelle formation.[1–6)]

The thermodynamic quantity known as the partial molal volume has proved to be a very useful tool in elucidating the interactions occurring in solutions. Studies of the partial molal volume of surfactants have been used to examine the behavior of surfactant solutions.[7–12)] They have also proved useful in determining the effect of the pressure on the micelle formation.[7,13,14)] With regard to the partial molal volume in a mixed solvent, Lee and Hyne[15)] have determined the partial molal volumes of tetraalkylammonium chlorides in ethanol–water mixtures in order to examine ion–solvent interactions in aqueous solvent mixtures. They also discussed the structural changes accompanying the addition of ethanol to water.

In this study, the partial molal volume of sodium dodecyl sulfate (SDS) has been determined above and below the CMC as a function of the cosolvent composition. Methanol was chosen as the cosolvent because it penetrates the micelle only slightly and chiefly changes the solvent property of water. The partial molal volumes of a homologous series of sodium alkyl sulfates have also been determined in the range of concentrations below the CMC in methanol–water mixtures. On the basis of these results, the interactions among water, methanol, and the hydrocarbon chain of a surfactant have been discussed.

Experimental

The SDS and its homologous salts used in this study were synthesized and purified by a method described previously.[16)] The water was redistilled from an alkaline permanganate solution. The methanol was distilled before use.

The partial molal volume was determined partly by a density method and also partly by a direct dilatometric method.[7)] The values of the partial molal volumes obtained by the two methods were in good agreement with each other. The densities of a series of solutions were simultaneously measured by using seven pycnometers with a capacity of about 20 ml; the errors in measurement was within $\pm 1\times 10^{-5}$ g/cm^3. The thermostatted bath was controlled to 25(±0.005) °C. The volume of solution per 1000 g of the solvent (water+methanol) was plotted against the molality of the surfactant, resulting in a straight line in the ranges of concentration below and above the CMC, as is shown in Fig. 1. The partial molal volume of the surfactant in aqueous methanol solutions was taken as the slope of the line; it was determined by the least-squares method on the basis of the 7—14 density data. Since the partial molal volume is almost independent of the surfactant concentration over the concentration ranges studied here,[7,8)] the experimental values thus obtained have been assumed to be identical with those corresponding to an infinite dilution. The values of the partial molal volume in a pure aqueous solution were 237.5 for SDS below the CMC, 247.0 for SDS above the CMC, and 203.6 for sodium decyl sulfate (SDeS), 172.6 for sodium octyl sulfate (SOS), and 141.3 for sodium

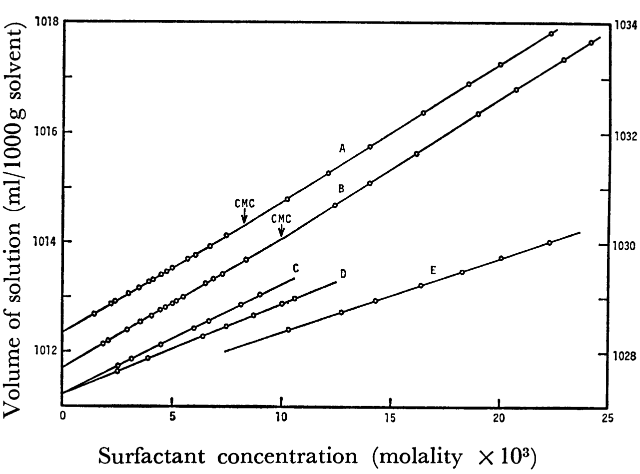

Fig. 1. Representative plots of the volume of solution per 1000 g solvent against the concentration of surfactant. A: SDS(3.31), B: SDS (9.04), C: SDeS (2.94), D: SOS (2.94), and E: SHS (2.87). The numerical values in parentheses indicate mol% of methanol in solvent. (Right scale shown is for B only).

hexyl sulfate (SHS) below the respective CMC's. These values are comparable to those of the literature.[7,8,16]

Results and Discussion

The partial molal volumes of four surfactants in the singly dispersed state and that of SDS in the micellar state are shown in Fig. 2 as functions of the solvent composition. The partial molal volume of the singly dispersed state ($\overline{V}_s$) for any surfactant decreases initially upon the addition of methanol and then increases up to 25 mol% methanol *via* a minimum at about 3 mol% methanol. On the other hand, the partial molal volume of the micellar state ($\overline{V}_m$) increases gradually upon the addition of methanol across the plateau region (3—15 mol% methanol). The $\overline{V}_m$ is slightly affected by the addition of both methanol and urea,[17] whereas the $\overline{V}_s$ is sensitive to such additives as urea[17—19] and alcohols.[15,20] This can reasonably be expected in view of the fact that the solute-solvent interaction, containing structural changes in water around the hydrophobic part of the surfactant, is included in $\overline{V}_s$.

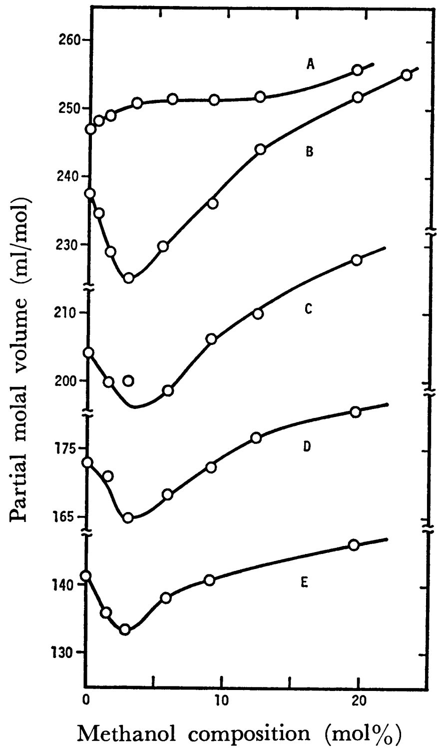

Fig. 2. Partial molal volumes of a homologous series of sodium alkyl sulfate in methanol–water mixtures at 25 °C.
Micellar state; A: SDS. Singly dispersed state; B: SDS, C: SDeS, D: SOS, and E: SHS.

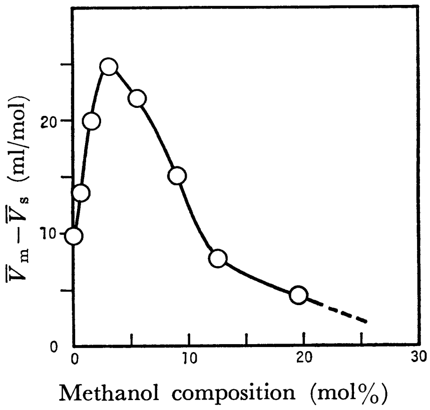

Fig. 3. The change of partial molal volume on micellization as a function of methanol content.

The change in the partial molal volume on micellization, $\Delta\overline{V}_m(=\overline{V}_m-\overline{V}_s)$, was calculated from the results shown in Fig. 2; it is shown in Fig. 3 as a function of the methanol content. The $\Delta\overline{V}_m$ in water is in good agreement with that of the literature.[7,8] As may be seem from Fig. 3, $\Delta\overline{V}_m$ initially increases upon the addition of methanol, and then it decreases *via* the maximum at 3 mol% methanol. The $\Delta\overline{V}_m$ is thermodynamically related to the pressure dependence of the CMC by the following expression, as has been described previously:[21]

$$\Delta\overline{V}_m = (1+\beta)\,RT\left(\frac{\partial \ln \mathrm{CMC}}{\partial P}\right)_{T,\Delta\overline{G}_m} \qquad (1)$$

where β is the constant which indicates the ratio of the number of the counterion to that of the surfactant ion in micelles. The results shown in Fig. 3 suggest that the CMC-increasing effect by compression reaches its maximum at 3 mol% methanol. In practice, the results of CMC measurements under high pressures in methanol–water mixtures have substantiated the above suggestion,[22] although the effect of added methanol on β has still not been elucidated. It can be seen from Fig. 3 that the extrapolation of $\Delta\overline{V}_m$ to a higher methanol content approaches zero at about 30 mol% methanol. This seems to indicate whether $\overline{V}_m$ is merely equal to $\overline{V}_s$ or whether no micelles are formed in about a 30 mol% methanol–water mixture. The latter is more likely from the facts that the CMC increases with the addition of methanol and is ultimately undeterminable at about 30 mol% methanol,[23] that the micellar weight decreases with the increase in the methanol content, and that at about 27 mol% methanol there is no evidence of micelle formation.[2,23]

It is generally known that, in alcohol–water mixtures, compounds containing the hydrophobic chain show a minimal partial molal volume at a water-rich composition and a maximal partial molal volume at a moderate composition of the solvent.[15,20] As may be seen from Fig. 2, the minimum of $\overline{V}_s$ for a homologous series of sodium alkyl sulfates was observed at a definite solvent composition (3 mol% methanol). The value of the minimal $\overline{V}_s$ is smaller by *ca.* 5% than the $\overline{V}_s$ in pure water. This contraction and the following expansion in $\overline{V}_s$ show the solute–solvent interaction characteristic of a system with methanol–water solvent mixtures. Since a surfactant molecule is composed of two parts with opposing properties, a hydrophobic and a hydrophilic group, the interactions between each part of the solute and the solvent should be discussed separately. Therefore, the split of $\overline{V}_s$ into the contributions of the ionic and the hydrophobic part was attempted as follows. By plotting $\overline{V}_s$ against the length of alkyl chain N, straight lines were obtained at various compositions of the solvent, as is shown in

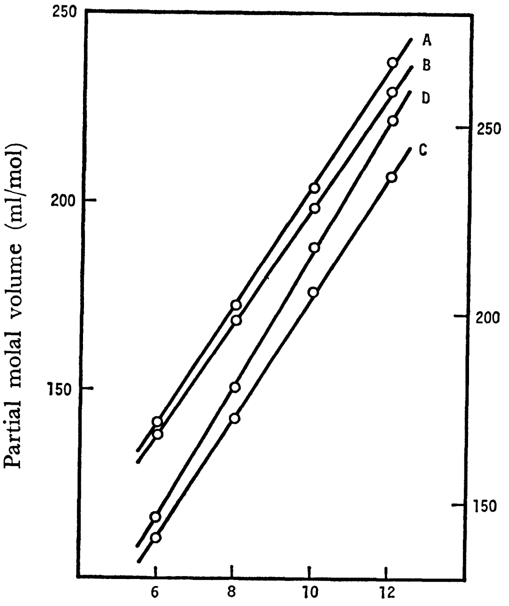

Fig. 4. Partial molal volumes of surfactants as a function of alkyl chain length. A linear relationship between $\overline{V}_s$ and N in mixed solvents of various compositions is typically shown. Methanol composition in mol%; A: 0, B: 5.87, C: 9.05, and D: 19.40. (Left scale shown is for lines A, B, and right scale for C, D.)

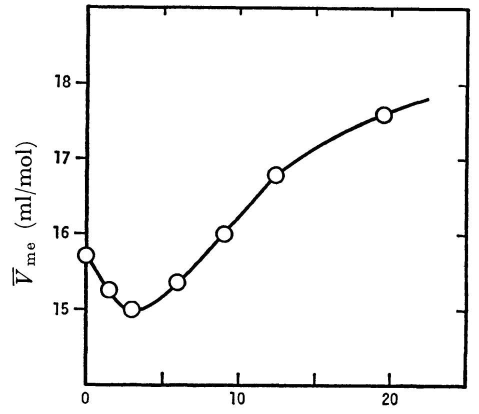

Fig. 5. The partial molal volume per one methylene group as a function of methanol content.

Fig. 4. Then the relation between $\overline{V}_s$ and N can be satisfactorily represented by the following expression.

$$\overline{V}_s=\overline{V}_i+\overline{V}_{me}N \qquad (2)$$

where $\overline{V}_{me}$ is the partial molal volume per methylene group and where $\overline{V}_i$ may be assumed to be the contribution of the ionic part, which is obtained by extrapolating N to zero in a linear plot of $\overline{V}_s$ *vs.* N. The value of $\overline{V}_i$ in water (47.0 ml/mol) is in fair agreement with the value estimated by Mukerjee for $NaHSO_4$ (47.5 ml/mol).[24] The value of $\overline{V}_i$ tends to decrease monotonously with an increase in the methanol content. This reduction of $\overline{V}_i$ may be qualitatively explained on the basis of the electrostrictive solvation effect, as was mentioned by Lee and Hyne.[15]

The $\overline{V}_{me}$ has its minimum at 3 mol % methanol, as is shown in Fig. 5. Thus, the variation in $\overline{V}_s$ with the solvent composition can be attributed to the behavior of the hydrophobic group in solutions. It is known that the transfer of hydrocarbons from a nonpolar environment to water results in a negative volume change,[25] which is considered to reflect the ordering of water molecules around the hydrocarbon chains or the "iceberg" formation.[26] Actually, the value of $\overline{V}_{me}$ in water, 15.7 ml/mol CH_2, is smaller than the contribution of the methylene group to the molal volume of normal alkanes at the C_8–C_{12} chain lengths, 16.7 ml/mol CH_2.[27] In an aqueous mixture of 3 mol % methanol, the $\overline{V}_{me}$ is more reduced than in water. This may be explained on the basis of the variation in the structure of the binary solvent with the composition.

Using the multilayer hydration models by Gurney,[28] Frank and Wen,[29] and Eigen and Wicke[30] for ion–water interactions, the partial molal volume of an ion at an infinite dilution, $\overline{V}^0_{ion}$, can be attributed to the following components:[31]

$$\overline{V}^0_{ion} = \overline{V}^0_{int} + \overline{V}^0_{elect} + \overline{V}^0_{disord} + \overline{V}^0_{caged} \qquad (3)$$

where $\overline{V}^0_{int}$ is the intrinsic partial molal volume, $\overline{V}^0_{elect}$ is the electrostriction partial molal volume, $\overline{V}^0_{disord}$ is the disordered partial molal volume, and $\overline{V}^0_{caged}$ is the caged or structured partial molal volume. Here, the $\overline{V}_{me}$ under consideration may be taken to contain only the contributions of $\overline{V}^0_{int}$ and $\overline{V}^0_{caged}$, and can be expressed by the following relation:

$$\overline{V}_{me} = \overline{V}^{int}_{me} + n_h(\overline{V}^h_0 - V_0) \qquad (4)$$

where $\overline{V}^{int}_{me}$ is the intrinsic partial molal volume for the methylene group, $\overline{V}^h_0$ is the partial molal volume of structured water around the hydrocarbon chain, V_0 is the molal volume of bulk water, and n_h is the number of hydrated or structured water molecules and is taken as 2 or 3.[26] As has been mentioned above, $\overline{V}^h_0 < V_0$ for structured water around the hydrocarbon chains. We assume that Eq. (4) is applicable to the $\overline{V}_{me}$ values in the aqueous solvent mixtures containing a small amount of methanol. In this case, V_0 should be taken as the mean molal volume of a mixture, and $\overline{V}^h_0$, as the mean partial molal volume of the solvent mixture around the hydrocarbon chain. The value of V_0 increases monotonously with an increase in the methanol content. Of course, $\overline{V}^h_0$ may be affected by the methanol added. The results shown in Fig. 5, however, show that the difference between $\overline{V}^h_0$ and V_0 reaches its maximum at the mixture of about 3 mol % methanol provided that n_h (the number of solvent molecules affected by one methylene group) changes only slightly and monotonously with the methanol content. This means that the initial addition of methanol is likely to be attributable to the structure-promotion of the solvent. By the addition more than 3 mol% of methanol, the difference between $\overline{V}^h_0$ and V_0 decreases gradually; that is, the increase in $\overline{V}^h_0$ with the increase in the methanol content overcomes that of V_0. This indicates that the addition more than 3 mol% of methanol will begin to break down the characteristic water structure.

There is an alternative explanation for the minimal $\overline{V}_{\mathrm{me}}$ at 3 mol % methanol. We assume that methanol is unaffected by the hydrocarbon chain; *i.e.*, the partial molal volume of methanol around the hydrocarbon chain is the same as that of methanol in the bulk binary solvent. Thus, in Eq. (4), V_0 should be taken as the partial molal volume of water in the binary mixed solvent, and n_{h}, as the number of water molecules affected by one methylene group, which number probably varies in proportion to the volume fraction of water in the binary solvent. It is well known that, in the methanol–water binary system, the partial molal volume of water increases slightly with the initial addition of methanol and then decreases with an increase in the methanol content *via* a maximum at about 10 mol% methanol; on the other hand, the partial molal volume of methanol has its minimum at the corresponding composition in the binary system.[32] Therefore, it can be seen from Fig. 5 that the methanol composition at which the $\overline{V}_{\mathrm{me}}$ has its minimum is not consistent with the composition of the minimal partial molal volume of methanol in the binary system; it is rather low. The results shown in Fig. 5 indicate that the second term of the right-hand side of Eq. (4) reaches its minimum at 3 mol% methanol. This probably means that the decrease in $\overline{V}^{\mathrm{h}}_0$, together with the increase in V_0, is responsible for the initial decrease in $\overline{V}_{\mathrm{me}}$ upon the addition of methanol. Thus, it may be concluded that the solvent structure is maximally promoted around the hydrocarbon chain of surfactant ions in the aqueous solvent mixture of 3 mol% methanol.

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