Thermodynamic and Viscometric Studies on the Solution State of Surfynol 465 in Water

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The vapor-pressure depression, surface tension, density and viscosity of the aqueous solution of Surfynol 465, nonionic surfactant, α,α′-[2,4,7,9-tetramethyl-5-decyne-4,7-diyl]bis[ω-hydroxy-poly(oxyethylene)], were measured at various concentrations and 298.15 K, indicating cmc at 11—14×10^{-3} mol kg^{-1} and a second cmc at *ca.* 30×10^{-3} mol kg^{-1}. From vapor-pressure depression, the association numbers of first and second micelles were approximately estimated at 4 and 13—16, respectively. From the results of density and viscosity measurements, the molar volume and Einstein's parameter, *k*, were calculated, respectively. The cohesion between the two hydrophobic chains in monomer was suggested by the analysis of molar volume. It was estimated on the molar volume and *k* of Surfynol 465 that the hydration of two hydrophilic poly(oxyethylene) chains is significant in monomer as well as micelles, but scarcely changes through micelle formation. The effect of concentration on *k* was discussed with respect to the shape and interaction of micelles.

In comparison with the usual surfactant, whose molecule has a single group each for hydrophilic and hydrophobic moieties, such as sodium dodecyl sulfate or alkylphenol with poly(oxyethylene) side chain, surfactant with more than two hydrophilic or hydrophobic groups reveals very different characteristics in monomeric state as well as in micellar one with respect to various physicochemical properties. It is well known that such a polyfunctionality plays an important role in many biological systems, *e.g.* the role of phospholipid molecule with two hydrophobic groups in the membranes of cell and neuron. Concerning phosphatidylcholine,[1-3] a typical phospholipid known as forming a similar bilayer structure to red blood cell, and on sodium 1,2-bis(2-ethylhexyloxycarbonyl)ethane sulfonate, Aerosol OT, as well as its homologues,[4,5] which are typical anionic surfactants with two hydrophobic alkyl groups, we have investigated their physicochemical properties so far and found the characteristic features caused by their structures, *i.e.* amphiphiles with two hydrophobic chains. On nonionic surfactants, Kuwamura and Takahashi studied their surface-chemical properties, using acetal-type compounds which have one hydrocarbon chain and two poly(oxyethylene) hydrophilic groups.[6] Based upon the above informations, we are now studying various physicochemical properties of nonionic Surfynols which have two sets of one branched hydrocarbon chain and one poly(oxyethylene) chain at both sides of acetylene radical. In this work, we report the

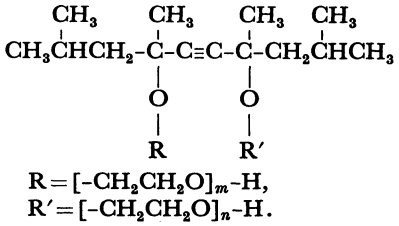

Fig. 1. Chemical structure of Surfynol 465. When m+n=10, the structure indicates Surfynol 465.

vapor-pressure depression, surface tension, density and viscosity of the aqueous solution of Surfynol 465, α,α′-[2,4,7,9-tetramethyl-5-decyne-4,7-diyl]bis[ω-hydroxyl-poly(oxyethylene)] with *ca.* ten oxyethylene segments in total (Fig.1).

Experimental

Materials. Surfynol 465 was obtained from Air Products and Chemicals, USA. NaCl was from Wako Pure Chemical Industries, Ltd., Japan. Deionized and twice-distilled water was used.

Procedures. The vapor-pressure depressions of Surfynol 465 and NaCl (reference) aq were measured with a Molecular Weight Apparatus model 115, Hitachi Ltd., Japan. Surface tension, σ, was measured by a drop-weight method, following Harkins, & Brown's correction.[7] Density, ρ, was determined with a digital precision densimeter (DMA 602/DMA 60, Anton Paar K.G., Austria) using air and water as calibration standards. Viscosity, η, was measured with a usual Ostwald viscometer. All measurements were carried out at 298.15 K±0.03 K for ρ and ±0.1 K for others.

Results and Discussion

Surfynol 465 is liquid and soluble in water at room temperature. The cloud point of 1—20 wt% aq solution exists in the range of 315—320 K, which was observed by the naked eye and plotted in Fig. 2. From the depression of vapor pressure in the very dilute aq solution, which is considered to be practically ideal, we estimated the number-average molar mass, *M*, of Surfynol 465 at 600 g mol^{-1}.

Using the molecular weight apparatus, we observed the difference in reading, Δ*R*, which indicates the vapor-pressure depression of water, against various molalities of Surfynol 465 in solution, *m*, and plotted the result in Fig. 3. The value of Δ*R* increased with *m*, approximately making a broken line, which had two breaks. The first sharp break is considered to indicate cmc (13.8×10^{-3} mol kg^{-1}) according to Brady *et al.*[8] The

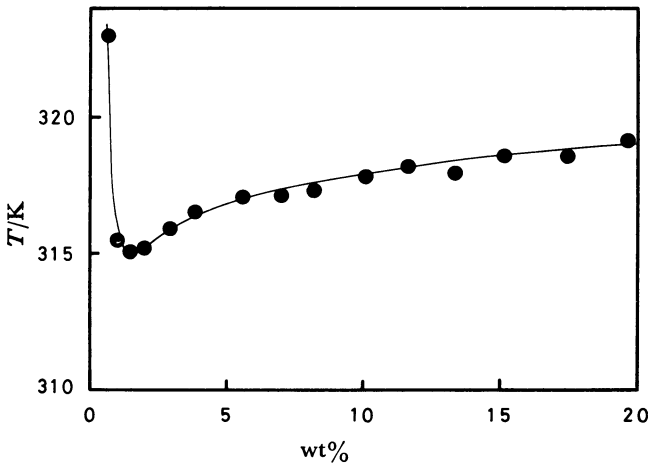

Fig. 2. Cloud point *vs.* wt% for Surfynol 465.

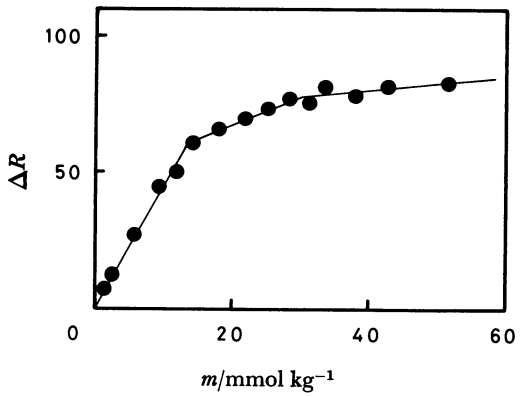

Fig. 3. Plots of ΔR *vs.* molality.

second slight break or bend suggests a second cmc.[4,5] Next, by the further analyses of the ΔR *vs.* m relation, we obtained the thermodynamic parameters for Surfynol 465, as follows. Since a real solution deviates from ideality with the increase of solute concentration, we must determine the activity coefficient of Surfynol 465, even if below cmc. Under the isopiestic condition between two solutions of reference and surfactant,

$$\nu_r m_r \phi_r = \nu m \phi, \tag{1}$$

where ν, m, and ϕ are the stoichiometric coefficient, molality and osmotic coefficient of water, respectively, for surfactant and those with suffix, r, are corresponding quantities for reference solute.[9,10] Adopting NaCl as reference, whose osmotic coefficient on $\nu_r=2$ is known over the necessary concentration range, and setting $\nu=1$, we obtained the ϕ *vs.* m relation shown in Fig. 4. The concentration, where ϕ dropped markedly, corresponds to cmc. The feature indicating the second cmc was scarcely recognized.

The activity coefficient, γ, and the activity, a, of surfactant can be calculated by Eq. 2 and 3.

$$-\ln \gamma = 1 - \phi + \int_0^m (1-\phi)/m \cdot dm \tag{2}$$

and

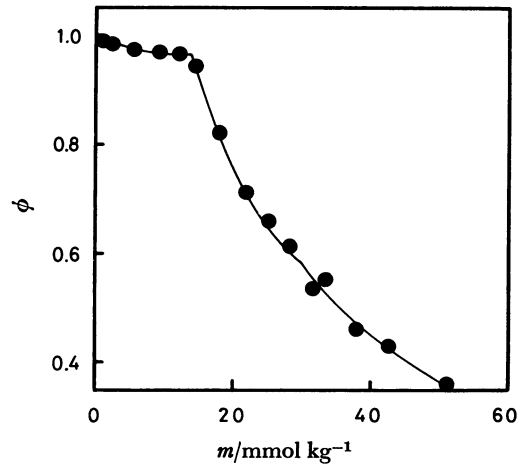

Fig. 4. Osmotic coefficient of water *vs.* molality.

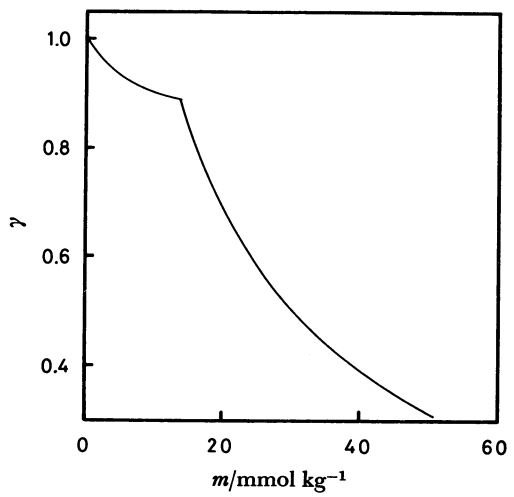

Fig. 5. Activity coefficient *vs.* molality.

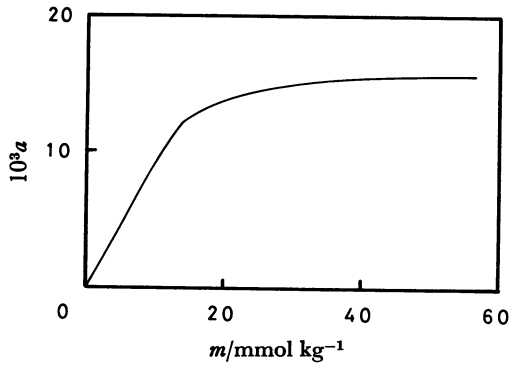

Fig. 6. Activity *vs.* molality.

$$a = \gamma m. \tag{3}$$

With the increase of m, γ decreased similarly to ϕ, also showing an abrupt fall at cmc (Fig. 5). As a result, above cmc the value of a became considerably restrained from increasing, hitherto almost proportionally to m (Fig. 6). The relation of a *vs.* m seems to be almost perfectly similar to the original relation of ΔR *vs.* m, in spite of the complex intermediates between them.

The similarity can be attributed to the nearly unit value of ϕ or the ideal nature of solute in low m.

Taking into consideration the general tendency that nonionic solutes behave more ideally than ionic solutes in water and in order to estimate the association number of Surfynol 465 in micelle, we approximately treated its aqueous solution as an ideal binary solution consisting of monomer and micelle, each of which has unit activity coefficient. As micellar species, we adopted a single kind of micelle with the association number, n, which is an average in the case of polydispersity. Then, we applied the Raoult's law to the ralation between ΔR and m (Fig. 3). The value of ΔR can be considered to be linear to the effective concentration of solute, C_{eff}, which is in an ideal solution the sum of molalities of surfactant in monomer and micelle, m_{mon} and m_{mic}, respectively, when C_{eff} is expressed in molality. Thus,

$$C_{\text{eff}} = m_{\text{mon}} + m_{\text{mic}}. \tag{4}$$

The molality of surfactant, which does not discriminate micelle from monomer, can be divided as

$$m = m_{\text{mon}} + nm_{\text{mic}}. \tag{5}$$

Then,

$$C_{\text{eff}} = m_{\text{mon}} + (m - m_{\text{mon}})/n. \tag{6}$$

The linearity of ΔR *vs.* m between cmc and second cmc can be simply explained, if both values of m_{mon} and n are assumed to be constant, m_{mon} being cmc. Calculating n as the ratio of two slopes of lines below and above cmc on ΔR *vs.* m, we obtained, *ca.* 4 for it.

For the analysis of ΔR *vs.* m relation above second cmc, the following two alternative approximations seems to be sufficient. First, approximating that the surfactant solution is an ideal ternary solution consisting of monomer, first micelle (hitherto simply called micelle) and second micelle, whose concentrations are cmc, second cmc minus cmc and m minus second cmc, respectively, we estimated the association number of second micelle at *ca.* 16 as the ratio of two slopes of lines below cmc and above second cmc on ΔR *vs.* m.[4,5] In this case, the linearity of ΔR *vs.* m holds at a constant association number of second micelle.

The second approximation assumes an ideal binary solution consisting of monomer and the second micelle, which forms from the transition of first micelle and grows in size, number or both with the increase of m above second cmc.[11] The association number of second micelle on the second approximation is not so easy to estimate directly from the slope of ΔR *vs.* m as the value on the first approximation, but is supposed to be somewhat smaller, owing to the consolidation of first micelles into second micelles at the second approximation.

Next in place of the above-mentioned phase-separation model, we considered an association equilibrium between monomer and micelle. For simplicity, we assumed also the monodispersity of micelle. Then,

$$(m_{\text{mic}}/\text{mol kg}^{-1})/(m_{\text{mon}}/\text{mol kg}^{-1})^n = K, \tag{7}$$

where K is the equilibrium constant. Combining Eq. 7 with Eqs. 4 and 5, which still hold, we have

$$\{(nC_{\text{eff}} - m)/\text{mol kg}^{-1}\}^n \cdot (n-1)^{1-n} = \{(m - C_{\text{eff}})/\text{mol kg}^{-1}\}/K, \tag{8}$$

or

$$n \ln \{(nC_{\text{eff}} - m)/\text{mol kg}^{-1}\} - (n-1) \ln (n-1) = \ln \{(m - C_{\text{eff}})/\text{mol kg}^{-1}\} - \ln K, \tag{9}$$

Converting ΔR into C_{eff} of Eq. 9 and calculating on a trial and error method, we obtained 15 for n, as seen in Fig. 7. To this value the association number of second micelle on the previously mentioned second approximation might be close.

From the inspection of σ *vs.* ln m curve, we assigned 11.1×10^{-3} mol kg^{-1} and 26.0 mN m^{-1} to cmc and the surface tension at cmc, σ_{cmc}, respectively (Fig. 8).

The surface excess, Γ, and the surface molecular area, A, of surfactant were calculated, by applying Gibbs' isotherm, Eq. 10, to the relation of σ with a, which had been calculated using Eq. 3.

$$\Gamma = -1/RT \cdot d\sigma/d\ln a, \tag{10}$$

and

$$A = 1/(L\Gamma), \tag{11}$$

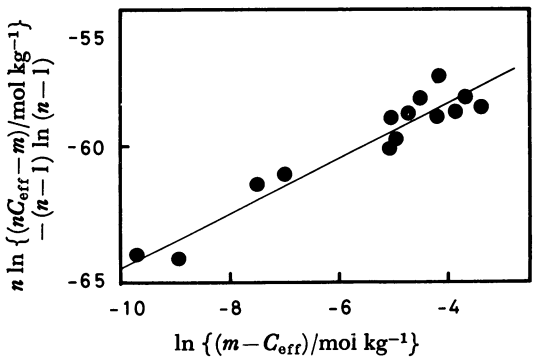

Fig. 7. Plot for the determination of association number.

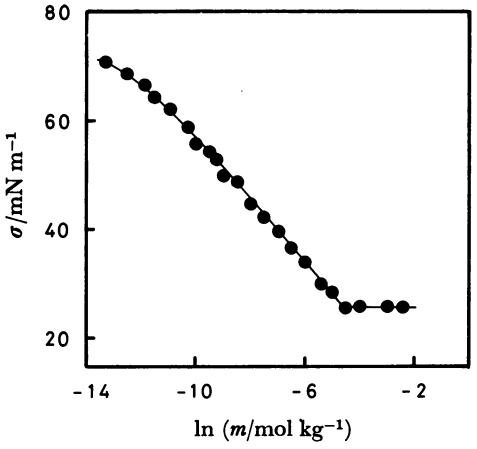

Fig. 8. Surface tension *vs.* logarithm of molality.

where L is Avogadro's number. We had 2.6×10^{-6} mol m^{-2} and 64.1 Å^2 molec^{-1} for Γ and A, respectively, near cmc.

In the course of study on acetal-type nonionic surfactant, Kuwamura and Takahashi[6] have reported that the cmc, σ_{cmc} and A of $CH_3(CH_2)_{12}CH(O(C_2H_5O)_5H)_2$, *i.e.* AG-14(10), at 293.15 K were 1.7×10^{-5} mol dm^{-3}, 36.2 mN m^{-1} and 54.5 Å^2 molec^{-1}, respectively. While the numbers of carbon, oxyethylene and poly (oxyethylene) chain of Surfynol 465 are same to those of AG-14(10), respectively, Surfynol 465 is about 650 times high in cmc, low by 10.2 mN m^{-1} in σ_{cmc} and large by 9.6 Å^2 molec^{-1} in A, each compared to AG-14(10). These discrepancies are considered to arise from the difference in the conformation of molecule in solution, wich is caused by the difference in the type of segment that connects two hydrophilic poly(oxyethylene) chains.

The relation between ρ and m makes two separate half lines, whose intersection gives cmc (12.4×10^{-3} mol kg^{-1}), as seen in Fig. 9. Owing to the lack of measurements beyond the second cmc, we could not describe the behavior of ρ or derived quantity *vs.* m at the formation of second micelle.

To obtain the apparent and partial molar volumes of surfactant, $^{\phi}V$ and V_s, respectively, we used the following relations.

$$^{\phi}V = \{(1+mM)/\rho - 1/\rho_o\}/m, \tag{12}$$

and

$$V_s = {}^{\phi}V + m(\mathrm{d}^{\phi}V/\mathrm{d}m), \tag{13}$$

where ρ_o is the density of water. The value of $^{\phi}V$ is plotted against m in Fig. 10.

Below cmc, surfactant exists only in monomeric form. There, the value of $^{\phi}V$ equals the apparent molar volume of monomer, $^{\phi}V_m$. According to Eq. 13, at infinite dilution the value of $^{\phi}V_m$ reduces to the standard partial volume of monomer, V_m°. From the inspection of Fig. 10, the following approximation can be expected at any concentration.

$$^{\phi}V_m \cong V_m^{\circ}. \tag{14}$$

Above cmc, assuming that $^{\phi}V$ is the average of monomeric and micellear contributions, we have

$$^{\phi}V = \mathrm{cmc}\cdot{}^{\phi}V_m/m + (m-\mathrm{cmc})^{\phi}V_M/m, \tag{15}$$

where $^{\phi}V_M$ is the apparent molar volume of surfactant in micelle. The $^{\phi}V$ of micelle formation, $\Delta_{mic}{}^{\phi}V$, is defined by Eq. 16.

$$\Delta_{mic}{}^{\phi}V \equiv {}^{\phi}V_M - {}^{\phi}V_m. \tag{16}$$

Then,

$$^{\phi}V = -\mathrm{cmc}\cdot\Delta_{mic}{}^{\phi}V/m + \Delta_{mic}{}^{\phi}V + {}^{\phi}V_m, \tag{17}$$

or

$$(m-\mathrm{cmc})/({}^{\phi}V - {}^{\phi}V_m) = m/\Delta_{mic}{}^{\phi}V. \tag{18}$$

From plots of $^{\phi}V$ *vs.* $1/m$ (Fig. 11) and $(m-\mathrm{cmc})/(^{\phi}V-{}^{\phi}V_m)$ *vs.* m (Fig. 12), we can ascertain the validity of Eqs. 17 and 18 or retrospectively the assumption of Eq. 15, on the basis of the constancy of $^{\phi}V_M$ as well as $^{\phi}V_m$. From the above situation,

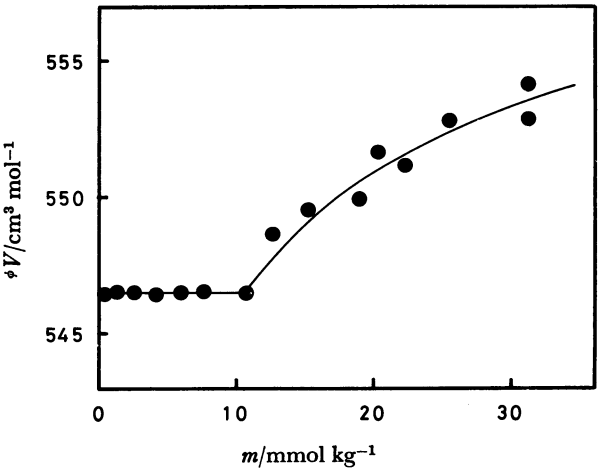

Fig. 10. Apparent molar volume *vs.* molality.

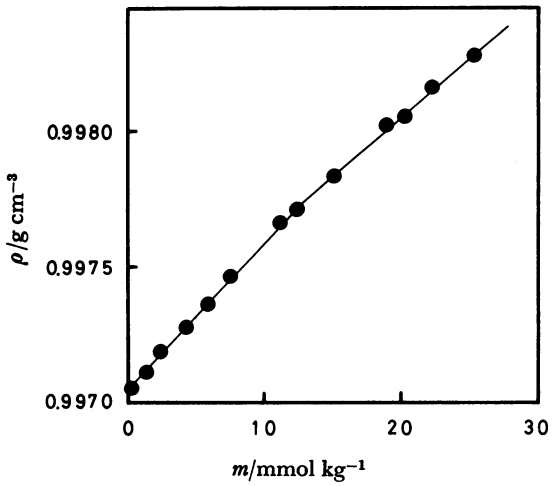

Fig. 9. Density *vs.* molality.

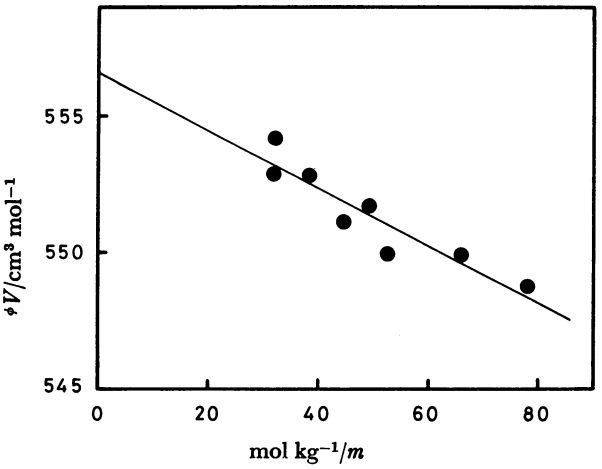

Fig. 11. Apparent molar volume *vs.* reciprocal of molality.

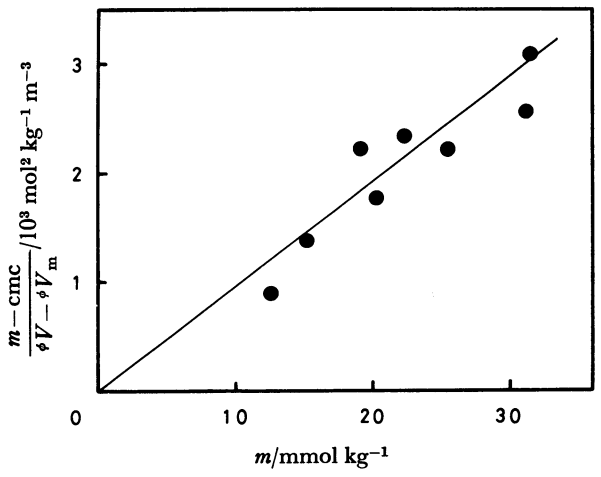

Fig. 12. $(m-\mathrm{cmc})/(^{\phi}V-^{\phi}V_{\mathrm{m}})$ *vs.* molality.

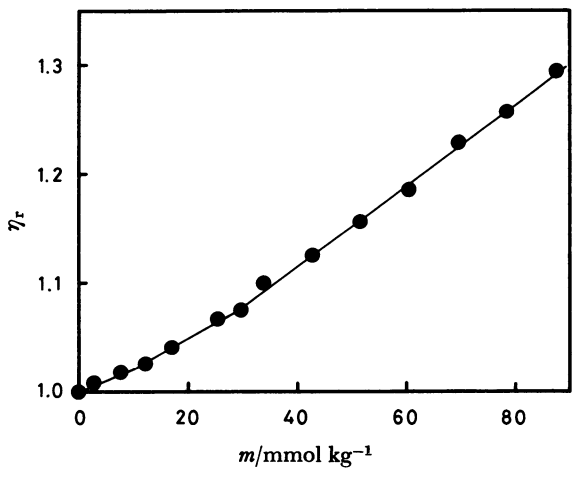

Fig. 13. Relative viscosity *vs.* concentration.

we can regard $^{\phi}V_{\mathrm{M}}$ and $\Delta_{\mathrm{mic}}{}^{\phi}V$ to be approximately equal to the standard partial volume of surfactant in micelle and of micelle formation, V°_{M} and $\Delta_{\mathrm{mic}}V^{\circ}$, respectively. From the analyses of Fig. 11 and 12, we estimated the V°_{m}, V°_{M}, and $\Delta_{\mathrm{mic}}V^{\circ}$ of Surfynol 465 at 546.5, 556.6, and 10.1 cm^3 mol^{-1}, respectively. As the optimal value of cmc for the above estimation, we used 10.6×10^{-3} mol kg^{-1} as cmc, which is slightly lower than the value estimated directly on the plot of ρ *vs.* m.

On the other hand, it is known with respect to $\Delta_{\mathrm{mic}}V^{\circ}$ that the contribution of methylene segment in one alkyl group is on the average *ca.* 1.5 cm^3 mol^{-1}, [12,13] which coincides with the molar volume change of methylene segment in paraffin at the transfer from solution state in water to liquid,[14] and the contribution of oxyethylene segment is considered to be negligible.[15] If the effect of acetylene group is ignored, the value of *ca.* 10 cm^3 mol^{-1} as $\Delta_{\mathrm{mic}}V^{\circ}$ of Surfynol 465, which has two hydrocarbon chains each with six carbons, suggests an entangling cohesion between the two chains in the surfactant molecule, dispersed in monomeric state, although the branching of hydrocarbon chains would also make the value of $\Delta_{\mathrm{mic}}V^{\circ}$ less in some degree. The above suggestion can be supported by the same case of Aerosol OT, which was studied by one of the authors and his co-worker using thermodynamic and spectrometric measurements.[4,5]

In order to study the micellar structure of Surfynol 465 from the rheological point of view, we measured the viscosity of its aqueous solution, η, against various m. The value of η increased rather monotonously with the increase of m, making only faint features near cmc and second cmc, as shown in Fig. 13 concerning the relative viscosity, η_r, *vs.* m. To make the effect of solute more conspicuous, we adopted the parameter of Einstein's formula, k, which is akin to reduced viscosity and defined by Eq. 19.[16]

$$k = (\eta_r - 1)/f, \tag{19}$$

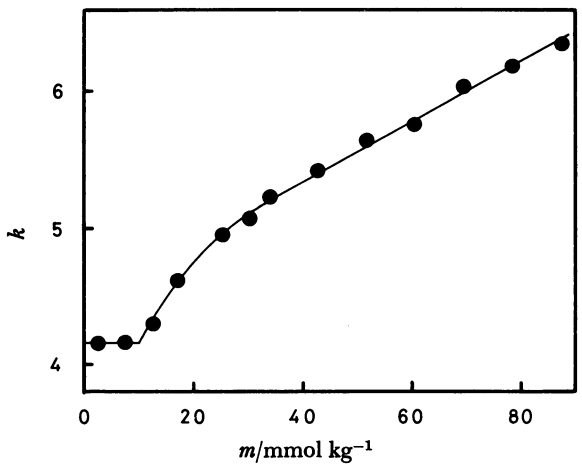

Fig. 14. Parameter of Einstein's viscosity formula *vs.* molality.

where f is the volume fraction of surfactant and can be approximately identified as the fraction of total apparent volume of surfactant, *i.e.* amount of surfactant, n_s, times $^{\phi}V$, in the volume of solution, V. Then,

$$f \cong n_s{}^{\phi}V/V = 1 - \rho/\{(1+mM)\rho_o\}, \tag{20}$$

The values of k were calculated from the results on η_r and ρ at various m and plotted in Fig. 14. Below *ca.* 10×10^{-3} mol kg^{-1}, which is approximately close to the previously described values of cmc, the value of k was constant at *ca.* 4, which is fairly higher than the theoretical value of 2.5 for spheres dispersed indepently of each other in medium. For its explanation, the deviation of molecular shape from sphere alone seems to be insufficient, since the monomer of Surfynol 465 dose not exist much differently from sphere, owing to the cohesion between its hydrophobic chains, which was previously mentioned. It is suggested that remarkable hydration occurs on the poly(oxyethylene) groups of Surfynol 465. As m increased above cmc, k increased and drew a parabola with a slight bend near second

cmc and a linear tail after it, showing the occurrence and multiplication of micelle having higher value of k than monomer. From the cause of higher k for micelle, the change in the hydration of poly (oxyethylene) group at micelle formation would be excluded, because the change is considered to be not significant, which was estimated on the analysis of $\Delta_{mic}V^{\circ}$, and might decrease k, even if it occurred, due to the dehydration and subsequent decrease of effective micellar size at micelle formation. Then, for the cause of higher k, there remain the following two factors: the shape and interaction concerning surfactant monomer and micelle.

In a dilute solution, the interaction between solutes can be excluded from discussion. Then, the shape of micelle is supposed to be significantly deviated from sphere in comparison with that of monomer, which is considered to be nearly spherical. With small n, the first micelle between cmc and second cmc is estimated to have the shape of either disk or short rod. The increase of k in this region with m is considered to result from the relative decrease of monomeric contribution to k, implying the convergence of k to the value of micelle itself. After passing through second cmc, the rate of increase in k on m recovered to show the linear increase of k, without any sign of convergence. Besides the long rod- or wide disk-like shape of second micelle with higher n, we might take into consideration the possible role played by the interaction between micelles, which facilitates a scaffold-structure, resulting in the so-called structural viscosity. Also, the possible increase of n with m might be the cause of increasing k. However, it seems to be necessary to study the micellar state above second cmc, or speaking with reserve, in a very higher concentration of Surfynol 465.

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