Conductometric and Volumetric Studies on the Inonization, Hydration, Aggregation, and Coagulation of AOT in Dodecane

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For the sodium 1,2-bis(2-ethylhexyloxycarbonyl)ethanesulfonate (AOT)/water/dodecane system, the conductivity (κ) of the solution as well as the partial molar volume of water was determined at 25 °C as a function of the water concentration (C_W) at a given concentration of AOT (C_A). The value of (κ) increased stepwise through 2 peaks before water-phase separation. Each step was assigned as follows. Upon the initial additions of water at all of the C_A's studied ($C_A < 0.2$ mol kg^{-1} (dodecane)), κ remained zero, indicating the formation of unionized hydrate, AOT(H_2O)$_2$. The critical composition of the solution for reversed micelle formation was estimated to be C_A=ca.0.02 and C_W=ca.0.04 mol kg^{-1} (dodecane). After hydrate formation, micelles were formed in equilibrium with the hydrate, at which point κ increased abruptly to the 1st peak. Coagulation of the micelles occurred above another critical composition (C_A=0.120 and C_W=0.612 mol kg^{-1}), at which point κ increased with a steep slope up to the 2nd peak. The partial molar volume of water in the same system also indicated the formation of AOT(H_2O)$_2$.

Sodium 1,2-bis(2-ethylhexyloxycarbonyl)ethanesulfonate (AOT) is an ionic surfactant which is miscible with nonpolar organic solvents, and forms thermodynamically stable aggregates, such as reversed micelles and microemulsion by the successive addition of water until phase separation occurs to form a W/O emulsion. In the solution, the water is located in the polar center (so-called water pool or micelle core) of the aggregates. The main factors concerning the aggregation are considered to be hydration and ionization of the ionic head group of the AOT molecule. Extensive studies on AOT solutions have been carried out, and various physicochemical properties have been measured as a function of *R* (the molar ratio of water to AOT) in order to elucidate the solubilization mechanism of AOT and water. In most cases, the physicochemical values remarkably change up to around 10 of *R*, and then asymptotically to the values of pure bulk water,[1—6] although the characteristic values of *R* depend not only on solvents, but also on the determination techniques.[4] The results reflect the existence of two kinds of water, providing a two-state model of water solubilization. One is bound water which strongly interacts with the ionic head group; the other is bulk-like free water which hydrates further to the bound water.[3,7,8]

In a lower water content region (the bound water region), some definite characteristic values of *R* have also been found, where each value implies the hydration number to the head group. For instance, the water ($R<6.5$) in dodecane was not frozen.[9] One of the lowest *R* values studied until now was determined by Goto et al.[5] They found that the heat of solution of water in an AOT/isooctane (2,4,4-trimethylpentane) solution changed from exothermic to endothermic at $R=2$, and was athermal above $R=11$. They thus proposed a three-state model.

It is well known that some ordinary inorganic electrolytes form stoichiometric hydrates in solid states, i.e., in unionized states. This fact suggests that AOT can form such a hydrate without ionization in nonpolar solvents in the presence of a very small amount of water. So far, however, only little attention has been paid to the ionization and hydration of AOT at such very low water contents. Thus, one of the purposes in the present study was to confirm the formation of the unionized hydrate of AOT in a nonpolar solvent.

A conductometric study concerning AOT/water/oil is useful for elucidating the ionization of AOT and interactions among AOT aggregates (micelles or microemulsion), which are insulated by a nonpolar medium. It was therefore attempted to determine the detailed conductivity dependence on the water content at a given concentration of AOT in dodecane over a wide range of concentrations of both AOT and water. The partial molar volume of water in the AOT solution was also determined in order to estimate the states of water hydrating to AOT.

Experimental

Materials. Sodium 1,2-bis(2-ethylhexyloxycarbonyl)-ethanesulfonate (AOT) was purchased from Tokyo Kasei and purified according to the following procedure. AOT (100 g) was dissolved in methanol (300 cm^3). After adding activated carbon powder, the solution was allowed to stand for one night. The carbon was filtered out through a millipore filter. After adding 200 cm^3 of water, the aqueous solution was washed five times with 100 cm^3 of petroleum benzine. It was then evaporated to remove the solvents. A viscous sample containing water was first frozen and freeze-dried, and then dried in vacuo at 110 °C for 24 h. The water content (0.0444 wt%) of purified AOT was determined by Karl Fischer titration. Dodecane (Tokyo Kasei) was distilled under reduced pressure. Water was deionized through an ion-exchange resin and then distilled for use. Its specific conductivity was less than 2 μS cm^{-1} at 25 °C.

Conductivity Measurements. The structure of conductivity cells having different volumes (cell constant= 0.2238, 0.3715 cm^{-1}), were designed to be free from moisture. Each cell was sealed with a glass cap, and having an injection aperture sealed with rubber, through which small amounts of water could be successively injected. A cell containing a dodecane solution at a certain concentration of AOT was immersed in a water thermostat, of which the temperature was controlled to be 25±1/100 °C. The conductivity was measured on a conductivity meter (HP: 4129A) operating at 1 kHz.

Partial Molar Volume Measurements. The dilatometer was of the same type as that used in a previous study.[10] It comprised a uniform capillary sealed with a glass cap, a bulb containing a magnetic stirring bar, and an injection aperture sealed with rubber. The bulb was filled with a dodecane solution of AOT. Small amounts of water were injected using a microsyringe. The partial molar volume of water ($\overline{V}_{\mathrm{W}}$) was determined from the volume increment (ΔV) and the mole number of injected water (Δn), being $\overline{V}_{\mathrm{W}}=\Delta V/\Delta n$. Measurements were carried out at 25±1/1000 °C.

The solutions were all prepared by weight. The concentrations of AOT and water, denoted by C_{A} and C_{W}, respectively, are expressed in the units of mol kg^{-1} (dodecane).

Results and Discussion

A general aspect of the dependence of the specific conductivity (κ) of an AOT solution on the water content, expressed in terms of the molar ratio R (=water/AOT), is illustrated in Fig. 1. For calculating R, the water contained in the sample AOT, itself, was taken into account, though its contribution was not substantial. At a given concentration of AOT (C_{A}), κ changed in the following manner. Upon the initial additions of water up to around R=2, κ remained virtually zero (the lowest limit of the measurable value on the conductivity meter) for all of the AOT solutions studied ($C_{\mathrm{A}}<0.2$ mol kg^{-1}). Above R, κ started increasing to a maximum above which κ slightly decreased, at low C_{A}. When C_{A} was higher, a second peak appeared and the first peak became a shoulder. After a slight decrease above the peaks, κ increased with a steep slope, and the solution became turbid due to W/O emulsion formation. Once the emulsion had formed, the measured values of κ became unstable. Figure 1 apparently shows that respective peaks are situated at around 4 and 10 of R, irrespective of C_{A}, and that at a given R, κ is higher at a higher C_{A}, except for the non-conducting region.

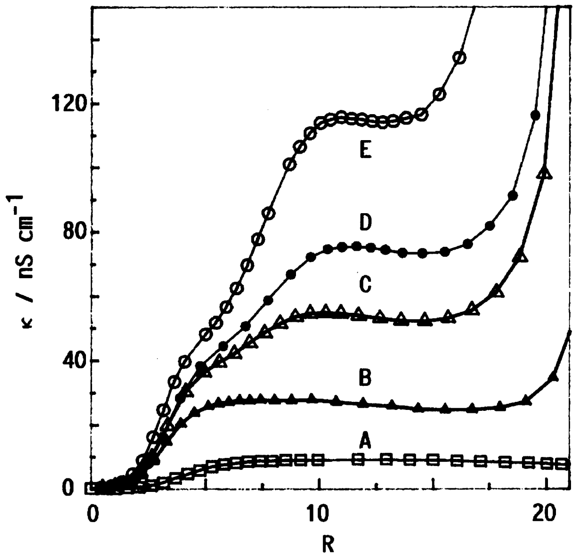

Fig. 1. The dependence of κ on R in AOT/water/dodecane system. C_{A}/mol kg^{-1}: A (0.05185); B (0.1219); C (0.1660); D (0.1795); E (0.1970).

So far, some conductometric studies[11—13] have been carried out on the systems of AOT/water/oil. The main subject of the studies was to elucidate the mechanism of the percolation transition of a microemulsion which occurs just before a phase separation due to W/O emulsion formation. Upon the transition, κ suddenly increases. Against that, in the region of low concentrations of both AOT and water, such a detailed concentration dependence on κ as the present one has not been determined. The present curves provide some novel characteristics, in addition to the percolation transition, as is now described.

In order to estimate the effect of added water on κ, the dependence of the concentration of water (C_{W}) is more effective than R, since R is an overall quantity. Thus, κ was plotted against C_{W}, as shown in Figs. 2 and 3. In these figures, and also in Fig. 1, the nearest-neighbor points are simply connected with a straight line for drawing each curve. In cases of low C_{A} (Fig. 2), each curve gives only one peak between the nonconducting region and the abruptly increasing region of the W/O emulsion, even though a monotonous increase in κ is observed at some lowest C_{A}'s (e.g., 0.02424 mol kg^{-1},

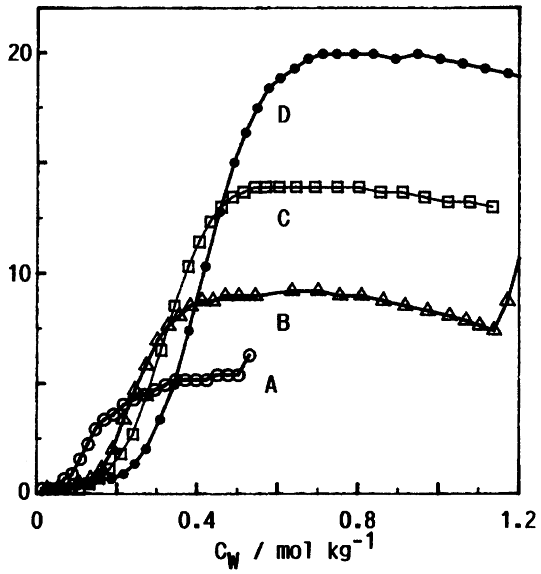

Fig. 2. The dependence of κ on C_W. C_A/mol kg^{-1}: A (0.02424); B (0.05185); C (0.07467); D (0.1012).

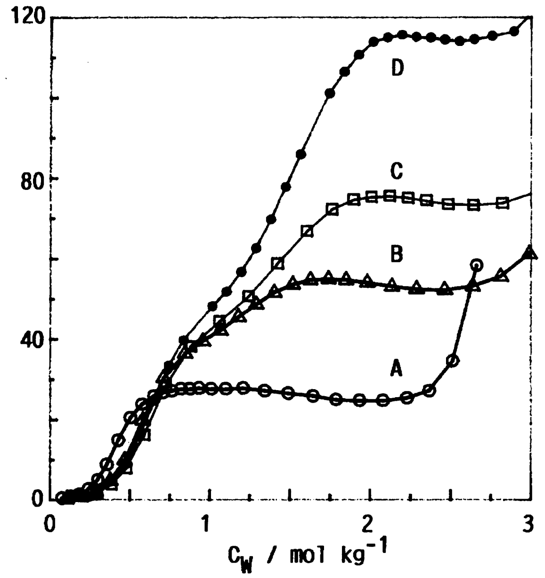

Fig. 3. The dependence of κ on C_W. C_A/mol kg^{-1}: A (0.1219); B (0.1660); C (0.1795); D (0.1970).

line A in Fig. 2). When C_A becomes higher (Fig. 3), a second peak of κ appears, above which a slight decrease is followed, as in the case of the first peak in Fig. 2; the first peak becomes a shoulder.

Some characteristic values of C_W at each C_A were determined by the linear interpolation shown in Figs. 2 and 3 in the following manner. C_{W0} is the C_W at the crossing point of the abscissa with an increasing straight line below the first peak; C_{W1} is determined from the straight line and a horizontal line through the first peak, C_{W2} from an increasing straight line below the second peak and a horizontal line through the second peak, and C_{W3} by a slightly decreasing straight line above the second peak and a steeply increasing line in the phase-transition region. A plot of each characteristic C_{Wi} against C_A gives a phase diagram, as shown in Fig. 4. Each line in Fig. 4 can be regarded as being linear. Both values of the slope ($\overline{R}_i$) and the intercept (IC$_i$), estimated by a least-mean-squares method for each C_{Wi} are listed in Table 1. The $\overline{R}_i$ indicates the partial molar ratio of water to AOT, in contrast to the overall molar ratio (R). These four lines divide the area on the phase diagram into five realms; respective areas are indicated by I—V in Fig. 4.

Kawai et al.[14] provided the same type of a phase diagram at 30 °C for systems of AOT/water/some organic solvents including dodecane, at C_A<0.1 mol kg^{-1}. They used some spectroscopic techniques in order to obtain information concerning hydrogen bonding, and the Karl Fischer titration to determine the solubility of water.

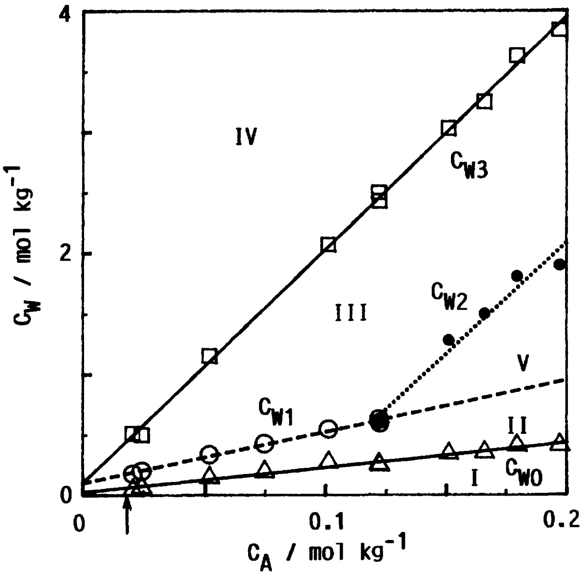

Fig. 4. The phase diagram of AOT/water/dodecane system at 25 °C. For characteristic C_W (C_{W0}, C_{W1}, C_{W2}, C_{W3}), and realm I—V, see in text. Arrow indicates C_A^m.

Table 1. The Characteristic Concentrations and Molar Ratios in AOT/Water/Dodecane System at 25 °C

i	C_{Wi}	$\overline{R}_i$[a]	IC$_i$[b] mol kg^{-1}
0	C_{W0}	2.04	0.0269
1	C_{W1}	4.24 (4.7)[d]	0.104
2	C_{W2}	18.3	−1.58
3	C_{W3}	19.3 (15.9)[d]	0.105
CMC[c]	$0.0168<C_A^m< 0.0206$		(0.0076)[d] mol kg^{-1}
	$0.0342<C_W^m< 0.0420$		(0.027)[d] mol kg^{-1}
CCC[c]	C_A^c=0.120 mol kg^{-1}		
	C_W^c=0.612 mol kg^{-1}		

a) $\overline{R}_i$: Slope (partial molar ratio: H_2O/AOT). b) IC$_i$: C_W at intercept. c) CMC, CCC: see in text, $C_W^m=\overline{R}_0*C_A^m$. d) Value in parenthesis is from Ref. 14.

The diagram is basically consistent with present one, and has the following aspects: (1) It does not have the C_{W0} line. (2) Their diagram consists of three straight lines, two of which correspond to the lines of C_{W1} and C_{W3}. The respective slopes are in agreement with $\overline{R}_1$ and $\overline{R}_3$, as given in Table 1. Another line (L),with a slope of 11.8, which is not found in the present diagram, lies between the two lines. (3) The solubility curve corresponding to C_{W3} breaks at a certain C_A, at which $C_A=0.0076$ and $C_W=0.027$ mol kg^{-1} (Table 1). The break was taken to be a critical composition of the solution for reversed micelle formation. (4) In the water pool of micelles formed below the C_{W1} line, the water directly hydrates to head group of AOT molecule. Between the C_{W1} line and L, swollen micelles are formed in which water hydrates further to the hydrated water. Between L and the C_{W3} line, microemulsions are formed in which free water exists. In the following discussion the states of hydration as well as aggregation are taken into account.

It is well known that aggregates of AOT grow from a reversed micelle to a microemulsion, and finally to a W/O emulsion with increasing water content. Generally speaking, the head group of AOT molecules, located in the water pool of each aggregate, must be dissociated into Na^+ and $-SO_3^-$ by the addition of water, resulting in an increase in κ. However, in realm I shown in Fig. 4, κ remains zero despite the addition of water, as can be seen in Figs. 1, 2, and 3. In addition, the value of $\overline{R}_0$, which indicates the hydration number, is very close to 2. Accordingly, it is concluded that the nonionized hydrate, AOT$(H_2O)_2$, is formed if it can form stoichiometrically. The unionization of the hydrate is also ascertained due to the interesting fact given in Fig. 2, that at a given C_W just above the nonconducting region, κ becomes higher as C_A (i.e., the electrolyte concentration) decreases; however, in Fig. 1, κ is lower as C_A is lower at a given R. This tendency is reversed to that of an ordinary aqueous solution of electrolytes. The reversed tendency is more definitely recognized from the curves for even lower C_A's, as given in Fig. 5. At some higher C_A's (lines B—D), κ starts increasing at a certain C_W after being nonconducting. The C_W at the break point becomes lower as C_A decreases. In other words, comparing κ at a given C_W above the break points, κ decreases along with an increase in C_A. The reversed tendency indicates that if AOT is successively added into dodecane containing an amount of water the concentration of freely ionized ions decreases. Thus, the reduction of κ is consistent with the formation of the hydrate of AOT, just as the widely known solid hydrate of ordinary electrolytes.

Unionized hydrate formation is supported by the following findings. Lucassen and Drew[15] confirmed by X-ray diffraction that homologous sodium 1,2-bis(alkyloxycarbonyl)ethanesulfonates (C_6—C_8 in alkylchain) form stable di-hydrates as well as unstable mono-hydrates. Peyrelasse and Boned[2] concluded that for $R<2$ the charge effect is small, based on dielectric complex permittivity data of the AOT/water/dodecane system. Another piece of evidence is that up to about 1.5 water molecules hydrating to a AOT molecule do not contribute to the vapor pressure of water in the AOT/water/isooctane system.[16] In addition, the characteristic molar ratios obtained in a calorimetric study ($R=2$,[5] $R=3$[17]) and an NMR study ($R=2$)[4] in some oils also show that about 2 water molecules are strongly bound to one AOT molecule. Compared to these studies, the present study bears out more definitely the formation of an unionized hydrate, AOT$(H_2O)_2$, in oil, irrespective of the AOT concentration.

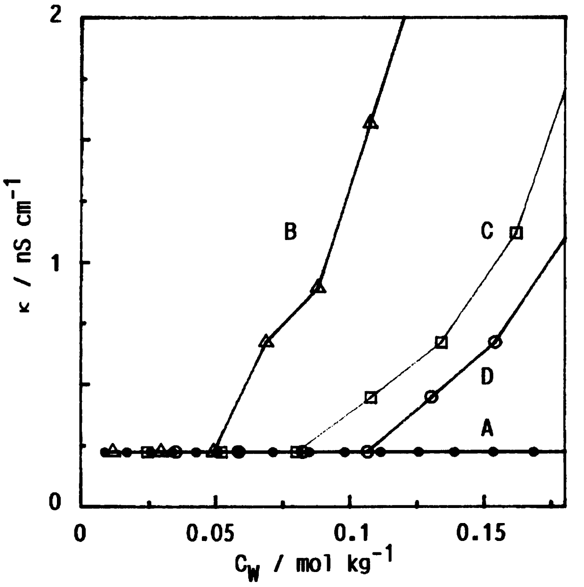

Fig. 5. The dependence of κ on C_W. C_A/mol kg^{-1}: A (0.008662); B (0.02424); C (0.05185); D (0.07467).

For the lowest C_A's studied (0.008662 and 0.01676 mol kg^{-1}), as for line A in Fig. 5, in the course of water addition at these C_A's up to the highest C_W's studied (0.1843 and 0.2729 mol kg^{-1}, respectively), κ remains zero over the solubility of water. It was difficult to visually or conductometrically confirm the solubility of water, since the solution very slowly became turbid. The two types of curves, which provide increasing (lines B—D) and nonincreasing (line A) tendencies in Fig. 5, show that a sudden increase in κ is observed at a critical C_A if κ is plotted against C_A at a given C_W, based on the data given in Fig. 5. The critical C_A value, denoted by C_A^m, lies between 0.01677 (line A) and 0.02059 mol kg^{-1} (line B). C_A^m is the lowest concentration of AOT for the solution to give a non-zero conductivity. It is therefore reasonable for C_A^m to be taken to the critical concentration of AOT for reversed micelle formation.

On the other hand, the critical concentration of water (C_W^m) for reversed micelle formation is estimated from $\overline{R}_0$ to be $C_A^m * \overline{R}_0$, considering that micelles are formed above the C_{W0} line in Fig. 4. The value of C_W^m

must be located between 0.0342 and 0.0420 mol kg^{-1}, which are calculated as C_A*R_0 for the respective C_A's (lines A and B) studied on both sides of C_A^m, as can be seen in Fig. 5. If the critical composition (represented by CMC) for reversed micelle formation is specified by both C_A^m and C_W^m, the C_{W1} line should intersect with the C_{W0} line at C_A^m, as in the phase diagram[14] mentioned above. However, the value of IC$_1$ is positive and higher than IC$_0$ (Table 1). Some of the possible reasons why these lines do not intersect at CMC are as follows: κ essentially increases abruptly from CMC on the C_{W0} line to the C_{W1} line, the values of C_{W1} estimated by the present method are too high, or estimation uncertainty for C_{W1}. No matter what the reason may be, the two types of the conductivity tendencies indicate the existence of CMC. The values of C_A^m and C_W^m are higher than the literature values,[14] as shown in Table 1. In addition, it is claimed that reversed micelle formation is a necessary condition for conducting. A question is thus whether AOT molecules aggregate or not below CMC. It was reported that in water-free binary systems of AOT/oil there exists critical concentration for AOT to form small aggregates: 0.5 mM,[18] 2.3 mM[19] in benzene, and 0.7 mM[18] in isooctane. It seems that even if AOT aggregates below C_A^m its aggregation number would be very small, and that the properties of the aggregates are different from that of the reversed micelles formed above CMC.

In realm II, upon the successive addition of water from C_{W0} to C_{W1} at a given C_A, the AOT hydrates turn to the reversed micelles and the concentration of the micelle becomes higher. One possible explanation for the rapid increase in κ from C_{W0} to C_{W1} is proposed. Provided that in realm II the micelles bear a molar ratio of $\overline{R}_1$, and they are in equilibrium with the unionized hydrates with $\overline{R}_0$, the added water is supposed to displace the equilibrium in favor of the ionized micelles. During this displacement, κ continues to rapidly increase up to the first peak as long as the hydrate exists. Once all of the hydrates are exhausted at C_{W1}, any further added water reduces the concentration of dissociated ions in the water pool; as a result, κ begins to decrease in realm III.

If the ratio ($\overline{R}_1=4.24$) is converted to the concentration of the head group of AOT, i.e., $-SO_3Na$, in water, by assuming that the water locates completely in the water pools, the concentration is calculated to be 13.1 mol kg^{-1} (H_2O). This concentration is remarkably high compared to that of an ordinary aqueous solution. However, the hydration numbers of normal 1 : 1 and 2 : 1 electrolytes in their dilute aqueous solutions are at around 10.[20] The $\overline{R}_1$ value is less than half of the hydration number. At such a high concentration, it must be difficult to freely ionize the ions in the water pool. They are probably in an ion-pair like state, and thus the water hydrates directly to ions.[14] Thus, the slightly decreasing tendency of κ above the first peak in Fig. 2 (i.e., in realm III) is interpreted in terms of the following two competing factors. The successively added water dilutes the solution in the water pool, resulting in a decreasing κ. Against that, any decreasing effect should in some parts be cancelled due to the destruction of the ion pair, i.e., complete ionization. In this case, the water is bonded to the water hydrated directly to each ion to form swollen micelles. As a result, the decreasing tendency is very slight (Fig. 2). Along this consideration of equilibrium, the size of the micelles should remain constant in realm II, and become larger in realm III. This prediction is supported by the fact that, according to Kawai et al.,[14] the aggregation number of AOT remains constant in isooctane as well as in cyclohexane at 30 °C up to $R=$ca. 5, close to $\overline{R}_1$; an increase is then followed by an increase in R, where the aggregation number at $R=0$ is lower than the constant value. It is therefore concluded that the increase in κ below the first peak is not due to a simple acceleration of the dissociation of the head group, but is due to displacement of the equilibrium between the hydrates and the micelles. In realm III, the reversed micelles are swollen by accommodating a greater amount of water, resulting in growth to microemulsions in which free water appears; finally, the W/O emulsion forms in realm IV.

It is noticed in Fig. 4 that the linear relations for C_{W1} and C_{W2} cross at a point at which the composition is denoted by CCC. The linear extension of the C_{W1} line over CCC is reasonable, because each point on the extended line falls on an inflection point of each corresponding curve in Fig. 3. The concentrations at CCC are denoted by C_A^C and C_W^C, where $C_A^C=0.120$ and $C_W^C=0.612$ mol kg^{-1} were calculated from the linear relations. Realm V has not been known until now. In this realm, κ increases over the first peak. Such a stepwise increase in κ suggests another mechanism of conductivity. Concerning the conductivity mechanism for AOT/water/oil systems, the following two factors which promote the migration of ions can be considered: (1) to increase the concentration of dissociated ions and (2) to facilitate the migration of ions through a nonpolar medium. The first factor refers to the inside of aggregates. The increasing molar ratio of water to AOT in the water pool accelerates ionic dissociation of the AOT head group, as described for realms II and III. The second factor concerns the interaction among aggregates. By encounterring aggregates insulated by the nonpolar medium the ions are able to migrate from one aggregate to another. A typical example of the second factor is the percolation mechanism[12] by which many aggregates are clustered in line to form a path for ion migration when the volume fraction of aggregates (AOT+water) attains a critical value. So far, the percolation transition mechanism has been applied to a microemulsion just before W/O emulsion formation, i.e., just below the line C_{W3}.[11—13,21] This is the point at which κ increases abruptly, as shown in Figs. 1, 2, and 3. In realm V, however, the volume fraction is too low to be related to a percolation transition.

Quite recently, Hasegawa et al.[22] found an interesting fact by using a fluorescent substance as a probe. At a high water content ($R=20$) isolated AOT micelles in heptane tend to coagulate with increasing C_A. The solution compositions correspond to those in realm V. The coagulation participates in the increase of κ in realm V, concerning the second factor of ion migration. Judging from this fact, it is presumed that a micelle (M_1) with $\overline{R}_1$ and that (M_2) with $\overline{R}_2$ can coagulate in the following manner. By the addition of water into a solution of M_1 at a given C_A, M_2 is formed in realm V. A M_2 links some M_1's, or a M_2 is surrounded by some M_1's to form a second-order aggregate (M_3). Further, various M_3 coagulate with each other, resulting in the facilitation of ion migration. This speculation provides a correlation among the molar ratios (R_2 (the over-all molar ratio on the C_{W2} line), $\overline{R}_1$, and $\overline{R}_2$) as

$$R_2 = (\overline{R}_1 * C_{A1} + \overline{R}_2 * C_{A2})/C_A. \tag{1}$$

The ratio (C_{A1}/C_{A2}) is calculated from Eq. 1 as

$$C_{A1}/C_{A2} = (\overline{R}_2 - R_2)/(R_2 - \overline{R}_1), \tag{2}$$

where C_{A1} and C_{A2} are the C_A for M_1 and M_2, respectively, on the C_{W2} line. The calculated value of C_{A1}/C_{A2} decreases asymptotically from infinity at C_A^C to zero with increasing R_2. Based on this consideration, the decrease in κ above the second peak in realm III might be due to a breakdown of the coagulates. It is worth noting that $\overline{R}_2=18.3$ is coincidence with $\overline{R}_3=19.3$. That is, since M_2 is rich in water as a microemulsion in realm III, the head group of AOT in M_2 must be completely ionized. This coincidence implies that, besides the break down, i.e., the second factor of migration, the dilution effect, i.e., the first factor, contributes to the decrease of κ.

In previous studies, the hydration numbers of solid hydrates for inorganic salts[23,24] an enzyme,[10] a polyelectrolyte,[25] and cyclodextrins,[26] were determined based on the partial molar volume ($\overline{V}_W$) of hydrated water. In this case $\overline{V}_W$ increases stepwise at each characteristic hydration number along with an increase in the amount of water added to the unhydrated solid substances immersed in dodecane; then, once the substrates start dissolving in water, $\overline{V}_W$ increases asymptotically to the molar volume of water. Accordingly, if AOT molecules are hydrated in an unionized state, $\overline{V}_W$ is presumed to be independent of the water content until $\overline{R}_0$, and then to increase asymptotically. Thus, the same method has been applied to the present system. $\overline{V}_W$, determined for homogeneous solutions, is plotted against R in Fig. 6. The difference of $\overline{V}_W$ between different C_A's at a given R can be ignored within the determination uncertainty. This fact suggests that the state of water in the water pool is mainly governed not by C_A, but by R. At first glance, $\overline{V}_W$ increase asymptotically toward the molar volume of liquid water along with an increase in R. The increasing tendency reflects the ionization of the AOT head group as well as dilution of free ions by the free water in the water pools with increasing R, as in the case of ordinary electrolyte solutions.[23,24] However, judging from the constancy of $\overline{V}_W$ for solid hydrate of ordinary electrolytes,[23,24] it is possible to consider that $\overline{V}_W$ remains constant (mean value, 17.2 cm^3 mol^{-1}, denoted by $\overline{V}_{W0}$) until $\overline{R}_0$, as shown in Fig. 6. The $\overline{V}_{W0}$ value is rather higher than those for the solid hydrate of electrolytes (around 10—13 cm^3 mol^{-1}).[23,24] This is because AOT dissolved in dodecane is not in a solid state, but in a liquid state in a monomerical form, or in a small aggregate. Such volumetric studies[7,27,28] have been carried out, although no attention has been paid to the volumetric behavior in the very low water-content region. The present value ($\overline{V}_{W0}$) compares reasonably well with the extrapolated values of the apparent molar volumes given in these reports to a limiting dilution for water; 17.75[27] (in carbon tetrachloride, 20 °C), 16.4,[28] and 16.2—16.8[7] (in n-heptane, 25 °C) cm^3 mol^{-1}. After all, the volumetric results are compatible with the conductometric ones, although the latter provide more definite information than the former.

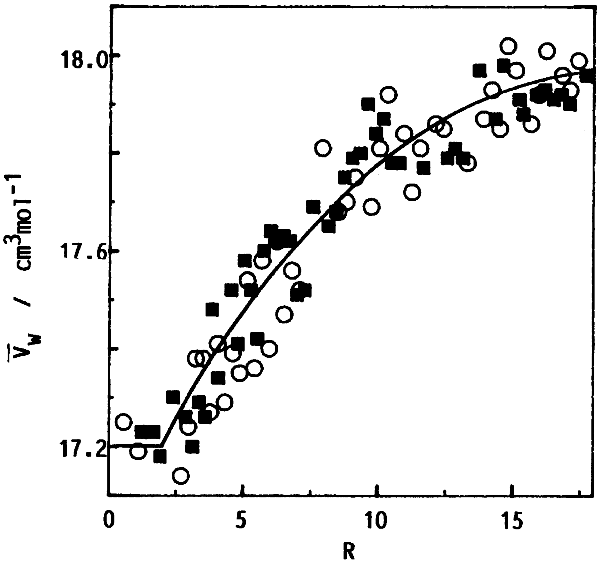

Fig. 6. The dependence of $\overline{V}_W$ in AOT/dodecane solution on R. C_A/mol kg^{-1}: open circle (0.06673); closed square (0.1489).

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