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The formation of molecular aggregation structures in ternary system: Aerosol OT / water / iso-octane

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With 4 figures and 1 table

Introduction

Sodium di-2-ethylhexylsulfosuccinate, Aerosol OT (AOT) is an anionic surfactant, which is characterized by its favorable hydrophilic and lypophilic balance in its molecular structure. This compound is accordingly well soluble either in water, a typical polar solvent, or iso-octane, a typical apolar solvent. It is also remarkable that AOT forms reversed micelles or swollen micelles in iso-octane with certain amounts of solubilized water, so-called microemulsion, which is considered thermodynamically stable. On the formation and nature of such molecular aggregation structures in apolar media extensive studies have been carried out by *Eicke* and his collaborators from both experimental and theoretical viewpoints (1). In their studies the specific importance of the role of water in forming such structures has been pointed out (2).

In the present study we attempted to establish the phase equilibrum diagram for the ternary system: AOT / water / iso-octane in order to know the extension of phase area of reversed micellar solution as well as that of liquid crystal and also to enquire, particularly, the mechanism of the transition form micellar structures to liquid crystalline structures.

In the course of our study, the phase equilibria studies on the same ternary or binary systems have independently been made by *Shinoda* and his collaborator, in which it was pointed out that the phase regions of aqueous micellar solution, apolar inverse micellar solution and liquid crystal are distinctly dependent on temperature and also that they are influenced by the purity of the sample AOT (3). Phase equilibria studies of other binary and ternary systems containing AOT as one component were also carried out by *Ekwall, Mandell* and *Fontell*, in which molecular aggregation structures of lyotropic liquid crystals were analysed in detail (4).

In our present study, however, experiments on the phase diagram and some physicochemical properties of certain phase regions have been done at isothermal condition of 25 °C in order to discuss the mechanism of the transition from swollen inverse micellar structures into liquid crystalline structures as well as its equilibrium conditions.

Experimental and results

Materials: AOT, the product of Wako Pure Chemicals Co., was purified in the following procedure according to *Shinoda* (5); 20 g of the sample is dissolved in 120 cm³ pure benzene, into which 7–8 cm³ of water being added and after strong shaking the mixture, the upper solution is separated from the lower one. This process was repeated three times in order to make AOT free from the salt, sodium sulfate, contained in the original sample. Then, after evaporating up benzene, the residue is dissolved in aqueous methanol (25%) and the solute is extracted by petroleum ether, the process being also repeated three times. The sample of pure AOT thus obtained by evaporation of petroleum ether is kept in P_2O_5- deccicator. Iso-octane was the product of special purity (b.p. 99.1 °C) and water was treated by ion-exchanger and then twice distilled.

Phase diagram: It was determined by following procedure; AOT-iso-octane solutions of various concentrations are prepared into which water is added stepwise and the mixtures sealed in pyrex ampoules are kept in a thermostat (25 °C) for 24 hours. The phase types of mixtures are detected visually or by applying crossed polaroids as well as polarizing microscope. X-ray analysis was also applied for detecting structures of liquid crystals.
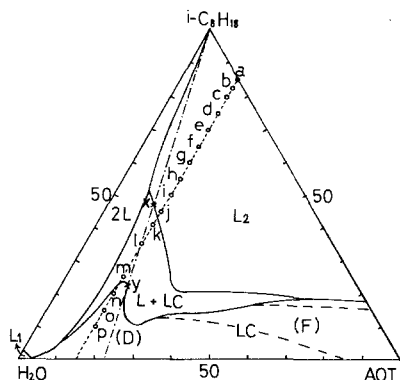
Fig. 1. Phase diagram of aerosol OT / water / iso-octane-system at 25 °C

Fig. 3. Relation between relative viscosity (η_r) or reduced viscosity ($[\eta]$) and water content for microemulsion at 25 °C

The phase diagram thus obtained is illustrated in figure 1, where L_1 means aqueous micellar solution, 2L emulsion, L_2 reversed micellar solution, LC liquid crystal whose structure being divided into lamellar (D) and hexagonal (F) types. L + LC means the phase region where liquid crystal exists in equilibrium with solution (chiefly L_2).

In this figure, it is noticed that the region of reversed micellar solution or microemulsion (L_2) widely extends in the phase diagram over about 40 to 60% of water content and also that liquid crystal phase (LC) covers a wide area along water-AOT axis. However, these phase regions change in their extensions according to temperature as *Shinoda* et al. confirmed (3).

Measurement of electric conductivity and viscosity: In connection with the work done by *Christen, Eicke* and *Rehak* (6) we measured electric conductivities and viscosities of ternary mixtures containing a definite amount of AOT and varying amounts of water and iso-octane. Starting from AOT-iso-octane solution (0.28 M) noted by *a*, we prepared mixtures AOT / iso-octane / water of compositions corresponding to notes: *b, c, d, e, f, g, h, i, j, k, l, m, n, o, p* in the phase diagram and we measured their properties. The phase transition from L_2 to L + LC takes place between points *j* and *k* and the transition from L + LC to LC occurs between points *m* and *n*.

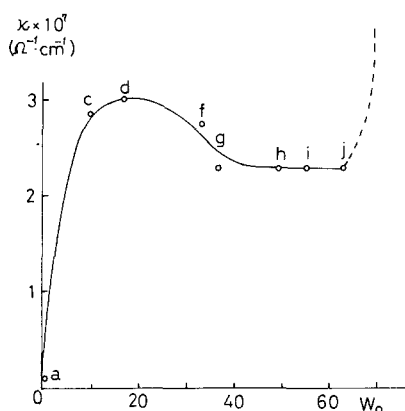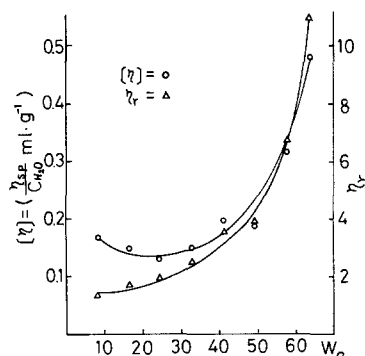The measurement of electric conductivity was made by the apparatus of CM-1DB type of TOA Co. (100 v. 60 Hz) and that of viscosity was made by a horizontal capillary viscometer as far as the viscosity of samples is not greater than 0.1P and by a Couette-type Autoviscometer for samples of greater viscosities. The experimental results for electric conductivity and viscosity are illustrated in figures 2 and 3, respectively.

Figure 2 shows the relation of specific conductivity ($\varkappa$) vs. W_o which means water content in mole per mole of AOT, namely, [H_2O] / [AOT]. Figure 3 gives the relation of relative viscosity (η_r) or reduced viscosity ($[\eta]$ i. e. η_{sp}/C_{H_2O}) vs. W_o.

The relation between shear rate and shear force for the flow of microemulsion corresponding to the point *j* and that for liquid crystal corresponding to the point *l* were determined by the rotational viscometer. It was found that the flow type of microemulsion is *Newton*ian, having viscosity of < 0.1P, whereas the flow type of liquid crystal is non-*Newton*ian, having apparent viscosity of about 1P and *Bingham* yield of about 110 dyn·cm⁻². The value of the viscosity of liquid crystal is thus about 10 times greater than that of microemulsion. The liquid crystal here examined is lamellar in its structure, the lamellar width being estimated 21 Å by X-ray diffraction patterns.

Discussion

The characteristic relations between specific conductivity or viscosity and water content shown in figure 2 and 3 will be discussed in comparison with the data previously obtained by *Christen, Eicke* and *Rehak* in their work on microemulsions of the same ternary system (6).

Comparing the figures in figure 3 and 4 with the corresponding ones given in the paper of above mentioned authors, respectively, we find remarkable resemblances between them, except for the data of higher water contents ($W_o > 40$). The relation between specific conductivity ($\varkappa$) and water content (W_o) demonstrates in both cases that $\varkappa$ rises sharply with W_o in the range of

Fig. 2. Relation between specific conductivity and water content for microemulsion at 25 °C

0–20 and also that $\varkappa$ decreases gradually with W_o in the range of 20–40. However, in the range of W_o: 40–60, $\varkappa$ is almost constant in the present case, while it still slowly decreases and then rises again in the case of *Eicke* et al. For samples of greater than $W_o > 60$ it was found in our case that the value of $\varkappa$ increases abruptly to about thousand times greater values $(10^{-3}\ \Omega^{-1} \cdot cm^{-1})$ for liquid crystalline phase, whereas in the case of *Eicke* et al. there was still a slight increase of $\varkappa$ at $W_o \simeq 60$. In our case the liquid crystalline phase (LC) separates out from the microemulsion (L_2) at $W_o \simeq 60$, but in the case of *Eicke* et al. the microemulsion transforms into the emulsion (2L) at the same water content. Such differences for both cases are considered due to the difference in AOT concentrations of samples applied: namely, 0.28 M in our case and 0.1 M in another case.

The relations for relative viscosity (η_r) or reduced viscosity $([\eta])$ vs. water content given in this paper (fig. 3) and those in *Eicke* et al.'s paper are also similar in their main features; namely, relative viscosity increases almost linearly with water content in the range of 10–40 and increases exponentially in the range of 40–60, while reduced viscosity first decreases and then increases more sharply with the increase of water content in the corresponding ranges. It is common for both our and *Eicke* and his collaborator's results that a minimum appears in reduced viscosity between water contents W_o: 20 and 30. The differences in absolute values of electric conductivity or viscosity found between our case and another one are also due to the difference in AOT concentrations of samples examined in both cases.

Now, on the mechanism of the change of molecular aggregations in our experimental results given in figure 2 and 3, analogous considerations as proposed by *Eicke* et al. will be given in the following. The sharp increase of specific conductivity in the range of W_o: 0–10 corresponds to the formation of hydrated reversed micelles, and the gradual decrease of $\varkappa$ after passing the maximum in the range of W_o: 20–40 corresponds to the coalescence of micelles, i.e. the decrease in number of micelles. The constancy of K in the range of W_o: 40–60 is considered due to the swelling process of micelles with the increase of water, during which the number of micelles being supposed to be kept constant.

The decrease of reduced viscosity in the range of W_o: 10–20 shown in figure 3 is corresponding to the decrease of specific conductivity in the same range of water content and considered due to the decrease of micelle numbers. The increase of η_r or $[\eta]$ in the range of W_o: 40–60 is considered to be attributed to the increase of micelle-sizes due to the swelling process. The fact that relative viscosity increases first linearly with W_o for 10–40 and then exponentially for 40–60 is also in accord with the change of molecular aggregations above assumed. Furthermore, it is to be noticed that at $W_o \simeq 60$ liquid crystal separates out from microemulsion to form the phase area L + LC as seen in the diagram (fig. 1) and that at this point both conductivity and viscosity exhibit an abrupt change.

In the phase region of L + LC, microemulsion is in equilibrium with liquid crystal, whose chemical compositions are different. For example, at the point l in the diagram (fig. 1) the sample has a total chemical composition: (AOT 15, H_2O 50, i-C_8H_{18} 35[%]). This will be separated into two parts: x (L_2) and y (LC), having compositions: (AOT 13, H_2O 40, i-C_8H_{18} 47 [%]) and (AOT 17, H_2O 60, i-C_8H_{18} 23[%]), respectively, which exist in equilibrium. The separation of these two parts is practically difficult and only succeeded by applying a strong centrifugal force for a long time. For the sample of liquid crystal thus obtained we determined its AOT-content by *Epton*'s ion antagonistic method and water-content by *Karl Fischer* reagents with the result of its composition: AOT 17.3, H_2O 59.6, i-C_8H_{18} 23.1, which is in good accord with the above expectation. The corresponding experimental data for the L_2 phase showed however some deviations from the calculated values, owing to the difficulty of complete separation of LC phase from the solution.

Comparing now values of molar ratios: $[H_2O] / [AOT]$ for L_2 (x) and LC (y) which are in equilibrium, we obtain following approximate values: 55 for L_2 and 91 for LC, which means that the content of water in LC is about 1.5 times richer per mole AOT than that in L_2. Furthermore, the molar ratios [i-C_8H_{18}] / [AOT] for L_2 (x) and LC (y) are 12.6 and 6.1, respectively; this means that LC is about 2 times poorer in iso-octane per mole AOT than L_2 in equilibrium.

From the above considerations it is supposed that there is a certain limit for the number of water molecules which can be contained in the inner core of a micelle formed by a definite number of AOT molecules in a stable microemulsion. When the relative number of water molecules exceed such a limit, reversed micelles will be collapsed and consequently, microemulsion will transform into liquid crystalline structure.

The equilibrium:

$$L_2 \rightleftarrows LC$$
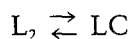
is dependent on temperature. We tried to examine how the formation of LC phase changes with temperature. With samples of various compositions: (15, 65, 20); (15, 60, 25); (15, 55, 30) for AOT, H_2O, i-C_8H_{18}, respectively, the existence of LC phase in these mixtures was observed at temperatures between 10–30 °C and was found that higher the temperature, the more favored for LC formation, as shown in table 1. The formation of liquid crystalline phase from microemulsion is accordingly endothermic. The temperature increase will accelerate the molecular rearrangement due to thermal motion. This conclusion leads us to thermodynamic considerations for the above equilibrium. In the relation:

$$\Delta F = \Delta H - T\Delta S$$

if $\Delta H > 0$ (endothermic) it should be $\Delta S > 0$, provided that $\Delta F = 0$ for the equilibrium. The transition of L_2 into $L_2 + LC$ is thus considered to be accompanied by an entropy increase, which might be attributed to the state change of water molecules, from „bound state" to „free state", inspite of the probable entropy decrease due to lamellar arrangement of AOT molecules
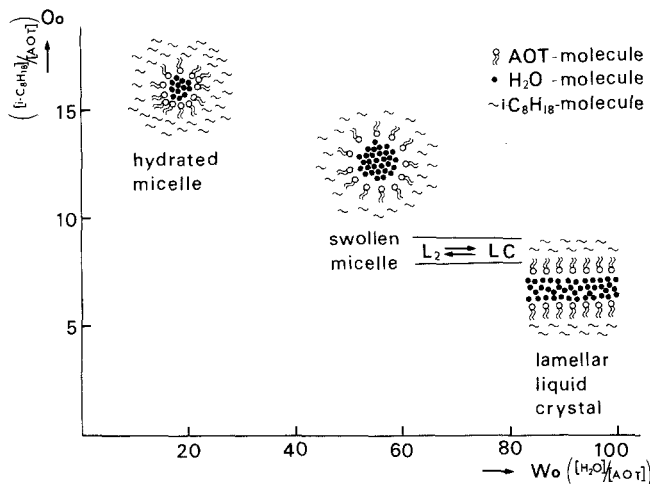

Fig. 4. Schematic illustration for transition from microemulsion to lamellar liquid crystal

in LC-phase which takes place at the same time. However, the former effect will overcome the latter one in absolute units.

The mechanism of such changes of molecular association structures occurring in the ternary system: AOT / water / iso-octane according to the change of water content, as above considered, may be schematically illustrated in figure 4, after the manner of *Eicke* and *Christen* (7).

There is still a problem to be discussed what kinds of molecular interaction forces are concerned in such changes of structures. If we add our considerations on this problem here shortly, it is supposed that for the formation of hydrated micelles or swollen micelles electrostatic forces (attractive as well as repulsive) or hydrogen bonding forces (attractive) between AOT polar groups and water molecules may play an important role, while for the formation of lamellar liquid crystalline structures dispersion forces (long range attractive) and solvation forces (repulsive) among hydrocarbon chains may play an important role. Regarding such considerations, articles written by *Friberg* (8) on "Lyotropic Liquid Crystals" may be referred to.

Summary

The phase equlibrium diagram for the ternary system: Aerosol OT / water / iso-octane is established at 25 °C. In this diagram it is noticed that the reversed micellar solution or microemulsion phase extends in its area so far as the water content reaches 50–60 (wt.%) at which liquid crystalline phase begins to appear. On the experimental data of electric conductivity, viscosity, optical birefringence, etc. for the samples containing a definite amount of AOT (0.28 M), and

Table 1. Temperature dependence of liquid crystalline phase formation. The number added means volume ratio between L and LC.

AOT/water/iso-octane (wt %)			10°C	16°C	20°C	25°C	30°C
15	65	20	L + LC 2/1	L + LC 1/20	LC	LC	LC
15	60	25	L + LC 15/1	L + LC 1/1	L + LC 1/20	L + LC	LC
15	55	30	L + LC 30/1	L + LC 1/3	L + LC 1/1	L + LC	LC
15	35	50	2 L	L_2	L_2	L_2	L_2

various relative amounts of water and iso-octane, the mechanism of the transition of reversed micellar structures into lamellar liquid crystalline structures is discussed from the viewpoint of thermodynamics and molecular kinetic theories.

Zusammenfassung

Das Phasendiagramm vom ternären System: Aerosol OT / Wasser / Iso-octan bei 25 °C ist angegeben. In diesem Diagramm ist zu bemerken, daß die Phase der inversen mizellaren Lösung oder Mikroemulsion so weit entwickelt ist, daß ihr Wassergehalt 50–60 (gew.%) erreicht, wobei flüssige Kristalle erscheinen. Auf Grund der experimentellen Daten der elektrischen Leitfähigkeit, Viskosität, optischen Doppelbrechung usw., von den Proben mit dem bestimmten AOT-Gehalt (0,28M) wird der Mechanismus der Umwandlung von inversen mizellaren Strukturen zu lamellaren flüssigen Kristallen aus dem Gesichtspunkt der Thermodynamik und molekularkinetischen Theorie diskutiert.

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