Abnormal Dielectric Response of Aerosol OT W/O Microemulsion in Cyclohexane at 298.15 K

Reiji Tanaka,* Kaori Okazaki, and Hideo Tsuzuki†
Department of Chemistry, Faculty of Science, Osaka City University, Sugimoto, Sumiyoshi-ku, Osaka 558
†*Central Workshop of Osaka City University, Osaka City University, Sugimoto, Sumiyoshi-ku, Osaka 558*

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A dielectric constant for W/O microemulsions consisting of sodium bis (2-ethylhexyl) sulfosuccinate (AOT), water and cyclohexane was measured at 1 MHz and at 298.15 K. Minima were found in the dielectric constant when a molar ratio of water to AOT was 15 irrespectively of the AOT concentration. This minimum would be related to symmetric hydration of ions, therefore, water pool in the microemulsion becomes more nonpolar around the ratio of 15.

The structure and properties of water solubilized in W/O microemulsion (water-dispersed-in-oil emulsion) are very unique since the water is pooled in a limited microscopic domain. It is expected that the property of solubilized water alters with changing composition of surfactant and also of water. We measured a dielectric constant ε, for W/O microemulsion composed of sodium bis (2-ethylhexyl) sulfosuccinate (Aerosol OT, AOT), water and cyclohexane at 298.15 K as functions of concentration, m, of AOT in cyclohexane and also molar ratio r of water to AOT.

The dielectric constant was precisely measured with a successive dilution technique. An apparatus was newly designed for this measurement, which was similar to that developed by Stokes and Marsh.[1] The unique point in our apparatus is that mercury is not used to introduce liquids into the cell. The electric capacitances were measured at 1 MHz by using a resonance method. The electric terminals of the dielectric cell consist of three nickel- cylindrical-plates fixed in a glass vessel. Size of the central terminal plate is 9 cm in length and 32 mm in diameter. The capacitance of the cell in vacuum is about 180 pF. Capacity of the cell is about 85 cm^3. The liquid is circulated with a gear pump through a mixing bulb, a piston burette (50 cm^3 at maximum), and the dielectric cell with a flow rate of about 500 cm^3 min^{-1} and stirred. Initial volume of cyclohexane is about 170 cm^3. The liquids are introduced from the Teflon plug of the mixing bulb. Amount of the poured liquid is determined by weighing. A microsyringe is used for addition of the solute. To achieve measurements for an extremely dilute region a solution, the typical concentration of which is 0.2 mol kg^{-1}, is added stepwise into the liquid stored in the apparatus. In this way extremely low concentration to 10^{-5} mol kg^{-1} could be easily established. Since the changes of capacitance due to the added components were measured successively without drying the cell for every test, an excellent precision of 10^{-5} in ε could be obtained.

AOT (100 g) from Aldrich was stirred in benzene (200 cm^3) with water (60 cm^3). The benzene solution was decanted and the procedure is repeated with water of about 30 cm^3. After the benzene was evaporated, AOT was dried at 60 ℃ in vacuum for more than 100 h. The purity of AOT was certified from HPLC method. The mole fraction of water contained in AOT was determined by Karl Fisher's method and was 0.04. Cyclohexane and water were purified by usual method.

Figure 1 shows change in ε with r for the system of (AOT + H_2O + cyclohexane) with m of 0.03156, 0.05997 , and 0.09035 mol kg^{-1}, respectively. Generally, an increment in ε is observed when a polar solute is added in a nonpolar solvent unless the dipole moments of solute molecules are compensated to the utmost extent due to the formation of aggregates. The dielectric constant increases by increasing the amount of water up to $r = 5$ because the hydration of polar sites of AOT is asymmetry and the emulsion core has a dipole moment. In the present systems, however, by increasing the amount of water further the value of ε decreases around the r values between 5 and 15. In each curve a maximum appears at $r = 5$, and a minimum appears at $r = 15$ irrespectively of the concentration of AOT, and then ε increases with increasing r value again.

Hanai and Koizumi[2] have reported a very similar behavior in dielectric properties for (AOT + water + kerosine) at 293 K observed at low frequency, but no attention was paid to the abnormal results.

The present observation implies that the Na^+ and SO^{3-} ions are hydrated strongly so that the dipole moments of water are

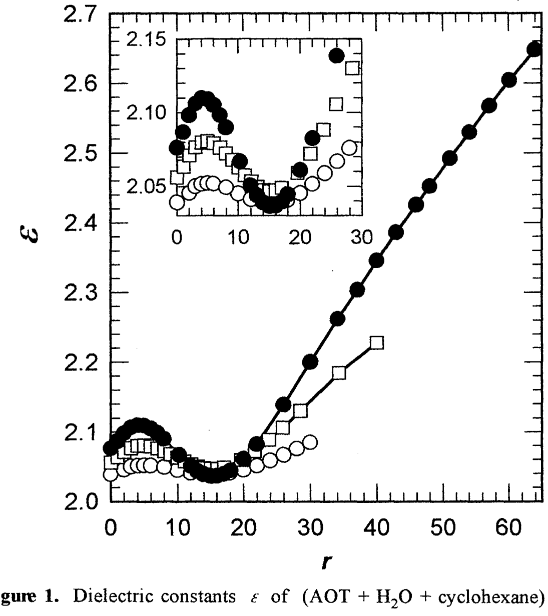

Figure 1. Dielectric constants ε of (AOT + H_2O + cyclohexane) at 1 MHz and at 298 K as functions of the molar ratio r of water to the AOT concentration m: ○, m = 0.03156 kg mol^{-1}; □, m = 0.05997 mol kg^{-1}; ●, m = 0.09035 mol kg^{-1}.

compensated each other in swollen micellar cores when the molar ratio of water is 15. An effective compensation of dipole moment of water is accomplished by the separation of Na^+ from the ionic group of AOT because water molecules can be bound to Na^+ ions symmetrically. Our results suggest that water of more than 5 moles per AOT is necessary for the dissociation of Na^+ from the polar group, and with 15 moles of water the hydration is completed. By adding water more than 15 in r, free water and ice-like water structure appear in the swollen micellar core so that the dielectric constant begins to increase again. Hauser *et al.*[3] concluded from DSC analysis that water in reversed micelles of AOT formed in isooctane is bound up to 13 times in molar ratio to the polar group of AOT-Na^+ and six water molecules of bound water molecules do not freeze at - 40 ℃. Our results are consistent with theirs.

Figure 2 shows the change of ε with AOT concentration m while r is fixed at 15.00 and also 25.00. In the case of r = 15.00, the value of ε increases linearly with m from 0 to 0.0002 mol kg^{-1} and then the slope decreases due to the formation of microemulsion. It is interesting that there appears a maximum in ε around m = 0.055 mol kg^{-1} and followed by a monotonous decrease reaching lower ε than that of cyclohexane. The amounts of emulsion particles and monomeric AOT which have non-zero dipole moment increase up to a molality near 0.055 mol kg^{-1}. However, beyond this concentration the dipole moment of swollen micelles, in which the most of water molecules are strongly bound to Na^+ and the other polar sites, becomes extremely small because the size of the micellar cores grows large and therefore the structure turns symmetric. In such higher AOT concentration only electric and atomic polarizations of solute and solvent contribute to the dielectric constant. The refractive index n of water is about 1.33 which is smaller than that of cyclohexane (1.42) at 298 K, and that of AOT is 1.46.[4] With a very simple estimation by using the Debye equation, the dielectric constant which does not arise from dipole orientation calculated for (AOT + $15H_2O$) becomes lower than that of cyclohexane.

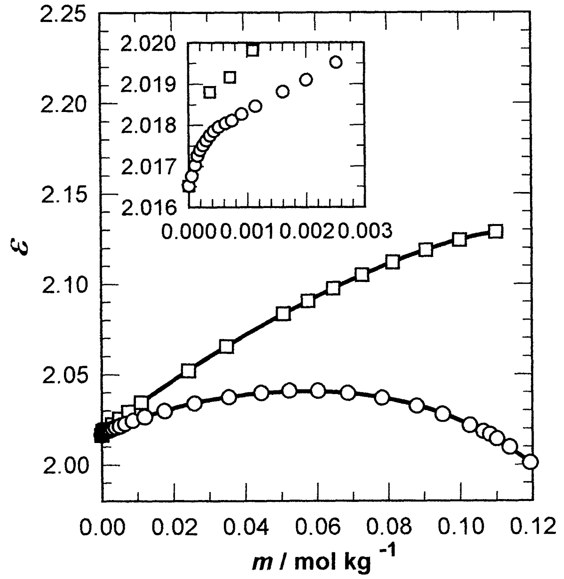

Figure 2 . Dielectric constants ε of (AOT + H_2O + cyclohexane) at 1 MHz and at 298 K as functions of AOT concentration m with two constant molar ratio r : ○, r = 15; □, r = 25.

There are large number of reports concerning the dielectric properties of colloid suspensions characterized by dielectric dispersions. Although we have not measured dielectric dispersion nor dc-conductivity, Robertus *et al.*[5] reported the dielectric relaxation for a similar system (AOT + water + decane). In their results up to a typical composition of r = 25 and m = 0.1 mol kg^{-1} change in ε due to dielectric loss was not serious.

The abnormality of dielectric property for r = 15 is obvious from a comparison with the results for r = 25. In the system of r = 25 abnormal decrease in ε is not seen up to 0.11 mol kg^{-1} in spite of the core of emulsions becomes larger. With more than 15 water molecules per AOT, ε increases monotonously with increasing m of AOT because free water and also structured ones which have a dipole moment exist in the micellar core. The dielectric constant of the water pool in microemulsions including 15 times water molecules than AOT is very low. It is expected that the micro-phase consisting of water molecules up to r = 15 may offer a unique field for chemical reactions as well as for the physicochemical properties of aqueous systems.

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