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Micelle Formation of Purified Dinonylnaphthalenesulfonates in Benzene

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Synopsis. The removal of trace amounts of unsulfonated dinonylnaphthalene contained in sulfonates by rubber membrane dialysis in pentane increased the apparent aggregation number of the micelles of dinonylnaphthalenesulfonate measured using vapor-pressure osmometry. The interaction between the cation and sulfonate ion was a factor affecting the aggregation, in addition to the steric factor of the hydrocarbon group and the solute-solvent interaction.

The micelle formation of metal salts of dinonylnaphthalenesulfonic acid (DNNS) in nonpolar solvents has been extensively studied using many methods, such as fluorescence depolarization,[1,2] viscometry,[3] ultracentrifuge separation,[4] and vapor-pressure osmometry.[5] It has been considered that the micelle formation of DNNS in nonpolar solvents is mainly due to the strong interaction between polar groups.[6] Furthermore, considerations of the steric or geometric factor and the solute-solvent interaction are also important. Kaufman and Singleterry[2] have studied the effect of cations on the micelle formation and the apparent molar volume of DNNS anions in benzene. However, the effect of the cation on the aggregation number for DNNS salts, which is a direct measure of the strength of the interaction between polar groups, has not been determined. In the present paper, the effect of the cation on the aggregation number for DNNS salts is reported and the importance of purification of the DNNS salts for vapor-pressure osmometry are also discussed.

Experimental

Alkali and alkaline-earth metal salts of DNNS were synthesized as described previously.[7] Metal salts of DNNS were further purified by rubber-membrane dialysis[8] for 72 h in pentane. This purification period was found to be sufficient to gain the limiting value of the aggregation number. The final product was freed from the solvent by evacuation at 70 °C for 24 h. The benzene used as the solvent for the vapor-pressure osmometric measurements was passed through activated alumina in order to remove water and polar contaminants. The water content in the benzene was determined using the Fischer titration method and was found to be less than 0.01%. The vapor-pressure osmometric measurements were carried out with a Mechrolab Model 301A vapor-pressure osmometer at 38 °C.

Results and Discussion

The relation of the apparent aggregation number for DNNS sodium salt (NaDNNS) and its concentration in benzene are shown in Fig. 1. The apparent aggregation number for NaDNNS was increased by the removal of the trace amount of unsulfonated dinonylnaphthalene contained in the NaDNNS using rubber-membrane dialysis in pentane. Although vapor-pressure osmometry is the most advantageous and accurate technique for investigating the aggregation of a surfactant in a nonpolar and volatile solvent, the result is strongly affected by the presence of trace amounts of low molecular-weight impurities. In addition to the effect mentioned above, the residual impurity in a surfactant which is similar to the surfactant in shape and structure should affect the state of aggregation by solubilization or the formation of co-micelle. To avoid this problem, purification by rubber-membrane dialysis is available for determining the micelle formation of high molecular-weight detergents, such as oil-soluble sulfonates.

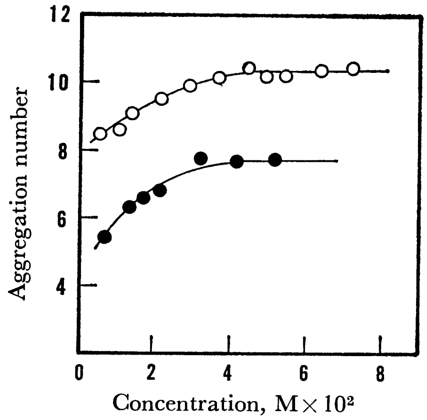

Fig. 1. Effect of purification of sodium dinonylnaphthalenesulfonate by rubber membrane dialysis on the aggregation number in benzene at 38 °C.
(—●— Before dialysis, —○— after dialysis).

Little and Singleterry[5] have studied the micelle formation of DNNS salts in various nonpolar solvents using vapor-pressure osmometry and have reported that the micelle aggregation number in benzene is 7 for Li and Na salts, and 6 for Cs salt. From the consideration that the aggregation of an ionic surfactant in a nonpolar solvent is mainly due to the interaction between the gegenion and the surfactant ion in the micellar cores, it is difficult to understand that the cations have little effect on the micelle aggregation number. Therefore, the present authors reexamined the micelle formation of DNNS salts, which were purified using vapor-pressure osmometry. The effect of the cation radius on the aggregation numbers of metal salts of DNNS in benzene is shown in Fig. 2. The aggregation number plotted in Fig. 2 shows the saturated value in the curve of the concentration-aggregation number as in Fig. 1. A strong correlation is found between the saturated aggregation number and the reciprocal of e^2/r_i for each cation studied, where e and r_i are the charge and radius of the cation, respectively. Kitahara and Kon-no[9] have reported the same effect of halogen ions on the aggregation number of didodecyldimethyl ammonium

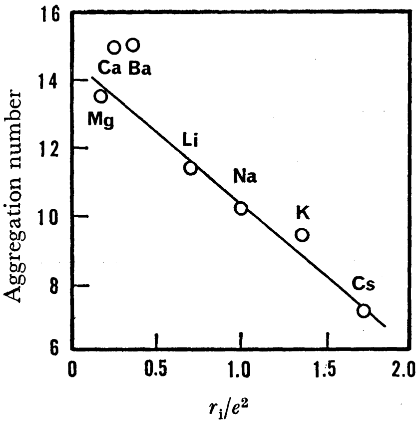

Fig. 2. Effect of cations of dinonylnaphthalenesulfonates on the aggregation number (acid residue/micelle) in benzene at 38 °C.

halides in benzene. Born[10] has suggested that e^2/r_i is proportional to the energy of hydration of gaseous spherical ions and that this value might be considered to be a measure of Lewis acidity. It is clearly seen in Fig. 2 that the driving force for the aggregation of micelles of DNNS salts in nonpolar solvents is the strong acid-base interaction between the polar groups in micellar cores. Kaufman and Singleterry[2] have also reported that such strong acid-base interactions cause a decrease in the apparent molar volume of anions of DNNS salts and an increase in the packing density from solution density measurements. A deviation from the linear relation in Fig. 2 is found in the case of alkaline-earth metal salts of DNNS. The deviation of the bivalent DNNS salts is ascribed to the increased polarity of their ionic head and the different contribution of the hydrocarbon group in the packing of the micelle from that of the monovalent DNNS salts.

Consequently, the micelle formation of DNNS salts in nonpolar solvents is mainly due to the strong interaction between polar groups in micellar cores, in addition to the steric factor and the solute-solvent interaction which have been discussed by Heilweil,[11] and Little and Singleterry,[5] respectively.

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