

Surface Active Anions in Polar Solvents: I. Conductometric Studies on Solutions of Sodium Decyl and Dodecyl Sulphate in Water, N,N-Dimethylformamide, and Dimethyl Sulfoxide

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ABSTRACT

Conductivity measurements of solutions of sodium decyl sulfate and sodium dodecyl sulfate were made in water, N,N-dimethylformamide, and dimethyl sulfoxide at 25 C. Within the concentration range 1 to 100 millimoles, the surfactants were found to form micellar aggregates. The critical micelle concentration values were found to depend on the dielectric constant of the medium and also on the hydrogen bonding nature of the solvent. The role of hydrogen bonding nature of the solvent in micelle formation is discussed.

INTRODUCTION

Micelle formation in organic solvents of high dielectric constant is little studied, even though the system is of much interest in view of the comparison with aqueous solutions which have been studied extensively. Previous work on micelle formation in nonaqueous solutions of sorbitan monostearate (span 60) has been carried out by Becher and others (1-2) in benzene, and later by Brown, Cooper, and Moore (3) in o-xylene and other organic solvents of low dielectric constant. They reported a similar type of behavior in all the organic solvents of low dielectric constant. Ram Gopal and his co-workers (4-5) studied the properties of large ions in solvents of high dielectric constant by conductivity and refractive index measurements. They concluded that the high dielectric constant of the medium, the hydrogen bonding nature of the solvent, and the dispersion forces operating in the higher concentration region are responsible for aggregation of long chain ions.

To better understand the role of dielectric constant of the medium, the hydrogen bonding nature of the solvent, and the dispersion forces in the micelle formation, we studied the behavior of anionic surfactants in sufficiently higher concentration range in polar solvents. This paper deals with the determination of critical micelle concentration (CMC) values of sodium decyl sulfate (DS) and sodium dodecyl sulfate (SDS) in water, N,N-dimethylformamide (DMF) and dimethyl sulfoxide (DMSO) at 25 C.

MATERIALS AND METHODS

DS and SDS were of British Drug House (BDH) (Poole, England) Anala R grade and were used after repeated crystallization from alcohol and then from acetone. The purity of samples was confirmed by the absence of minimum in the surface tension versus concentration curve (6). DMSO was obtained from Koch-Light Company (Coln-

brook Bucks, England), dried, and vacuum distilled. Only the middle fraction of specific conductivity, $1027 \times 10^{-6} \text{ Ohm}^{-1} \text{ Cm}^{-1}$, was used. DMF was obtained from BDH, dried over freshly ignited quick lime for 3 days, then vacuum distilled. The middle fraction used had a specific conductivity $1.76 \times 10^{-6} \text{ Ohm}^{-1} \text{ Cm}^{-1}$. Demineralized water, distilled twice in the presence of alkaline permanganate in an all glass Quickfit assembly, was used to prepare the solutions.

Fresh solution of the surfactant of known concentration in a desired solvent was kept immersed in a constant temperature bath for ca. 20 min. The conductivity of the solution then was measured by Phillips Conductivity Meter model PR 9500 using platinized electrodes. The unit incorporated a wheatstone bridge with measuring frequencies 50 c/s and 1000 c/s. The cell constant at a given temperature was calculated from the ratio of specific conductivity and the observed conductivity of 0.10 and 0.01 Mole KCl solutions. The specific conductivity of standard KCl solution was calculated from the relation:

$$K = A + Bt + Ct^2 \quad (I)$$

where, K = Specific conductivity ($\text{Ohm}^{-1} \text{ Cm}^{-1}$), t = temperature (C), and A, B, and C are the constants whose values

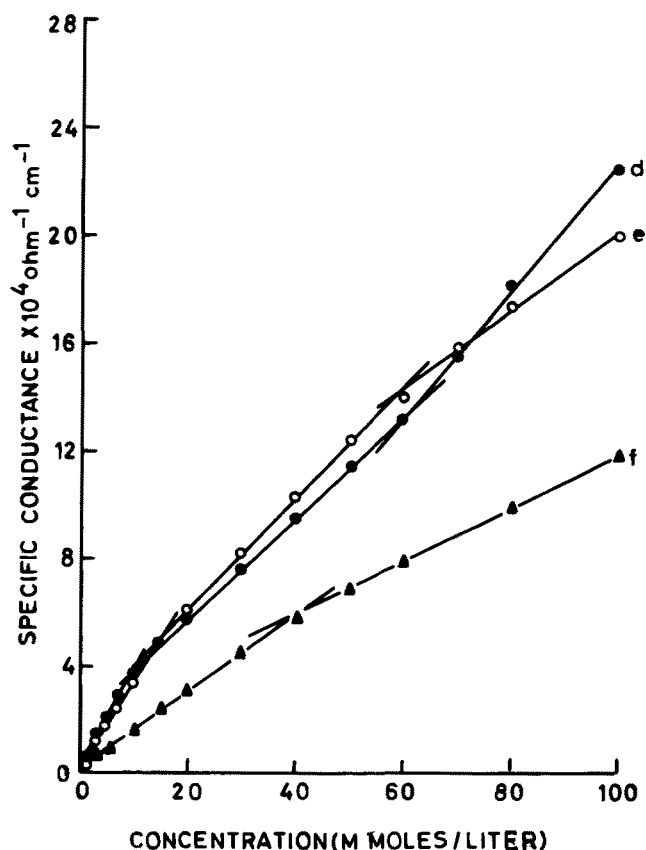


FIG. 1. Specific conductance versus concentration plot of sodium decyl sulfate in: (a) water (—○—); (b) N,N-dimethylformamide (—●—); and (c) dimethylsulfoxide (—▲—).

TABLE I

Values of Constants A, B, and C for Different Concentrations of Potassium Chloride Solutions

Constant	0.10 Mole KCl	0.01 Mole KCl
A	7.1295×10^{-3}	7.7284×10^{-4}
B	2.1178×10^{-4}	2.3448×10^{-5}
C	6.8500×10^{-7}	7.8160×10^{-8}

TABLE II

Critical Micelle Concentration (CMC) Values of Sodium Decyl Sulfate (DS) and Sodium Dodecyl Sulfate (SDS) in Different Solvents

Solvent	Surfactant			
	DS		SDS	
	1st CMC	2nd CMC	1st CMC	2nd CMC
Water	10.0	66.0	8.5	62.5
DMF ^a	17.5	63.0	14.5	60.0
DMSO ^a	43.5		40.0	

^aDMF = N,N-Dimethylformamide; DMSO = dimethyl sulfoxide.

for 2 concentrations of KCl solution are given in Table I.

The cell constant at 25 C was found to be 0.705 Cm⁻¹. The specific conductivity of the surfactant solution was calculated by multiplying the observed conductivity and the cell constant. To locate the CMC values, specific conductivity was plotted against surfactant concentration, as shown in Figures 1 and 2 for DS and SDS, respectively, in different solvents.

RESULTS AND DISCUSSION

A perusal of Figures 1 and 2 shows that the specific conductivity versus surfactant concentration plots do not vary linearly as in the case of simple binary electrolytes. Two inflections occur at definite concentrations of the surfactant in water and DMF, but only one in DMSO. The results in solvent water are in good agreement with those reported by other workers (6,7). This gives clear evidence of micelle formation in these solvents. The points of inflection at definite concentrations correspond to the CMC values of DS and SDS in water, DMF, and DMSO. The CMC values are given in Table II.

A perusal of Table II shows that the decrease in the first CMC of the surfactants in these solvents follows the order water < DMF < DMSO. One of the criteria for ionic micelle formation is the dielectric constant of the medium. The higher the dielectric constant of the medium, the greater will be the formation of the long chain anions which associate themselves by dispersion forces in higher concentration range to form charged micelles (8). Another factor responsible for the micelle formation is the long hydrocarbon chains which associate in polar solvents due to their hydrophobic nature, as explained by Nemethy and Scheraga (9). However, the dielectric constant of water, DMF and DMSO are 78.5 (10), 36.7 (11), and 46.6 (12), respectively. Therefore, it seems apart from the dielectric constant of the medium, hydrogen bonding and solvation capacity of the solvent also play an important role in the micelle formation. Because water possesses greater hydrogen bonding capacity than DMF, while DMSO has none, the variation between the observed CMC values for water, DMF, and DMSO is not unexpected. Therefore, it may be concluded that in water and DMF the micelles are formed by interlinking of long chain anions through hydrogen bonds between a hydrogen atom of water and a CH proton of DMF, together with the solvation of the positive end of the solvent dipole by the anion. This situation forces the alkyl chains of the surfactant anions to come into closer proximity to one another to form micellar aggregates. Therefore, it is quite reasonable to expect lower CMC values in water and DMF than in DMSO.

It is interesting to note that there occurs a change in the properties of surfactant in water and DMF solutions at a concentration above the first CMC, which is usually called the second CMC. The slope of specific conductivity concentration curve in DMF above the second CMC, for both the surfactants, bends toward the concentration axis. This

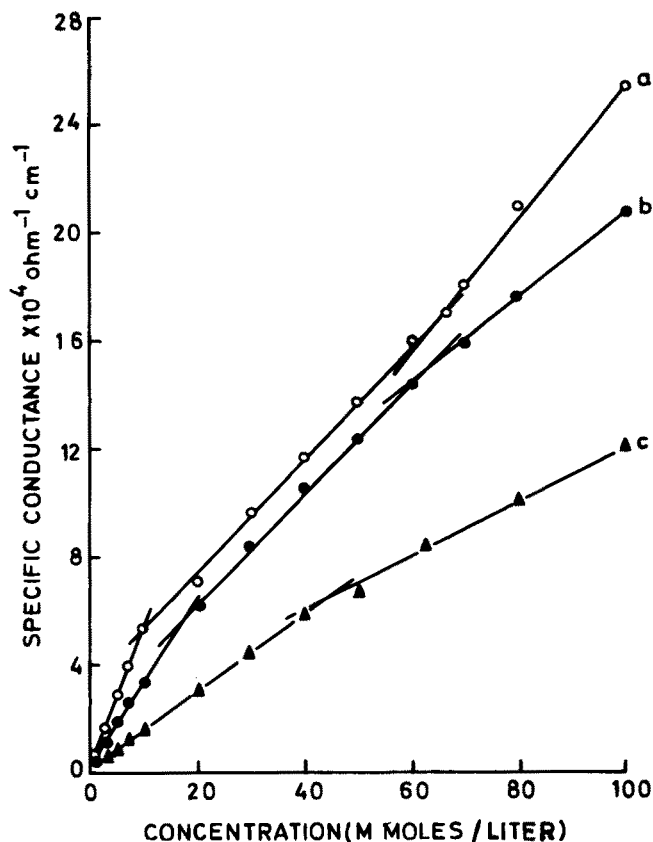


FIG. 2. Specific conductance versus concentration plot of sodium decyl sulfate in: (a) water (—○—) (b) N,N-dimethylformamide (—●—); and (c) dimethylsulfoxide (—▲—).

may well be due to the presence of some organic impurity in the solvent (6). The presence of the second CMC in aqueous surfactant solutions has been ascertained by Miura and coworkers by different methods (13). However, how the shape and size of the micelle vary at the second CMC is still little known. Our observed values of the second CMC in water and DMF are in the reverse order compared to the first CMC values in these solvents. This may afford a clue for elucidating the change in micelle structure at the second CMC caused by the variation in the type of aggregation.

Further investigation in this area promise additional information about the effects of additives and mixed solvents in the mode of micellization. Temperature investigations should also provide interesting data on structural variations of the micelles with concentrations.

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