Conductivity of Aqueous Potassium Dodecyl Sulfonate at Various Temperatures and with Solubilized Benzene

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Introduction

The somewhat abrupt change with concentration of many physical properties of solution of long-chain electrolytes has been attributed to the formation of micelles, and the concentration at which this change occurs has been termed " the critical concentration for the formation of micelles ".1)

Electrical conductivity is one of the properties which may be utilized for the determination of the critical concentration. It has been pointed out2,3), that if the specific conductivity be plotted against the concentration the critical concentration is given by the intersection of the resulting two straight lines.

We have determined the specific conductivity of aqueous solutions of potassium dodecyl sulfonate as a function of the concentration of the salt at temperatures ranging from 25 to 60°C and in the presence of varying amounts of solubilized benzene.

In this manner we have determined the critical concentration of potassium dodecyl sulfonate at several different temperatures and at several different concentrations of solubilized benzene. We also could obtain data for the effect of solubilized benzene on the relation between equivalent conductivity and concentration at constant temperature.

Experimental

Potassium dodecyl sulfonate was prepared by the reaction between dodecyl bromide and aqueous potassium sulfite. The salt was washed sev-

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1) See references quoted by M. L. Corrin, H. B. Klevens, and W. D. Harkins, *J. Chem. Phys.*, **14**, 480 (1946).

2) K. A. Wright, A. D. Abbott, V. Sivertz and H. V. Tartar, *J. Am. Chem. Soc.*, **61**, 549 (1939).

3) A. P. Brady and H. Huff, *J. Colloid Sci.*, **3**, 511 (1948).

eral times with petroleum ether, recrystallized twice from ethanol and twice from conductivity water and dried in vacuo. Benzene was of reagent grade and used without further purification.

Solutions containing solubilized benzene were prepared by adding weighed amounts of the salt to solutions of benzene in water. These solutions were made up by weight-volume.

Conductivity measurements were made in a Leeds-Northrup pyrex conductivity cell at 1000 cycles. A Leeds-Northrup Jones bridge and electronic amplifier and oscillator were used and the null points determined on an oscilloscope. An oil bath constant to 0.01°C was used for temperature control; cell constants were determined for each temperature. The electrodes were platinized.

Critical concentrations were determined graphically as the point of intersection of two straight lines in the plot of specific conductivity against concentration.

Results and Discussion

Plots of specific conductivity versus concentration at temperatures five degrees apart in the range of 25 to 60°C are given in Fig. 1. These are characteristic of solutions of long-chain electrolytes. Similar plots of the equivalent conductivity as a function of the square root of the concentration are given in Fig. 2. The form of these curves has been discussed by Wright, Abbott, Sivertz and Tartar2), by Wright and Tartar4), and by Ralston and Hoerr5). The rapid increase in equivalent conductivity at the higher salt concentrations has been attributed to "retrograde dissociation".

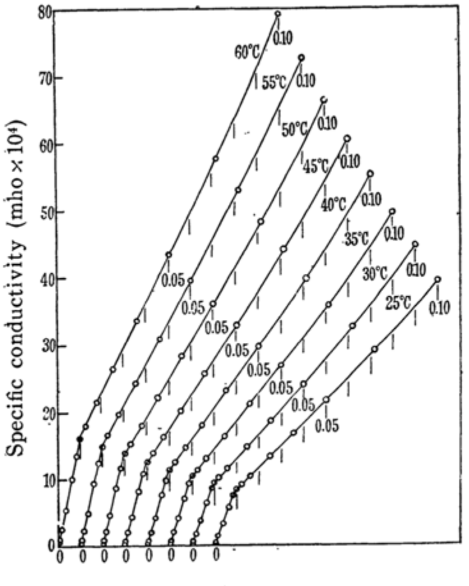

Fig. 1. Specific conductivity plotted against volume normality for aqueous solution of potassium dodecyl sulfonate

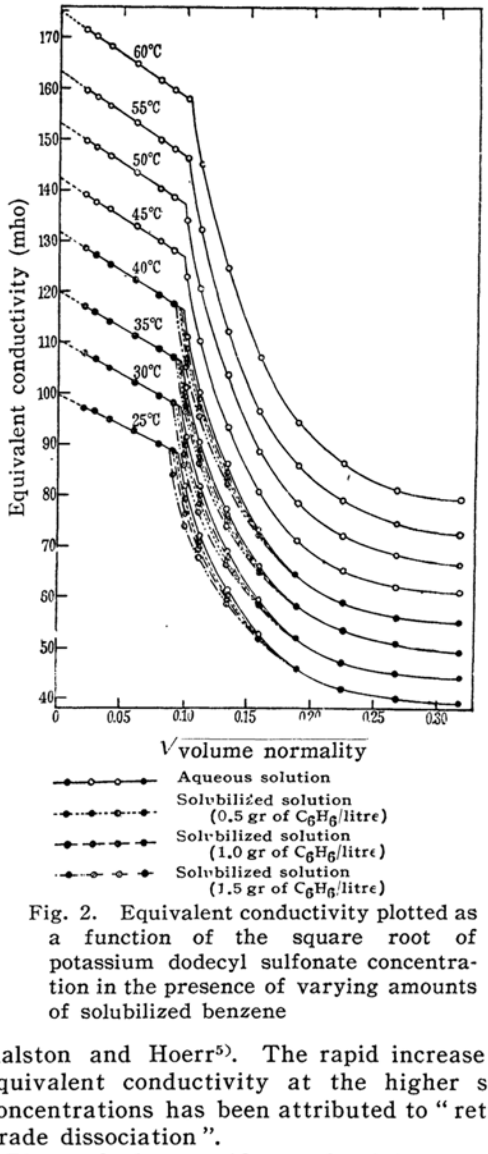

Fig. 2. Equivalent conductivity plotted as a function of the square root of potassium dodecyl sulfonate concentration in the presence of varying amounts of solubilized benzene

Plots of the specific conductivity versus salt concentration at several temperatures in the presence of varying amounts of solubilized benzene are given in Fig. 3. Similar plots of the equivalent conductivity as a function of the square root of the salt concentration at several temperatures in the presence of varying amounts of solubilized benzene are also given in Fig. 2. It is evident that (a) the solubilized benzene does not affect the conductivity at concentrations below the critical concentration, (In this range the salt is supposedly completely ionized and the Debye-Hückel-Onsager limiting law may be applied.), (b) the critical concentration is lowered by

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4) K. A. Wright and H. V. Tartar, *J. Am. Chem. Soc.*, **61**, 544 (1939).

5) A. W. Ralston and C. W. Hoerr, *J. Am. Chem. Soc.*, **64**, 772 (1942).

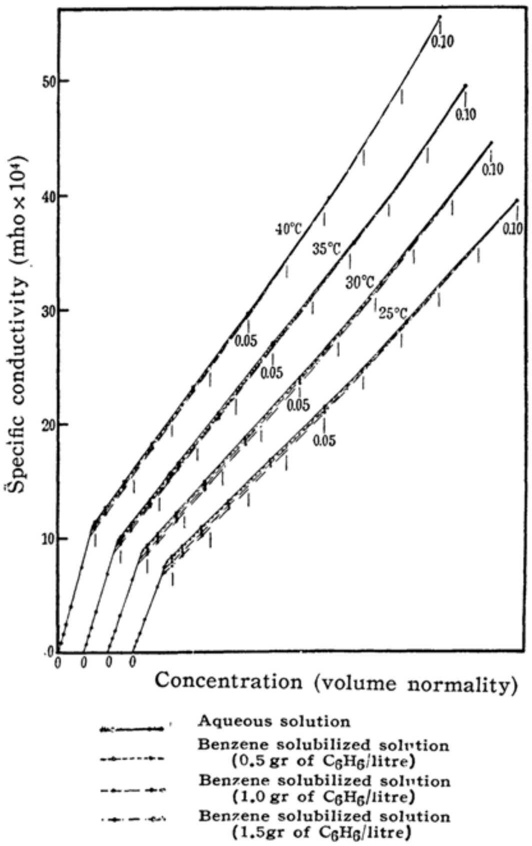

Fig. 3. Specific conductivity plotted against concentration of potassium dodecyl sulfonate in the presence of varying amounts of solubilized benzene

the solubilized benzene with the amount of lowering increasing with the increase of benzene concentration, and (c) the effect of added benzene becomes increasingly less as the salt concentration becomes greater.

Change of Critical Concentration with Temperature.—The variation in critical concentration with temperature has been discussed by several authors. Tartar and his coworkers have reported that with long-chain sulfonates in the range of 40 to 80°C the critical concentration increases with temperature[2]. Brady and Huff[3] found a decrease with temperature for lauryl sulfonic acid and potassium laurate in the range of 0 to 90°C. A similar decrease was noted by Scott and Tartar[6] for quaternary ammonium salts between 25 and 60°C. The above estimates were made from conductivity data. Using the dye method Herzfeld observed a minimum in the critical concentration as the temperature was varied from 0 to 80°C[7]. The results obtained in this study as shown in Table I and Fig. 4 are in agreement with those noted for the sulfonates by Tartar et al[2,6]; namely, that the critical concentration increases with temperature.

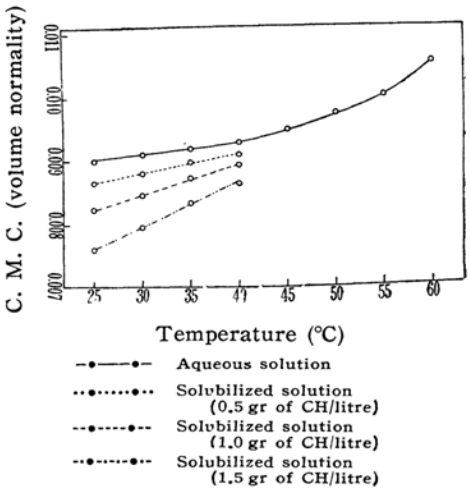

Fig. 4. Change of C. M. C. with temperature

TABLE I

CHANGES OF C. M. C. FOR AQUEOUS SOLUTIONS OF POTASSIUM DODECYL SULFONATE WITH CHANGE IN TEMPERATURE AND CONCENTRATION OF SOLUBILIZED BENZENE

Temperature	Amount of benzene solubilized (grams of C_6H_6/litre of aqueous solution)			
(°C)	0	0.5	1.0	1.5
25	0.0090^{0}	0.0086^{5}	0.0082^{5}	0.0076^{0}
30	0.0091^{0}	0.0088^{0}	0.0084^{5}	0.0079^{5}
35	0.0092^{0}	0.0090^{0}	0.0087^{5}	0.0083^{5}
40	0.0093^{0}	0.0091^{0}	0.0089^{0}	0.0086^{5}
45	0.0095^{0}	—	—	—
50	0.0097^{5}	—	—	—
55	0.0100^{0}	—	—	—
60	0.0104^{0}	—	—	—

The Effect of Benzene on the Critical Concentration.—The effects of various concentrations of solubilized benzene on the critical concentration of potassium dodecyl sulfonate are given in Table I and plotted in Fig. 5. At constant temperature the lowering of the critical concentration increases with the increase of benzene concentration. The lowering becomes less marked with increasing temperature.

These results are in essential agreement with those obtained by Lingafelter, Wheeler

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6) A. B. Scott and H. V. Tartar, *J. Am. Chem. Soc.*, 65, 692 (1943).

7) S. H. Herzfeld, Unpublished work

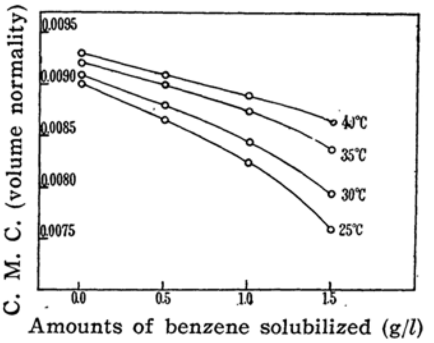

Fig. 5. C. M. C. plotted against amount of solubilized benzene

and Tartar[8] for benzene and several sodium alkylsulfonates by an interfacial tension method.

An interpretation of this work must rest upon the analysis of the various energy terms involved in micellization. Herzfeld, Corrin and Harkins[9] have suggested two such energy terms of major importance. First a decrease in free energy is brought about by removal of the long-chain ion from its aqueous environment into the interior of the micelle (environmental term). This term will be maximal when the removal of the non-polar chain from the water is as complete as possible. Second, short range repulsive terms come into play as the polar head groups are brought together in the micelle and this repulsive energy term must be taken into account. On the basis of this analysis the micelle would contain fewer ions than the limit set by steric factors.

In the presence of relatively non-polar additives such as benzene it might be expected that the environmental terms might be increased in magnitude and that the repulsive term might be decreased by the inclusion of benzene in the micelle. This would lead to (a) a decrease in critical concentration and (b) a change in the size or the number of long-chain ions per micelle or both. It would seem from the conductivity measurements reported here that the change in micelle size in the presence of benzene cannot be very great since at concentrations exceeding the critical concentration there is little difference between the conductivity terms in the presence and absence of benzene. It is possible, although unlikely, that a change in micelle size is exactly balanced by a change in micelle ionization.

We do not propose to discuss the conductivity curves completely at this time.

Summary

The specific conductivity of aqueous solutions of potassium dodecyl sulfonate has been measured as a function of concentration in the presence and absence of solubilized benzene in the temperature range between 25 and 60°C.

Below the critical concentration for the formation of micelles solubilized benzene has no effect on the conductivity. In the critical concentration range there is a marked effect which decreases with salt concentration and finally becomes negligible.

The critical concentration decreases in the presence of solubilized benzene; this effect becomes more marked as the benzene concentration is increased. The critical concentration increases with increasing temperature both in the presence and absence of benzene.

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[8] F. C. Lingafelter, O. L. Wheeler and H. V. Tartar, *J. Am. Chem. Soc.*, 68, 1490 (1946).

[9] S. H. Herzfeld, M. L. Corrin and W. D. Harkins, *J. Phys. & Colloid Chem.*, 54, 271 (1950).