[CONTRIBUTION FROM THE RESEARCH LABORATORY OF ARMOUR AND COMPANY]

Viscosities, Densities and Refractive Indices of Solutions of Dodecylammonium Chloride in Various Dilutions of Aqueous Ethanol

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The solubility of dodecylammonium chloride in aqueous ethanol[1] increases rapidly and then decreases as the solvent goes from pure water to pure ethanol, the maximum solubility being shifted toward a higher water content of the solvent with increase in the temperature. The equivalent conductance of a less concentrated solution is only slightly decreased by the addition of small amounts of ethanol. These behaviors are ascribed to micelle formation in solutions of this salt. Micelle formation is completely inhibited by the addition of large amounts of ethanol to

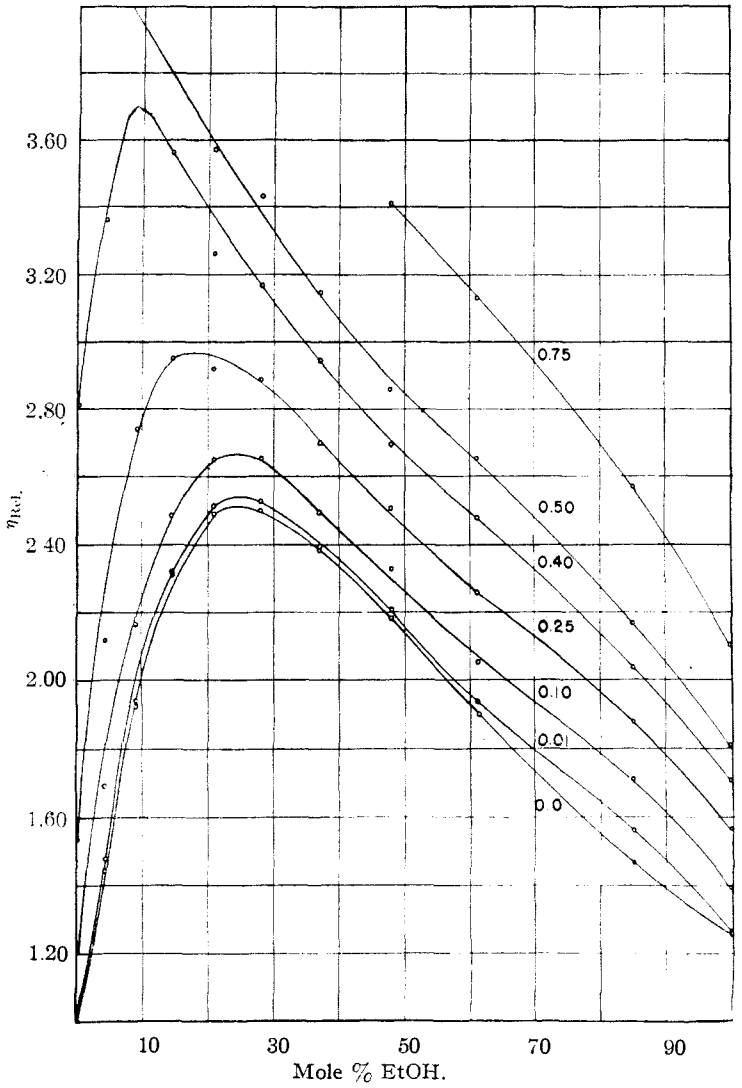

Fig. 1.—Relative viscosities of dodecylammonium chloride in aqueous ethanol at 30.0°. The numbers on the curves refer to the molarity of amine salt.

ductance of a concentrated aqueous solution of dodecylammonium chloride[2] is increased and the aqueous solutions of dodecylammonium chloride.

It has been shown that the density–composition curves of aqueous solutions of potassium octan-

(1) Ralston and Hoerr, THIS JOURNAL, **68**, 851 (1946).
(2) Ralston and Hoerr, *ibid.*, **68**, 2460 (1946).

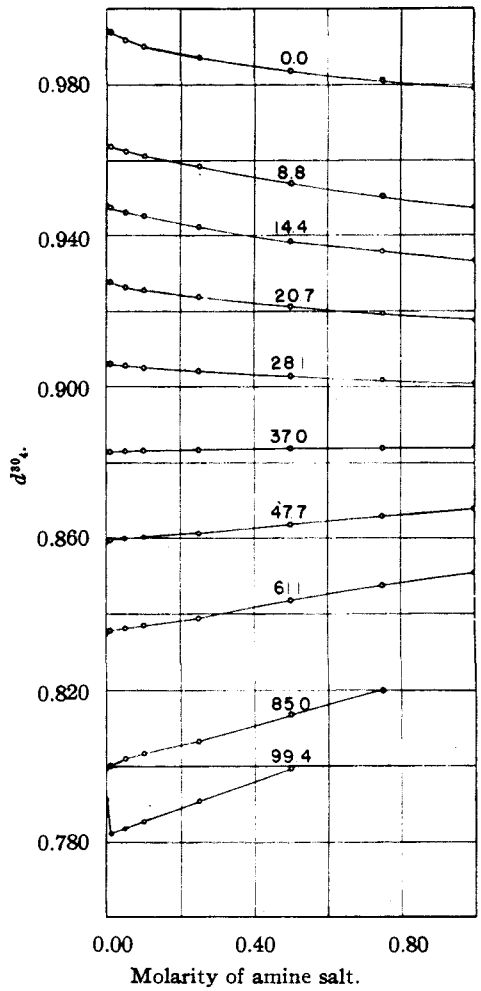

Fig. 2.—Densities of dodecylammonium chloride in aqueous ethanol at 30.0°. The numbers refer to the mole per cent. of ethanol.

oate[3] and of potassium dodecanoate[4] undergo decided changes at the critical point for micelle formation. More recently, Wright and Tartar[5] have reported that both the density–composition and viscosity–composition curves of aqueous solutions of sodium dodecylsulfonate undergo abrupt changes in slope at the critical point. In view of the changes in properties which accompany increases in the concentration of electrolyte in aqueous solutions of the colloidal electrolytes and of the apparent transition from a colloidal electrolyte to an ordinary electrolyte attending progressive additions of ethanol to solutions of dodecylammonium chloride, it was decided to investigate the changes in viscosity, density and refractive index which accompany the addition of ethanol to aqueous solutions of this latter salt.

(3) Dories and Bury, *J. Chem. Soc.*, 2263 (1930).
(4) Bury and Parry, *ibid.*, 626 (1935).
(5) Wright and Tartar, THIS JOURNAL, **61**, 544 (1939).

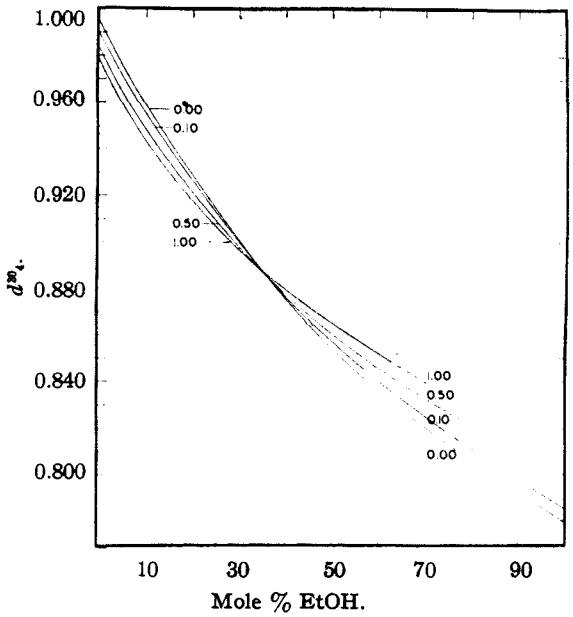

Fig. 3.—Densities of dodecylammonium chloride in aqueous ethanol at 30.0°. The numbers on the curves refer to the molarity of amine salt.

Experimental

The dodecylammonium chloride used in these experiments was from the same lot employed in the previous investigations.[1,2] The relative viscosities were determined in a standard Ostwald viscometer of such dimensions that the time of flow for 10.0 cc. of water was 129.3 sec. The densities were determined by means of a 25-cc. calibrated pycnometer, the weights being corrected for the buoyancy of air. The refractive indices were determined with an Abbé-type refractometer, the prism temperatures being maintained constant, within ±0.05°, by the circulation of water from a thermostatically controlled bath.

Results and Discussion

The relative viscosities at 30° of various concentrations of dodecylammonium chloride plotted against the mole per cent. of ethanol in the solvent are shown in Fig. 1. The plotted values include the relative viscosities of dodecylammonium chloride in water[6] and also the values for the various dilutions of aqueous ethanol. The latter values were calculated from the data in the "International Critical Tables."[7] It will be noted that the curve for aqueous ethanol contains a decided maximum at approximately 25 mole per cent. of ethanol. The presence of the amine salt shifts this maximum toward a lower ethanol content. Since the influence of viscosity upon the conductivity of a solution of a colloidal electrolyte is a moot question, the relationship of these curves to those previously published upon the equivalent

(6) Ralston and Hoerr, *ibid.*, **64**, 772 (1942).
(7) "International Critical Tables," Vol. V, p. 22 (1929).

conductances of these solutions[2] is not at present apparent.

The densities of solutions of dodecylammonium chloride in various dilutions of aqueous ethanol plotted against the molarity of the amine salt are shown in Fig. 2. The plotted data include the densities of solutions of the amine salt in water[8] as well as the values for the various dilutions of aqueous ethanol.[9] It will be noted that the progressive addition of amine salt to the 37 mole per cent. ethanol is not accompanied by any significant change in the density of the solution. Similar additions below this ethanol concentration result in substantial reductions in the densities, whereas above this concentration they result in appreciable density increases. The change in density with increase in amine salt concentration becomes greater as the solvent approaches either pure water or pure ethanol. Figure 3 shows the densities of several concentrations of dodecylammonium chloride plotted against the mole per cent. of ethanol in the solvent. The density curves intersect at approximately 34 mole per cent. of ethanol, which concentration is essentially similar to that which has been previously observed to preclude the formation of micelles in solutions of this amine salt.[2]

The refractive indices of solutions of dodecylammonium chloride in various dilutions of aqueous ethanol plotted against the molarity of the amine salt are shown in Fig. 4. The plotted points include the refractive indices of the various dilutions of aqueous ethanol.[10] The refractive indices of the amine salt solutions appear to be directly additive in proportion to the amount of amine salt present. When these refractive indices are plotted against the mole per cent. of ethanol the curves possess a rather flat maximum at concentration of about 50–60 mole per cent. ethanol. A slight shift of the maximum occurs at the higher concentrations of amine salt.

Acknowledgment.—The authors wish to express their appreciation to Mr. E. F. Binkerd for the preparation of the drawings.

(8) Ralston, Hoerr and Hoffman, THIS JOURNAL, **64**, 97 (1942).
(9) "International Critical Tables," Vol. III, p. 116 (1928).
(10) "International Critical Tables," Vol. VII, p. 67 (1930).

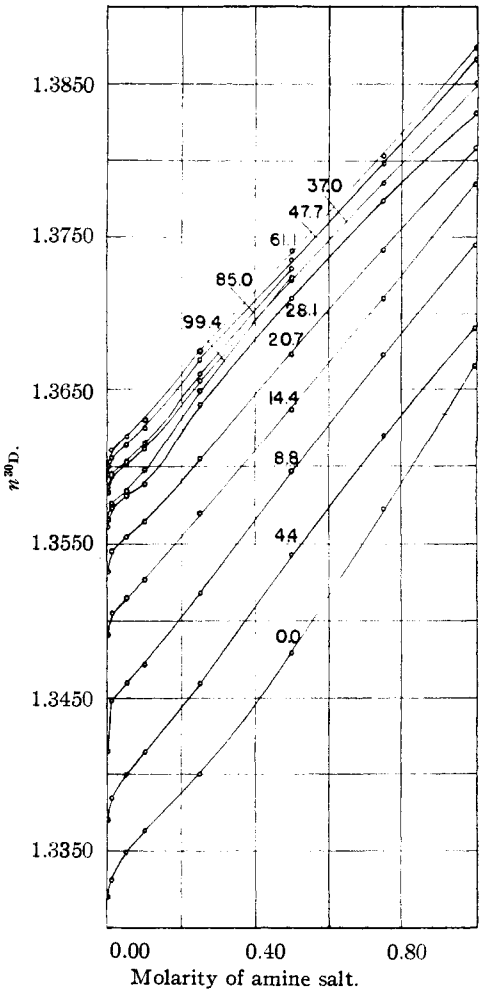

Fig. 4.—Refractive indices of dodecylammonium chloride in aqueous ethanol at 30.0°. The numbers refer to the mole per cent. of ethanol.

Summary

The viscosities, densities and refractive indices of solutions of dodecylammonium chloride in various dilutions of aqueous ethanol have been determined.

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