The Effects of Electrolytes upon the Conductivity of Aqueous Solutions of Dodecylammonium Chloride[1]

BY A. W. RALSTON AND D. N. EGGENBERGER

The presence of electrolytes is known to have a significant effect upon the behavior of aqueous solutions of colloidal electrolytes. In general, the effect of added salts is to magnify the colloidal properties of the colloidal electrolyte. This manifests itself in a lowered conductivity on the part of the colloidal electrolyte, a lowered concentration of colloidal electrolyte at the critical point, and an increased solvent power for a number of organic non-electrolytes. Several observations of these effects have been recorded in the literature. For example, it has been shown[2] that an increase in the sodium ion concentration materially reduces the concentration of sodium dodecyl sulfate at the critical point for micelle formation. Tartar and Cadle[3] have shown that the presence of sodium chloride reduces the aqueous solubilities of sodium dodecyl sulfate and sodium tetradecyl sulfate and increases their tendencies toward micelle formation. Hartley[4] has observed that the solubility of azobenzene in aqueous solutions of hexadecylpyridinium chloride is greatly increased by the presence of sodium chloride. The addition of salts to both dilute and concentrated soap solutions has been shown by McBain and co-workers[5] to materially increase the solubilizing power of such solutions for water-insoluble dyes. The osmotic studies of McBain and Brady[6] showed that the presence of either potassium chloride or potassium sulfate promotes micelle formation in aqueous solutions of potassium laurate. Quite recently, Corrin and Harkins[7] have described a method by which the critical point can be determined by titration with an aqueous dye solution, the critical concentration being indicated by a visual color change in the dye. This method was employed in an investigation[8] of the effect of the addition of electrolytes upon the critical concentrations of a number of anionic and cationic electrolytes. It was stated that the critical concentration is affected only by the concentration of the ion opposite in charge to that on the colloidal aggregate and that the concentration and nature of the other ion is without effect. More recently,

however, Harkins and associates[9] have observed that the increase in solubilizing power of soap solutions upon the addition of an electrolyte is dependent upon both the nature of the cation and the anion of the added salt. This present study reports the effects of several electrolytes upon the equivalent conductivity of aqueous solutions of dodecylammonium chloride. The effects observed are undoubtedly associated with the colloidal behavior of this amine salt.

Experimental

The preparation and properties of the dodecyl- and hexadecylammonium chlorides used in this investigation have been described elsewhere.[10] The conductivities were determined in the manner and with the equipment previously described.[11] The conductivity by difference was calculated by substracting the specific conductance of the added electrolyte from the specific conductance of the solution containing the electrolyte and the amine salt. For example, if a 0.005 N sodium chloride solution is employed as the solvent the specific conductance of this solution is subtracted from the observed values.

Results and Discussion

The conductivities of aqueous solutions of dodecylammonium chloride at 30° and the conductivities by difference of this colloidal electrolyte in 0.005 N and 0.015 N sodium chloride are shown in Fig. 1. The material reduction in equivalent conductivity of the amine salt occasioned by the presence of sodium chloride is clearly evident. This effect can be attributed to the increased chlorine ion concentration which reduces the ionization of the amine salt, the marked reduction of the critical concentration evidencing the presence of undissociated molecules at lower concentration of colloidal electrolyte. The magnitude of this common ion effect may overshadow other changes produced in the system by the presence of the sodium chloride such as dehydration of the micelles resulting from the lowered partial pressure of the water or any possible effects of the sodium ions. If the predominant influence of the sodium chloride is to retard the ionization of the amine salt a similar effect should be noted when the amine salt is a non-colloidal electrolyte. Figure 2 shows that the addition of sodium chloride to a solution of hexylammonium chloride materially lowers the conductivity attributable to the amine salt.

(1) Presented before the Physical Section, Fifteenth Midwest Regional Meeting of the American Chemical Society, Kansas City, Missouri, June, 1947.

(2) Wright, Abbott, Sivertz and Tartar, THIS JOURNAL, 61, 553 (1939).

(3) Tartar and Cadle, J. Phys. Chem., 43, 1173 (1939).

(4) Hartley, J. Chem. Soc., 1968 (1938).

(5) Merrill and McBain, J. Phys. Chem., 46, 10 (1942); McBain and Merrill, Ind. Eng. Chem., 34, 915 (1943); McBain and Johnson, THIS JOURNAL, 66, 9 (1944); McBain and Green, ibid., 68, 1731 (1946).

(6) McBain and Brady, ibid., 65, 2072 (1943).

(7) Corrin and Harkins, ibid., 69, 679 (1947).

(8) Corrin and Harkins, ibid., 69, 683 (1947).

(9) Stearns, Oppenheimer, Simon and Harkins, J. Chem. Phys., 15, 496 (1947).

(10) Ralston and Hoerr, THIS JOURNAL, 68, 851 (1946).

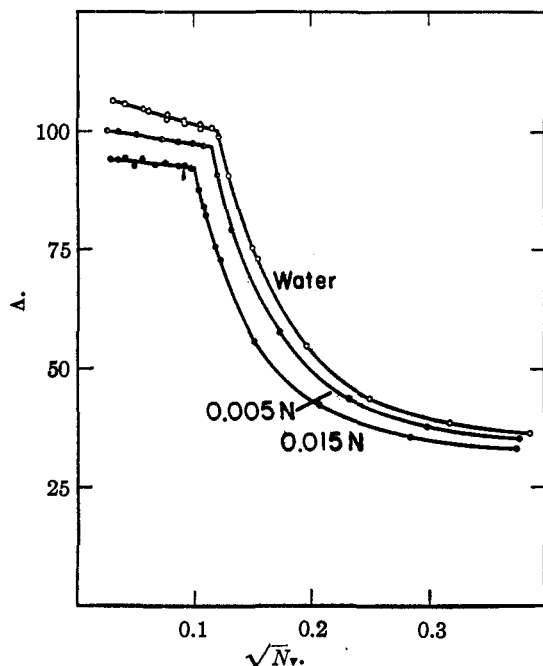(11) Ralston, Hoerr and Hoffman, ibid., 64, 97 (1942).

Fig. 1.—Conductance by difference of dodecylammonium chloride in sodium chloride at 30°. The numbers on the curves refer to the molality of sodium chloride.

A somewhat more involved problem is presented when we study the effect of electrolytes which do not possess an ion in common with the amine salt.[12] Much of the previous work upon the effect of salts on the physical behavior of solutions of colloidal electrolytes has been confined to salts having an ion in common with the colloidal electrolyte and the common ion effect has been used as the basis for interpretation of many of the observed phenomena. On the other hand, Corrin and Harkins[8] have shown that salts not possessing
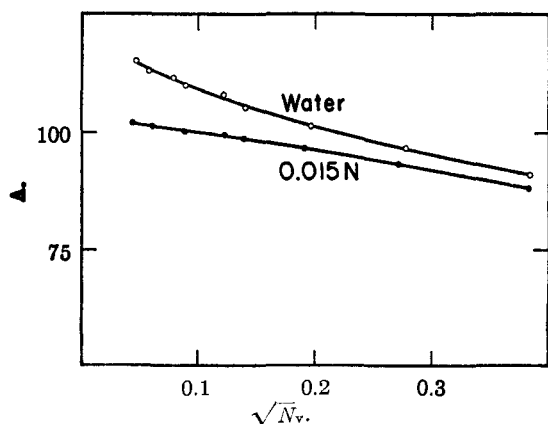

Fig. 2.—Conductance by difference of hexylammonium chloride at 30° in sodium chloride.

(12) See for example, Sherrill, THIS JOURNAL, **32**, 741 (1910); Mackay, *ibid.*, **33**, 308 (1911); Bray and Hunt, *ibid.*, **33**, 781 (1911); Smith and Gortner, *J. Phys. Chem.*, **37**, 79 (1933); Davies, *J. Chem. Soc.*, 448 (1938).

an ion in common with the colloidal electrolyte are as effective in lowering the critical concentration as those which have a common ion. Figure 3 shows the conductivity by difference at 30° of dodecylammonium chloride in 0.0261 N sodium acetate, 0.0169 N potassium acetate, and 0.0107 M calcium acetate. These salt concentrations were selected because they possess specific conductances comparable with the previously employed 0.015 N sodium chloride solution. The effects of these three salts upon the equivalent conductance of the colloidal electrolyte are approximately equal and are comparable with that of the 0.015 N sodium chloride solution. This indicates that the effect of a salt not possessing an ion in common with the colloidal electrolyte is similar to that of one which contains a common ion. It also shows that, for the salts investigated, the effect of the salt upon the electrical behavior of the cationic electrolyte is independent of the nature and concentration of the cation of the added salt.
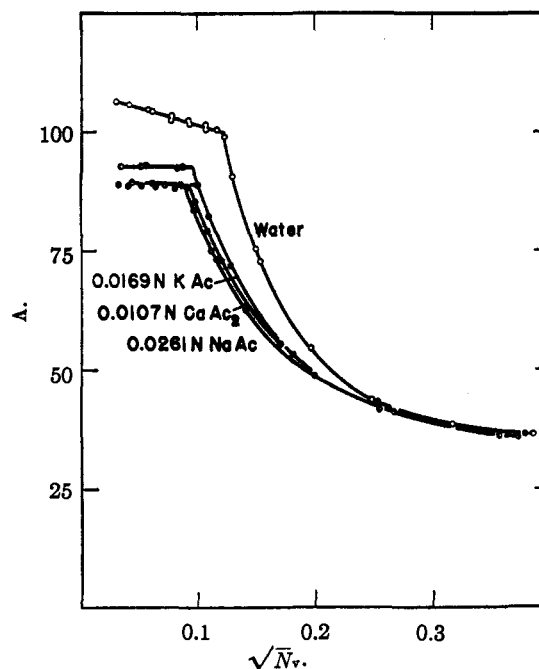

Fig. 3.—Conductance by difference of dodecylammonium chloride at 30° in presence of acetates.

The first of these conclusions is explainable on the basis of a general consideration of the behavior of solutions of colloidal electrolytes. Such solutions differ from solutions of ordinary electrolytes in that at a certain critical concentration the ions and undissociated molecules associate into colloidal particles. For colloidal electrolytes of similar structure the concentration at which this phenomenon occurs is a function of the chain length. The X-ray studies made by Harkins, Mattoon and Corrin[13] on aqueous solutions of mixtures of potassium laurate and potassium myri-

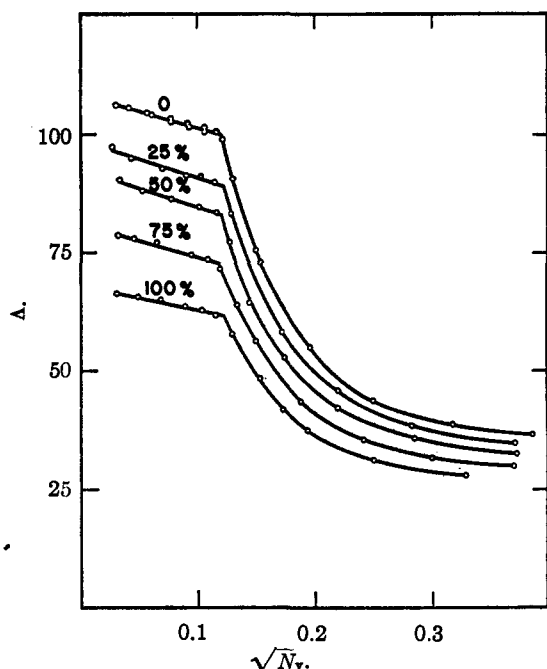(13) Harkins, Mattoon and Corrin, *ibid.*, **68**, 220 (1946).

Fig. 4.—Conductances of mixtures of dodecylammonium acetate and dodecylammonium chloride at 30°. The numbers on the curves refer to the weight per cent. of dodecylammonium acetate.

Fig. 5.—Conductance by difference of dodecylammonium chloride in hydrochloric acid at 30°.

state show only one maximum which is intermediate between the maxima exhibited by the pure soaps. Figure 4 shows the equivalent conductivities at 30° of solutions of pure dodecylammonium chloride and dodecylammonium acetate and of mixtures of these amine salts. These results show that the micelles formed from a solution of dodecylammonium chloride and its acetate incorporate both components and that the position of the critical point is not influenced by the nature of the anion. This is in conformity with previous observations[14] that the concentration of colloidal electrolyte at the critical point is a function of the chain length. When sodium acetate is added to an aqueous solution of dodecylammonium chloride an equilibrium will be set up which involves both the chloride and acetate of the colloidal electrolyte and, as a consequence, both the chloride and acetate ions are common to the components of the micelles. A similar situation will result when any salt is added to a solution of a colloidal electrolyte.

In view of the above-described effect of salts, it is surprising to find that the addition of acids to solutions of dodecylammonium chloride has only a negligible effect upon the position of the critical point. Figure 5 shows that, although the conductivities by difference at 30° of dodecylammonium chloride in 0.00145 and 0.00428 N hydrochloric acid are materially lower than that of the salt in pure water, the position of the critical point is not materially shifted. The lowered conductivity
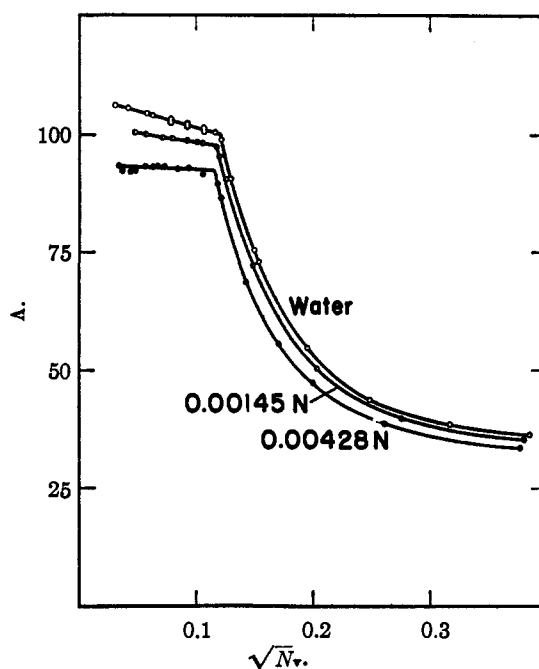
(14) Ralston and Hoerr, ibid., 69, 883 (1947).

can be ascribed to depression of the ionization of the colloidal electrolyte, since it was observed that the conductivity by difference of the non-colloidal electrolyte, hexylammonium chloride, in 0.0043 N hydrochloric acid is appreciably lower than its conductivity in pure water. We have no present explanation as to why this effect is not attended by a more significant shift in the critical concentration of the colloidal electrolyte.

The conductivities by difference of dodecylammonium chloride at 30° in 0.15 and 1.43 N acetic acid compared to that of the pure salt are shown in Fig. 6. It will again be noted that the addition of acetic acid does not influence the position of the critical point. At concentrations of dodecylammonium chloride beyond the critical point, the presence of acetic acid brings about an appreciable increase in the conductivity attributable to the colloidal electrolyte. It must, however, be borne in mind that the conductivity by difference incorporates all changes brought about in the system as a whole. Incorporation of undissociated dodecylammonium acetate into the micelles will remove it from solution and will result in an appreciable conversion of dodecylammonium chloride to its acetate. The increased conductivity may possibly be attributed to the simultaneous formation of hydrochloric acid attending this conversion.

The effect of tartaric acid upon the conductivity of dodecylammonium chloride is shown in Fig. 7 which compares the conductivity of the amine salt at 30° in pure water with its conductivity by difference in 0.0091 N tartaric acid. At concentrations higher than the critical point the effect
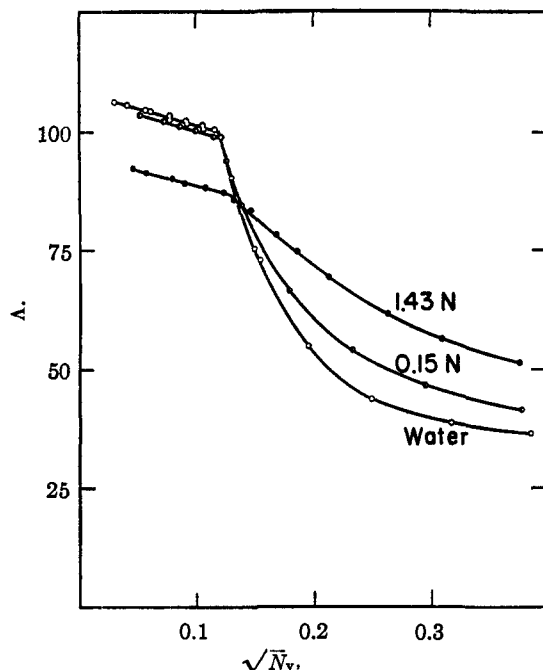
Fig. 6.—Conductance by difference of dodecylammonium chloride in acetic acid at 30°.
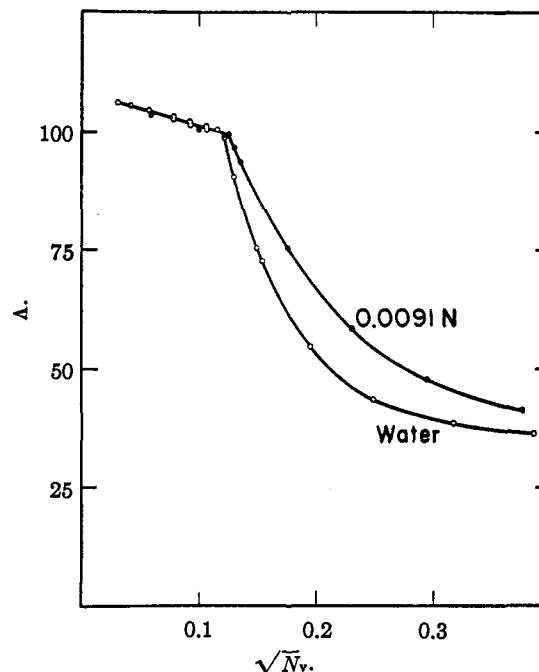

Fig. 7.—Conductance by difference of dodecylammonium chloride in tartaric acid.

of tartaric acid is qualitatively similar to that of acetic acid; however, at lower concentrations the presence of tartaric acid does not influence the conductivity of the colloidal electrolyte. In conformity with this latter observation we have found that the presence of tartaric acid does not lower the conductivity of aqueous solutions of the non-colloidal electrolyte, hexylammonium chloride.

The above observations show that the effect of the addition of acids upon the conductivity of dodecylammonium chloride differs in several respects from the effects resulting from the additions of salts. We have no present explanation for this

difference and feel that much more work is required before any explanation should be attempted.

Summary

The effect of the presence of sodium chloride, sodium acetate, potassium acetate, calcium acetate, hydrochloric acid, acetic acid and tartaric acid upon the equivalent conductivity of aqueous solutions of dodecylammonium chloride has been determined.

The results have been discussed in relation to the micelle theory.

The Effect of Organic Non-electrolytes upon the Conductivities of Aqueous Solutions of Cationic Colloidal Electrolytes

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The ability to solubilize water-insoluble organic non-electrolytes is one of the characteristic properties of aqueous solutions of colloidal electrolytes.[1] McBain and co-workers have made extensive investigations of the solubilization of water-insoluble dyes,[2,3,4] water-insoluble organic liquids,[5] and of hydrocarbon vapors[6] by aqueous solutions of col-

loidal electrolytes. In 1939, Kiessig and Philipoff[7] observed an increase in the size of the micelles of sodium oleate upon the addition of benzene to aqueous solutions of this soap and this has been subsequently interpreted[8] as indicating that the solubilized material is incorporated in layers within the micelles. A recent X-ray investigation[8] has shown that the thickness of micelles of potassium laurate or potassium myristate

(1) Hartley, J. Chem. Soc., 1968 (1938).
(2) McBain, Merrill and Vinograd, THIS JOURNAL, 63, 670 (1941).
(3) McBain and Johnson, ibid., 66, 9 (1944).
(4) McBain and Green, ibid., 68, 1731 (1946).
(5) McBain and Richards, Ind. Eng. Chem., 38, 642 (1946).
(6) McBain and O'Connor, THIS JOURNAL, 63, 875 (1941).

(7) Kiessig and Philipoff, Naturwissenschaften, 27, 593 (1939).
(8) Mattoon, Stearns and Harkins, J. Chem. Phys., 15, 209 (1947).