bility differences varying from 15–33% less than that in light water were observed.

3. Solubilities in water–deuterium oxide of cesium nitrate, potassium silver cyanide, potassium chlorate, sodium bromate, sodium oxalate and mercuric cyanide are given at 5° and that of lead chloride at 25°. The latter is 36.3% less soluble in deuterium oxide than in water.

4. The solubility of potassium dichromate in light and heavy water at 25° has been measured and is a linear function of the deuterium content of the solvent.

Conductivities of Alkylammonium Chlorides in Aqueous Solutions of Their Homologs

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

The effect of various salts and acids upon the equivalent conductivity of dodecylammonium chloride has been recently described,[1] the method employed being a determination of the conductivity by difference of the amine salt solutions in the presence of salt solutions of various concentrations. The presence of either salts or acids greatly decreases the equivalent conductivity of dilute solutions of alkylammonium chlorides. The critical concentration is markedly reduced by the presence of salts; however, the effect of acids upon the critical concentration is apparently much less. These results can be attributed to a decreased solubility of the long-chain ions in the presence of such electrolytes and can be related to the salting-out properties of the various ions.

The alkylammonium chlorides range from ordinary uni-univalent electrolytes to typical colloidal electrolytes depending upon the length of the alkyl chain. This transition has been shown[2] to occur at octylammonium chloride, since its lower homologs do not show evidence of micelle formation in aqueous solution, whereas its higher homologs progressively increase in colloidal properties with increase in molecular weight. A low molecular weight alkylammonium chloride, such as hexylammonium chloride, would be expected to affect the conductivity of a cationic colloidal electrolyte in the same manner as a salt. The effect of the presence of lower homologs upon the critical concentrations of anionic colloidal electrolytes has been investigated by Corrin and Harkins,[3] who reported that if the tendency of the components to aggregate is quite dissimilar, the soap with the lower aggregation value acts as a salt toward the other soap.

From the foregoing it is evident that the effect of an electrolyte such as an inorganic salt, an acid, or a lower molecular weight soap or alkylammonium salt upon the electrical conductance of a colloidal electrolyte is generally predictable. Much valuable information can be obtained, however, if the added electrolyte itself is a colloidal electro-lyte, and it is the purpose of this paper to present a study of the electrical conductivities of cationic colloidal electrolytes in the presence of various concentrations of other cationic colloidal electrolytes. This has been accomplished by determining the conductivity by difference of an alkylammonium chloride, such as dodecylammonium chloride, in a solution which contains a known concentration of another alkylammonium chloride, for example, tetradecylammonium chloride. It must be clearly realized that since the conductivity by difference is obtained by subtracting the conductivity of the solution employed as the solvent from the conductivity of the solution which contains both electrolytes, the conductivity by difference combines the total conductivity change occasioned by the addition of the second electrolyte. In certain instances, discussed herein, this leads to an unreal value for the conductivity of the added electrolyte. On the other hand, the conductivity by difference does show the mutual effect of the mixed electrolytes, and the proper interpretation of these effects can yield valuable information concerning the colloidal properties of one or both of the components.

Recent work upon the electrical conductivities of mixtures of cationic colloidal electrolytes has shown that both components of such mixtures are included in the micelles and that the change of slope at the critical concentration is as abrupt for mixtures as it is for pure compounds. A study of the equivalent conductivities of mixtures of dodecyl- and octadecylammonium chlorides[4] has shown that the conductance values and also the critical concentrations are intermediate between those of the two amine salts. The critical concentrations of compounds of similar structure are a function of the chain lengths,[1] and it has been observed that dodecylammonium chloride and dodecylammonium acetate and also mixtures of these salts possess identical critical concentrations. If, therefore, one determines the conductivity by difference of a higher alkylammonium chloride in a solution of a homolog which is also a colloidal electrolyte, the concentration of the original solution being below the critical concentration, the curve

(1) A. W. Ralston and D. N. Eggenberger, THIS JOURNAL, **70**, 980 (1948).

(2) A. W. Ralston and C. W. Hoerr, *ibid.*, **64**, 772 (1942).

(3) M. L. Corrin and W. D. Harkins, *J. Colloid Sci.*, **1**, 469 (1946).

(4) A. W. Ralston and C. W. Hoerr, THIS JOURNAL, **69**, 883 (1947).

obtained should show an abrupt drop at the point where mixed micelles are formed. Certain of the experiments recorded herein clearly show that this occurs.

The ability of micelles to solubilize water-insoluble, organic non-electrolytes is well known, and a study has recently been published[5] concerning the solubilization of a number of organic non-electrolytes by aqueous solutions of dodecylammonium chloride. In the study it was shown that the solubilization of water-insoluble, organic compounds reduces both the equivalent conductivity and the critical concentration of dodecylammonium chloride, the extent of reduction varying greatly with the nature of the compound solubilized. No reduction in conductivity was observed at concentrations lower than the critical point, thus evidencing that solubilization does not take place in the absence of micelles. It was further pointed out that in solutions of colloidal electrolytes at concentrations equal to or greater than the critical concentration the undissociated molecules of the colloidal electrolyte itself function as non-electrolytes and are solubilized by the associated ions, thus accounting for the abrupt drop in equivalent conductivity and the abnormal transference numbers. Further evidence of this solubilization can be obtained if one determines the conductivity by difference of an alkylammonium chloride in a solution of another alkylammonium chloride whose concentration is higher than the critical concentration. Solubilization would be manifested by an abnormally low equivalent conductivity of the added electrolyte in such a solution when compared to its conductivity in pure water. That this occurs is quite evident from the data presented in this paper upon the effect of the presence of dodecylammonium chloride upon the equivalent conductivity of tetradecylammonium chloride and *vice versa*.

Experimental

The preparation and properties of the hexylammonium chloride used in this investigation have been previously described.[6] The dodecylammonium chloride was from the same lot used in a conductometric investigation.[7] Tetradecylammonium chloride was prepared from tetradecylamine, f. p. 38.11°, which was synthesized by a previously described procedure.[8] A freezing point of 38.19° was reported[8] for pure tetradecylamine.

The conductivities were determined in the manner and with the equipment previously used in other conductometric work.[9] Solutions were prepared containing known amounts of an amine salt and these solutions were employed as solvents for the other amine salts. Decreasing concentrations were obtained by diluting more concentrated solutions with the amine salt solution. Thus, the concentration of one of the amine salts remained constant and the other varied. All the curves were checked by

(5) A. W. Ralston and D. N. Eggenberger, This Journal, **70**, 983 (1948).

(6) A. W. Ralston and C. W. Hoerr, *ibid.*, **68**, 851 (1946).

(7) A. W. Ralston and D. N. Eggenberger, *ibid.*, **70**, 436 (1948).

(8) A. W. Ralston, C. W. Hoerr, W. O. Pool and H. J. Harwood, *J. Org. Chem.*, **9**, 102 (1944).

(9) A. W. Ralston, C. W. Hoerr and E. J. Hoffman, This Journal, **64**, 97 (1942).

determining the conductivities of individually prepared samples. Conductivity water having a specific conductance of 1×10^{-6} mhos was employed for the preparation of the solutions. In order to minimize the effects of adsorption, the conductivity cell was allowed to remain in contact with several portions of the amine salt solution before the final conductivity value was recorded. The necessity for this precaution in conductometric work involving cationic colloidal electrolytes has been pointed out by Scott and Tartar.[10] The conductivity by difference was calculated as previously described.[1]

Results and Discussion

The equivalent conductivity of dodecylammonium chloride in pure water and in various concentrations of hexylammonium chloride is shown in Fig. 1. The latter salt has been shown to function as an ordinary uni-univalent electrolyte,[2] its equivalent conductivity falling linearly with the square root of the concentration.[11] The former salt is a recognized colloidal electrolyte. The presence of hexylammonium chloride reduces both the equivalent conductivity and the critical concentration of dodecylammonium chloride. The change of slope at the critical concentration is as abrupt in hexylammonium chloride solution as in pure water. A comparison of these curves with those obtained for dodecylammonium chloride in the presence of various salts[1] shows a striking similarity. It is, therefore, evident that the lower alkylammonium chloride has functioned as a salt toward its higher homolog. This effect has recently been ascribed[12] to a reduction in the solubility of the hydrocarbon
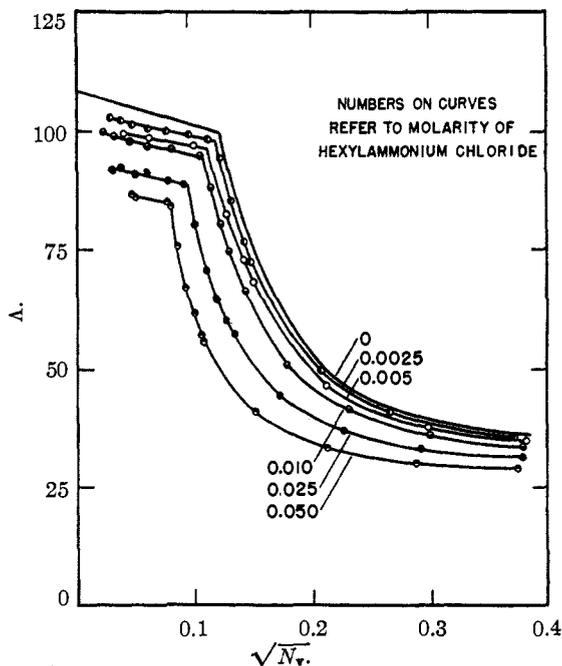
Fig. 1.—Conductivity by difference of dodecylammonium chloride at 30° in hexylammonium chloride.

(10) A. B. Scott and H. V. Tartar, *ibid.*, **65**, 692 (1943).

(11) A. W. Ralston and C. W. Hoerr, *ibid.*, **68**, 2460 (1946).

(12) A. W. Ralston and D. N. Eggenberger, paper presented before the Division of Colloid Chemistry, American Chemical Society, 113th Meeting, Chicago, Illinois, 1948.

portion of the long-chain ions in the presence of salts.
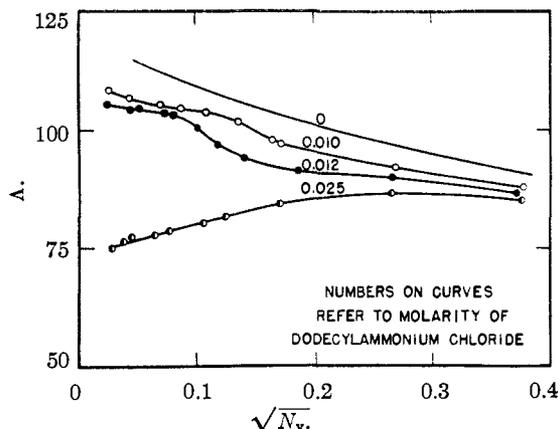

Fig. 2.—Conductivity by difference of hexylammonium chloride at 30° in dodecylammonium chloride.

The curves shown in Fig. 2 were obtained by determining the conductivity by difference of hexylammonium chloride in the presence of various concentrations of dodecylammonium chloride. The curves show the equivalent conductivity of hexylammonium chloride in pure water and the conductivity by difference in 0.010, 0.012, and 0.025 N dodecylammonium chloride solutions. The critical concentration of dodecylammonium chloride has been recently reported[7] to be 0.0144 N. The type of curve obtained under these conditions depends upon whether the amount of dodecylammonium chloride present in the solvent is higher or lower than the critical concentration. The curves for the conductivity by difference of hexylammonium chloride in 0.010 N and 0.012 N dodecylammonium chloride simulate those of colloidal electrolytes and show that the addition of the hexylammonium chloride causes its higher homolog to form micelles. Such an effect would be predictable from the curves shown in Fig. 1. The curve for the conductivity by difference of hexylammonium chloride in 0.025 N dodecylammonium chloride, a concentration beyond the critical point of the latter, rises slowly with increase in concentration and then drops slightly. The appreciable lowering of the equivalent conductivity of dilute solutions of hexylammonium chloride indicates that a portion of the added amine salt is solubilized by the micelles of dodecylammonium chloride.

Figures 1 and 2 contain several identical points as regards the concentration of the two amine salts. It is interesting to note that at these common points the conductivities of the systems are identical, thus showing that the final state of the system is independent of the order of addition of its various components.

Figure 3 shows the equivalent conductivity of tetradecylammonium chloride in pure water and

its conductivity by difference in the presence of its homolog dodecylammonium chloride. The curve obtained for the equivalent conductivity of tetradecylammonium chloride in 0.010 N dodecylammonium chloride shows that mixed micelles are formed by these two amine salts. The curve drops very abruptly over a limited concentration range to a minimum and then rises. The abruptness of the drop and the low values for the conductivity by difference at concentrations higher than that at which mixed micelles are formed indicate an extensive solubilization of undissociated tetradecylammonium chloride molecules by the mixed micelles.

The curve obtained for the conductivity by difference of tetradecylammonium chloride in 0.025 N dodecylammonium chloride, a concentration beyond the critical concentration of dodecylammonium chloride, is extremely interesting. The negative values for the conductivity by difference obtained over an appreciable concentration range of tetradecylammonium chloride mean that the addition of this amine salt has actually lowered the specific conductance of the dodecylammonium
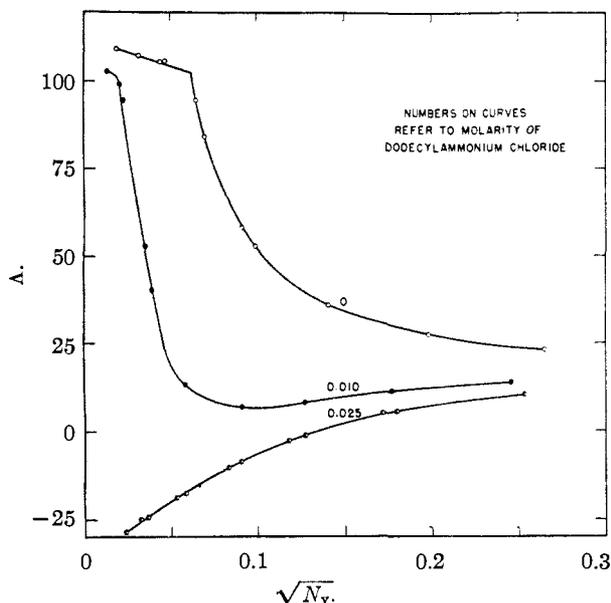

Fig. 3.—Conductivity by difference of tetradecylammonium chloride at 30° in dodecylammonium chloride.

chloride solution. This phenomenon is explainable on the basis of solubilization of the added amine salt by the micelles present in the solvent and is similar to that encountered when organic non-electrolytes are added to such solutions. Solubilization of a substantial portion of the added amine salt would greatly reduce the mobility of the micelles and consequently reduce the conductivity of the system.

That solubilization of the added amine salt is not complete in the more concentrated solutions is evidenced by the rise in the conductivity of the

tetradecylammonium chloride with increase in its concentration. It is well known that the tendency of the alkylammonium chlorides toward micelle formation increases markedly with increase in their chain lengths. Thus, the addition of tetradecylammonium chloride to a system in which micelles formed from dodecylammonium ions are present should result in the replacement of the dodecylammonium ions in the micelles by tetradecylammonium ions, with the formation of mixed micelles. In the above system it is probable, therefore, that as the concentration of tetradecylammonium chloride is increased the micelles are composed largely of tetradecylammonium ions and that it is actually the dodecylammonium chloride which is solubilized. This process may contribute to the gradual rise in the conductivity by difference with increase in the concentration of the tetradecylammonium chloride.

The equivalent conductivity of dodecylammonium chloride in pure water and in the presence of 0.0025 N and 0.020 N tetradecylammonium chloride is shown in Fig. 4. The curve for dodecylammonium chloride in 0.0025 N tetradecylammonium chloride indicates that mixed micelles are formed. The break after the critical point is much less abrupt than that observed for the reverse addition (Fig. 3). The conductivity by difference of dodecylammonium chloride in 0.020 N tetradecylammonium chloride, a concentration beyond the critical concentration of the latter, is still appreciable even in dilute solutions. Since dodecylammonium chloride is more highly conducting than its higher homolog it would be anticipated that its presence would raise the conductance of the system as a whole in spite of its partial solubilization. It would not be expected that dodecylammonium ions would replace tetradecylammonium ions from the micelle structure for reasons previously mentioned.

As in the case of hexyl- and dodecylammonium chlorides, Figs. 3 and 4 contain several identical points as regards the concentrations of the two amine salts. At these common points the electrical conductances are identical, thus showing that in systems involving two cationic colloidal electrolytes the final state of the system is independent of the order of addition of the components. This presents further evidence in support of the statement of McBain[13] that such systems are thermodynamically stable.
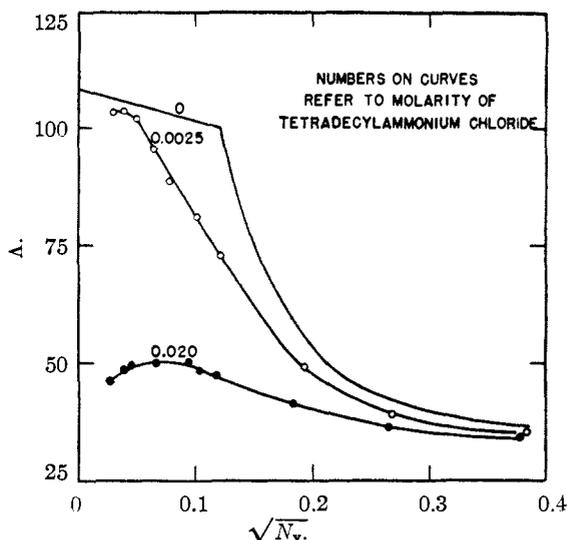

Fig. 4.—Conductivity by difference of dodecylammonium chloride at 30° in tetradecylammonium chloride.

Summary

The conductivities by difference of dodecylammonium chloride in the presence of hexylammonium chloride and of hexylammonium chloride in the presence of dodecylammonium chloride have been determined. It has been shown that the lower alkylammonium chloride acts as a salt toward its higher homolog.

Mixed micelles are formed when dodecylammonium chloride is added to a dilute solution of tetradecylammonium chloride and vice versa. The conductivity by difference of tetradecylammonium chloride in the presence of a solution of dodecylammonium chloride at a concentration beyond the critical concentration of the latter shows extensive solubilization of amine salt by the micelles. The reverse addition also indicates appreciable solubilization. It has been suggested that tetradecylammonium replace dodecylammonium ions in micelles. The final state of such systems is independent of the order of addition of the various components.

(13) J. W. McBain, Nature, 145, 702 (1940).