Fig. 6.—Conductance by difference of dodecylammonium chloride in acetic acid at 30°.
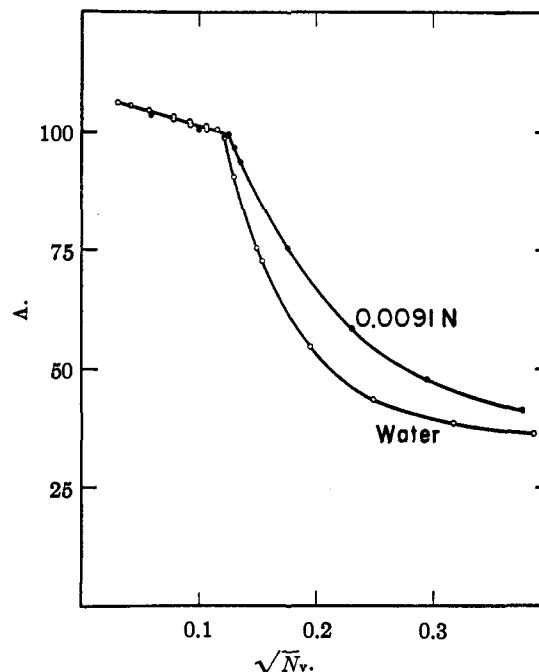

Fig. 7.—Conductance by difference of dodecylammonium chloride in tartaric acid.

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.

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

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

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 colloidal 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).

is materially increased by the presence of hydrocarbons such as hexane, benzene or ethylbenzene. The recent work of Harkins and associates[9] has given support to the opinion previously expressed by Hartley[1] that solubilization does not occur below the critical point for micelle formation. Factors such as molecular volume, molecular weight, polarity, and structure exert a marked influence upon solubilization.

Many conductivity measurements upon aqueous solutions of colloidal electrolytes have been published. It is universally accepted that the colloidal electrolytes exhibit conductivity behaviors which distinguish them from ordinary electrolytes. Since solubilization is occasioned by the incorporation of water-insoluble substances into the micelles, it follows that this process should materially influence the conductivities of solutions of colloidal electrolytes. We have, therefore, made a study of the effect of the presence of a number of organic non-electrolytes upon the conductivities of several cationic colloidal electrolytes. The data permit certain generalizations regarding the phenomenon of solubilization and also allow certain speculations regarding the mechanism of micelle formation in aqueous solutions of colloidal electrolytes.

Experimental

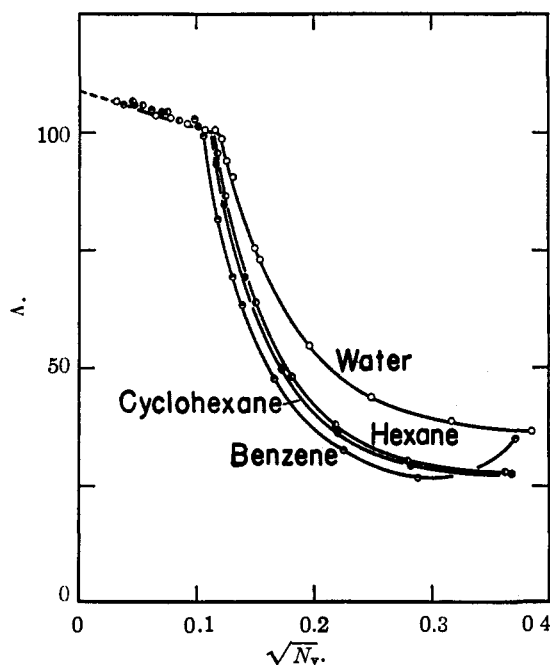The preparation of the hexadecyltrimethylammonium chloride used in this study has been

previously described.[10] The dodecyltrimethylammonium chloride was prepared by a similar procedure. The dodecylammonium chloride was from the same lot as that previously employed in recent conductivity determinations.[11] Conductivities were determined in the manner and with the equipment previously described.[12] In all cases the solution of the colloidal electrolyte was saturated with the organic non-electrolyte. This was accomplished by progressively adding the non-electrolyte to the solution, vigorously shaking, and allowing the system to come to equilibrium at the temperature of the determination. In several instances this process required from twelve to forty-eight hours. Excess of non-electrolyte is indicated by the formation of a separate layer which was removed. Conductivity water was used for dilution; however, in all cases care was exercised to make certain that the solution was saturated with the non-electrolyte. All the curves were checked by determining the conductivity of individually prepared samples, and the cell was permitted to come to equilibrium with the solution before any conductivity values were recorded.

Results and Discussion

The three six-carbon-membered hydrocarbons, n-hexane, benzene, and cyclohexane are solubilized in an aqueous solution of dodecylammonium chloride and Fig. 1 shows that their presence brings about an appreciable lowering of the conductivity of the colloidal electrolyte. It is interesting to note that all three of these hydrocarbons lower the concentration at the critical point which indicates that they assist in micelle formation. This is in agreement with the previous observations of McBain and others[2,13] that the presence of water-insoluble, organic, non-electrolytes lowers the critical concentration for micelle formation. The effect of hexane is less than that of benzene, whereas that of cyclohexane is intermediate. This shows that either the benzene is solubilized to a somewhat greater extent than cyclohexane or its effect when incorporated into the micelles is greater. In any event, the curves indicate that the structure of the compound solubilized is a factor in its effect upon the conductivity. The fact that the presence of these hydrocarbons lowers the critical point is explainable on the basis of their affinity for the hydrocarbon portion of the associated ions. Solubility determinations of benzene and cyclohexane in dodecane[14] show that both are extremely soluble in this hydrocarbon; however, the former is somewhat less soluble than the latter.

The influences of the higher straight chain hydrocarbons, octane, dodecane, heptadecane and octadecane upon the equivalent conductivity of

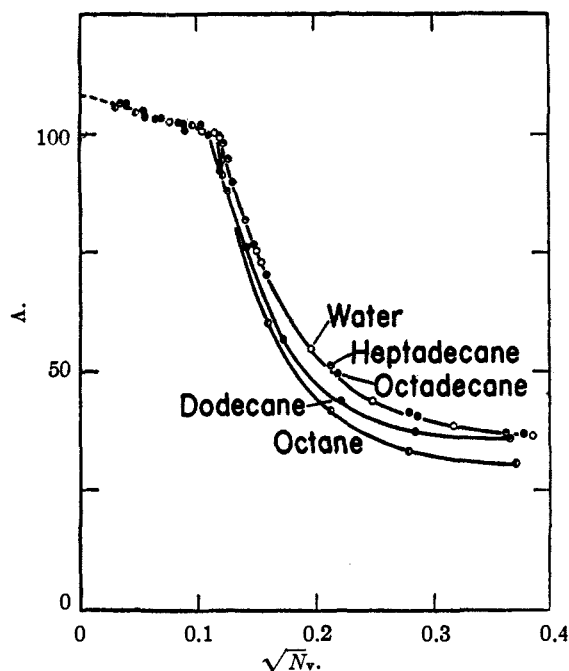Fig. 1.—Equivalent conductivities at 30° of dodecylammonium chloride in the presence of six-carbon-membered hydrocarbons.

Fig. 2.—Equivalent conductivities at 30° of dodecyl-ammonium chloride in the presence of straight-chain, saturated hydrocarbons.

Fig. 3.—Equivalent conductivities at 30° of dodecyl-ammonium chloride in the presence of polar aliphatic compounds.

dodecylammonium chloride are shown in Fig. 2. It is evident that their effects are appreciably less than those of the six-carbon-membered hydrocarbons, and that they decrease progressively with increase in chain length. Both heptadecane and octadecane are without apparent effect on the equivalent conductivity of this colloidal electrolyte. This shows that increase in chain length of the hydrocarbon is attended by a drastic reduction in its ease of solubilization and is in conformity with the previous findings of McBain and Richards[5] that hydrocarbons of high molecular weight are scarcely solubilized. An important observation with regard to the effect of hydrocarbons is that their presence does not significantly influence the conductivity values at concentrations lower than the critical concentration for micelle formation.

If the long-chain compound possesses a polar group, its presence lowers the equivalent conductivity of dodecylammonium chloride. Figure 3 shows that both stearonitrile and stearamide lower the conductivity of this amine salt, in contrast to octadecane, Fig. 2, which was observed to be without effect. The lowering of the conductivity by the presence of undecyl chloride, Fig. 3, is quite similar to that produced by octane and substantially greater than that resulting from the presence of dodecane, Fig. 2. This shows that even though the corresponding hydrocarbon is solubilized, the presence of a polar group increases either the amount of solubilization or the specific conductivity effect. None of the compounds shown in Fig. 3 appear to exert a significant influence on the
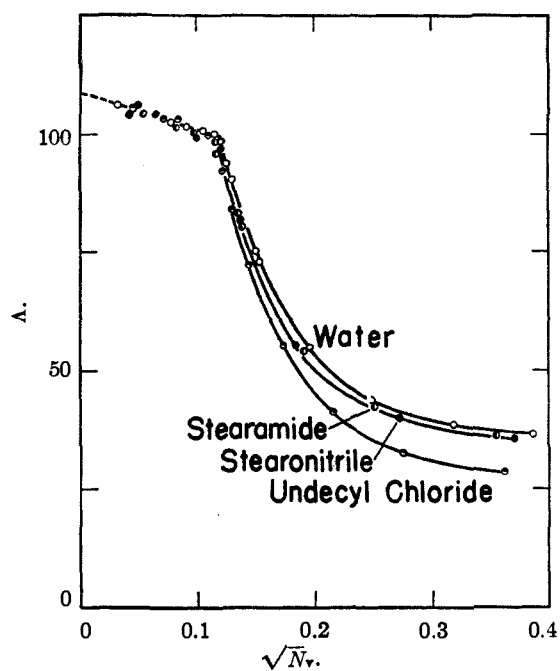
conductivity of the amine salt at concentrations lower than the critical concentration for micelle formation. This is contrary to our previously published results[15] which reported that dodecane, lauronitrile and N-methyllauramide lower the conductivity of aqueous solutions of dodecylammonium chloride at concentrations below the critical point.

The higher alcohols, hexanol, octanol, dodecanol and octadecanol have a profound influence upon the conductivity of dodecylammonium chloride. Figure 4 shows that these alcohols decidedly lower the conductivity over the entire range of concentration, the lowering being at a maximum with dodecanol and at a minimum with octadecanol. As the concentration of the amine salt is increased all these solutions go from milky liquids to sirupy liquids and finally to gels. We interpret these results as indicating that long-chain compounds which contain a hydrophilic group are not only solubilized but that they can also enter into the structure of the ionic micelles and thus assist in the solubilization process. McBain and McHan[16] have ascribed the solubilization of dodecyl alcohol in solutions of potassium laurate to the polar portion of the detergent.

The effect of the presence of organic non-electrolytes upon two long-chain alkyltrimethylammonium chlorides has been investigated. The results obtained with aqueous solutions of hexadecyltrimethylammonium chloride in the presence

(15) Ralston and Hoerr, THIS JOURNAL, 69, 883 (1947).

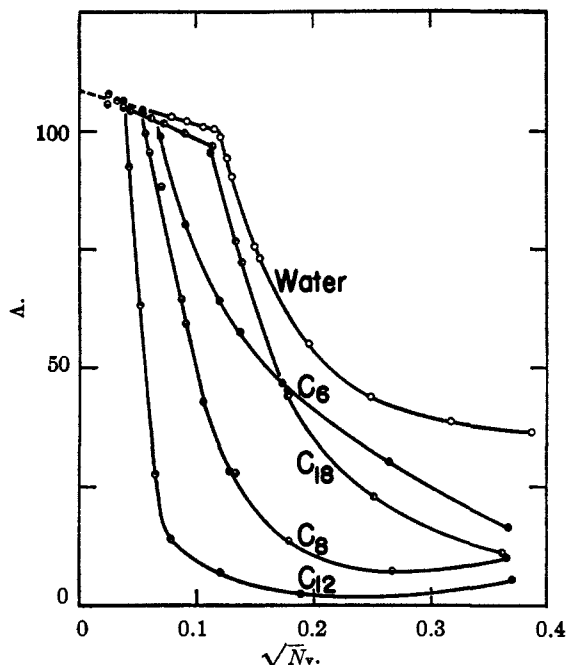(16) Paper presented before the Division of Colloid Chemistry, 112th Meeting, A. C. S., New York, Sept., 1947.

Fig. 4.—Equivalent conductivities at 30° of dodecylammonium chloride in the presence of aliphatic alcohols.

of dodecane, octadecane and lauronitrile agree quite closely with those which would be expected from the above-described observations upon dodecylammonium chloride. Figure 5 shows that the presence of dodecane and lauronitrile lowers the equivalent conductivity of aqueous solutions of dodecyltrimethylammonium chloride. The polar compound exerts the greater effect, and although both compounds lower the critical concentration, they do not significantly influence the conductivity within the first range. These results
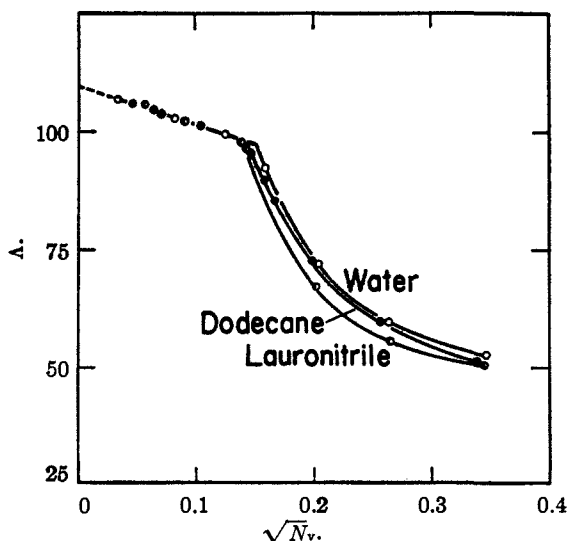

Fig. 5.—Equivalent conductivities of dodecyltrimethylammonium chloride in the presence of dodecane and lauronitrile.

are qualitatively similar to those observed with dodecylammonium chloride and indicate that the presence of the methyl groups in the colloidal electrolyte is without material influence.

In the above discussion we have assumed that the observed results are dependent upon the incorporation, by solubilization or otherwise, of the organic non-electrolytes into the colloidal aggregates. Although this assumption appears reasonable it certainly requires experimental verification. As a consequence, we have determined the effect of the presence of several organic non-electrolytes upon the conductivity of aqueous solutions of hexylammonium chloride. This salt has been previously shown[17] to function as an ordinary electrolyte even in concentrated solutions. Since it does not form micelles the conductivity of its aqueous solutions should not be influenced by the presence of water-insoluble substances. Figure 6 shows the conductivities of aqueous solutions of hexylammonium chloride and of solutions of this salt in the presence of dodecane, dodecanol, lauronitrile and N-methyllauramide. None of these compounds influence the equivalent conductivity of this amine salt and we are, therefore, safe in assuming that the effects noted above with its higher homologs are dependent upon the colloidal nature of the latter.
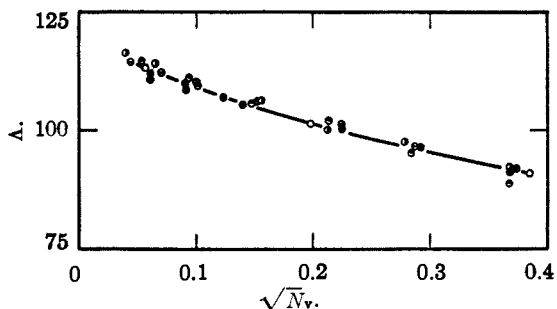

Fig. 6.—Equivalent conductivities of hexylammonium chloride in the presence of non-electrolytes: O, hexylammonium chloride; ⊖, methyllauramide; ◑, lauronitrile; ●, dodecanol; ◓, dodecane.

The phenomenon of solubilization appears to be of more fundamental significance than has hitherto been considered. The fact that the critical concentration for micelle formation in solutions of colloidal electrolytes is materially lowered by the presence of water-insoluble organic non-electrolytes indicates that the effect is more complex than a simple incorporation of the water-insoluble substance into a previously formed micelle. It is, therefore, possible that solubilization and micelle formation are allied phenomena. As the concentration of an aqueous solution of a colloidal electrolyte is increased, the number of undissociated molecules also increases and these undissociated molecules function as non-electrolytes. Their inclusion into the ionic micelles would be attended

(17) Ralston and Hoerr, ibid., 68, 2460 (1946).

by a marked and abrupt drop in the equivalent conductivity and by an abnormal increase in the cationic transference number in the case of the cationic colloidal electrolytes. It is well known that both of these effects are observed in aqueous solutions of colloidal electrolytes. The essential difference between ionic and lamellar micelles is that the latter has solubilized the undissociated colloidal electrolyte.

Transference data on the effect of non-electrolytes upon solutions of colloidal electrolytes would be extremely helpful in explaining the mechanism of micelle formation and studies are now underway to determine the effect of various non-electrolytes upon the transference numbers of solutions of dodecylammonium chloride.

Summary

The effect of the presence of benzene, cyclo- hexane, hexane, octane, dodecane, heptadecane, octadecane, hexanol, octanol, dodecanol, octadecanol, undecyl chloride, stearonitrile and stearamide upon the equivalent conductivity of aqueous solutions of dodecylammonium chloride has been determined. The influence of the presence of dodecane and lauronitrile upon the equivalent conductivity of aqueous solutions of dodecyltrimethylammonium chloride has also been investigated.

With the exception of heptadecane and octadecane all the compounds investigated lowered the equivalent conductivity and the critical concentration for micelle formation in the amine salt solutions.

The results have been discussed in relation to the micelle theory and it has been proposed that solubilization and micelle formation are allied phenomena.

The Dissociation of Diborane by Electron Impact

BY VERNON H. DIBELER AND FRED L. MOHLER

Introduction

The theory of the structures of some electron-deficient molecules, the hydroborons in particular, have recently received considerable attention. In 1942 the most fully developed valence theory of the hydroborons, as reviewed by Bauer,[1] assumed hydrocarbon-like structures. Because of inconsistencies between the hydrocarbon analogy and chemical and physical properties, Pitzer[2] and others further developed the four-membered-bridge bond originally proposed by Dilthey[3] to a "protonated double bond" theory in which two protons are placed symmetrically between the boron atoms, one above and one below an ethylene-like double bond. More recently, Burg,[4] in order to account for the lack of proton–deuteron exchange between ammonia and ammoniated diborane, proposed a "pseudoethane" structure in the form of a trigonal antiprism in which two sp^2 planar BH_3 groups are held together by resonating cross linkages between the B–B and B–H atoms. Another structure which he considers possible is a four-proton-bridge model in which the two boron atoms and four of the hydrogen atoms form the corners of a cube. The remaining two hydrogens extend outward along the diagonal of the cube connecting the two boron atoms.

Rundle[5] accepts Pitzer's developed theory in the case of the hydroborons with an interpretation of the protonated double bond as two hydrogen bridges consisting of "half-bonds." Each hydrogen bonds two boron atoms using its ls-orbital and one electron pair. Thus, the bridge contains two pairs of electrons and should have the properties of the ethylene-like double bond.

Hipple[6] has published a note on the mass spectrum of diborane. An analysis of this mass spectrum made by the authors differs significantly from the results reported by Hipple. As the results have a direct bearing on the structure of the diborane molecule we report in detail the analysis of this spectrum as compared with the mass spectra of ethane and ethylene.

Experimental

The Consolidated mass spectrometer used to obtain the mass spectra has been described elsewhere in detail.[7] The gas to be studied is admitted to the ionization chamber at about 10^{-4} mm. pressure and ionized by a beam of electrons at 50 or 70 electron volts energy. The positive ions formed in the electron beam are accelerated by an electric field and sorted into 180° arcs by a constant magnetic field used as a velocity analyser. By varying the electric field the ions are separately collected and recorded. The ionizing current is automatically maintained constant and the ionization chamber is thermostated to maintain a temperature of about 245°. Two samples of diborane were obtained. Sample 1 was prepared at the U. S. Naval Research Laboratory and supplied by Roman R. Miller. About 25 ml. of gas (S.T.P.) were removed from the liquid phase and transferred from the stainless steel cylinder into a glass bulb. The glass bulb was stored at −78° to minimize decomposition to hydrogen and heavy hydroborons. A mass spectrometric analysis of the original sample showed a purity of about 99.4% with small amounts of tetraborane, ethane and diethyl ether. Sam-

(1) S. H. Bauer, *Chem. Rev.*, **31**, 43 (1942).

(2) K. S. Pitzer, THIS JOURNAL, **67**, 1126 (1945).

(3) W. Dilthey, *Z. angew. Chem.*, **34**, 596 (1921).

(4) A. B. Burg, THIS JOURNAL, **66**, 747 (1947).

(5) R. E. Rundle, *ibid.*, **69**, 1327 (1947).

(6) J. A. Hipple, Jr., *Phys. Rev.*, **57**, 350 (1940), abstract.

(7) H. W. Washburn, H. F. Wiley, S. M. Rock and C. E. Berry, *Ind. Eng. Chem., Anal. Ed.*, **15**, 54 (1943).