acetophenone was taken. The spectrum is similar, and the intensity of absorption is of the same order as is exhibited by benzene derivatives with carbon–carbon double bonds conjugated with the benzene ring.

The absorption spectrum of α-phenylpropene oxide is very interesting. There is a marked similarity between its spectrum and that of acetophenone (see Fig. 3). The main differences seem to be that the intensity of both maxima of the oxide are about one-half of those of acetophenone, and that the maxima are shifted about 30 mμ lower. It appears obvious, however, that considéral conjugation exists between the benzene ring and the oxide grouping.[10] This is readily shown by further comparison with benzyl alcohol.

Care must be exercised in assigning structure to an unknown substance on the basis of spectra alone, since certain substituents (either on the ring or on the side chain) affect the characteristic spectra markedly. This may be seen from the data for anethole (9, Table I), methylatropic acid (14), which has a carboxyl group in conjugation with the double bond in the side chain, and cinnamic acid (13), with the carboxyl group in conjugation both with the double bond in the side chain and with the benzene ring. However, despite the shift in position (or disappearance) of the characteristic maxima, conjugation is indicated by the high order of the extinction coefficients.

The cyclic compound indene (Fig. 3 and Table I) also differs from the corresponding open-chain compound, propenylbenzene; however, the characteristic high maximum at 249 mμ is present.

Our results are in agreement with those of Ramart-Lucas and Hoch,[11] who compared the absorption spectra of indene and its open-chain analog, *o*-methylstyrene.

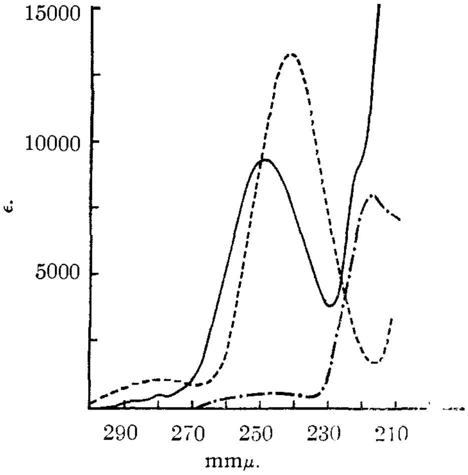

Fig. 3.—Absorption spectra of indene, —; acetophenone - - - -; and α-phenylpropylene oxide, —·—·—.

Summary

1. The absorption spectra of a number of unsaturated benzene derivatives have been studied and compared with the spectra of similar saturated derivatives.

2. It has been found that a double bond in conjugation with the benzene ring produces a very characteristic spectrum, by which this type of compound may be differentiated from saturated derivatives, and from unsaturated compounds without the double bond in conjugation.

LOS ANGELES, CALIFORNIA RECEIVED DECEMBER 3, 1946

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[10] Klotz [THIS JOURNAL, **66**, 88 (1944)] has presented spectroscopic evidence of a similar nature for conjugation between a cyclopropane ring and a carbonyl group or a carbon–carbon double bond.

[11] P. Ramart-Lucas and M. J. Hoch, *Bull. soc. chim.*, [5] **2**, 327 (1935).

[CONTRIBUTION FROM THE RESEARCH LABORATORY OF ARMOUR AND COMPANY]

The Electrical Conductivities of Aqueous Solutions of Mixtures Containing Alkylammonium Chlorides

BY A. W. RALSTON AND C. W. HOERR

The many studies which have been made upon homologous series of colloidal electrolytes clearly show the gradation in conductivity behavior which accompanies progressive increases in the chain lengths of the various members. Increase in the chain length of colloidal electrolytes of similar structure is attended by lowered equivalent conductivities of their aqueous solutions and by a shifting of the critical point for micelle formation toward a lower concentration of electrolyte. An example of this effect is found in the conductivity behavior of aqueous solutions of the alkylammonium chlorides,[1] and it has recently been found that in compounds of comparable structures, the chain length is determinative as regards the critical point for micelle formation.[2] Although the conductivity behavior of individual members of various series of colloidal electrolytes has been the subject of many studies, the conductivities of aqueous solutions of mixtures of homologous electrolytes have not been investigated. It has been assumed that the micelles formed in a solution of a specific colloidal electrolyte are of approximately uniform size, the size depending upon the nature of the electrolyte, the concentration, the temperature, and other factors. Where the

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[1] Ralston and Hoerr, THIS JOURNAL, **64**, 772 (1942).

[2] Unpublished observations.

solute comprises a mixture of two structurally similar colloidal electrolytes, it is extremely unlikely that each homolog will form its individual micelles. The micelles will, therefore, incorporate both components of the mixture and the conductivity behaviors of aqueous solutions of such mixtures will be intermediate between those of the pure components. The work herein presented upon the conductivities of aqueous solutions of mixtures of dodecylammonium chloride and octadecylammonium chloride indicates this assumption to be correct.

Since micelles can incorporate compounds of different chain lengths, it appeared of interest to investigate the electrical behavior of a mixture of two structurally similar homologs one of which functions as a simple electrolyte and the other as a colloidal electrolyte. Hexylammonium chloride and octadecylammonium chloride were selected as representing these two types of electrolytes. The former of these has been shown to function as an ordinary uni-univalent electrolyte[3] and the latter is a typical colloidal electrolyte. Our study of the conductivities of mixtures of octadecylammonium chloride and hexylammonium chloride shows that the critical concentration for micelle formation in aqueous solutions of octadecylammonium chloride is not influenced by the presence of hexylammonium chloride. This suggests that the latter compound is not incorporated into the micelles.

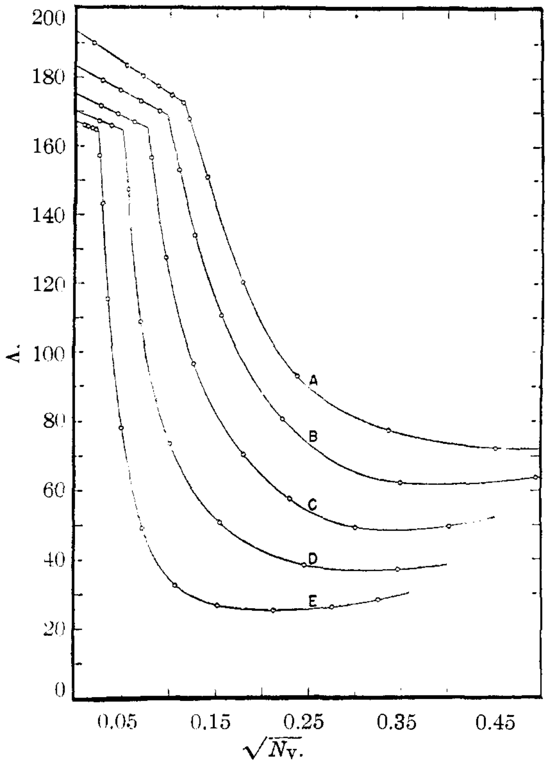

Fig. 1.—Equivalent conductivities of various mixtures of dodecyl- and octadecylammonium chlorides in aqueous solution at 60.0°. The curves represent the following: A, pure $C_{12}H_{25}NH_2{\cdot}HCl$; B, 75.0 mole % $C_{12}H_{25}NH_2{\cdot}HCl$ and 25.0 mole % $C_{18}H_{37}NH_2{\cdot}HCl$; C, 50.0 mole % $C_{12}H_{25}NH_2{\cdot}HCl$ and 50.0 mole % $C_{18}H_{37}NH_2{\cdot}HCl$; D, 25.0 mole % $C_{12}H_{25}NH_2{\cdot}HCl$ and 75.0 mole % $C_{18}H_{37}NH_2{\cdot}HCl$; E, pure $C_{18}H_{37}NH_2{\cdot}HCl$.

Since the micelles formed from alkylammonium chlorides are highly paraffinic in character, it appears reasonable to suppose that various long-chain non-electrolytes would be attracted to the micelles and can be incorporated into their structures. Such an effect would be attended by an increase in the size of the colloidal ion and, consequently, by a reduced mobility which would manifest itself by a lowered equivalent conductivity and possibly a shifting of the critical point for micelle formation toward a lower concentration of electrolyte. In this present investigation we have determined the equivalent conductivities of aqueous solutions of dodecylammonium chloride in the presence of three long-chain non-electrolytes, methyllauramide, dodecane and lauronitrile. The equivalent conductivity of an aqueous solution of dodecylammonium chloride is materially lowered by the presence of such non-electrolytes, methyllauramide exerting the least effect and lauronitrile the greatest. The critical point for micelle formation in aqueous solution of dodecylammonium chloride is shifted toward a lower concentration of electrolyte by the presence of these non-electrolytes. This suggests that in a system involving a colloidal electrolyte and a long-chain non-electrolyte both of the components are present in the micelles. The fact that the saturated hydrocarbon, dodecane, has an effect comparable with those of the polar compounds, methyllauramide and lauronitrile, evidences that the effect of the non-electrolyte is not dependent upon the presence of a polar group. A several-fold increase in the concentration of the non-electrolyte is without influence upon the conductivity properties of the system. It, therefore, appears that solubility considerations are involved and that the function of the non-electrolytes is dependent upon its solubility in the amine salt–water system.

Experimental

The amine salts used in this investigation were prepared by a method described elsewhere[3] and the conductivities were determined in the manner and with the equipment previously described.[4]

Results and Discussion

The conductivities of aqueous solutions of octadecylammonium chloride and dodecylammonium chloride and of mixtures of these two salts are shown in Fig. 1. The molar concentrations plotted in this figure are based upon the total amine salt content. The values for the equivalent conductivities of mixtures of these two electrolytes

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(3) Ralston and Hoerr, THIS JOURNAL, **68**, 851, 2460 (1946).

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

are intermediate between those of the components, and the same comments apply to the critical concentrations. In view of the above and also the fact that the critical points are as well defined for the mixtures as for their pure components it is apparent that both of these electrolytes have been included into the micelles.

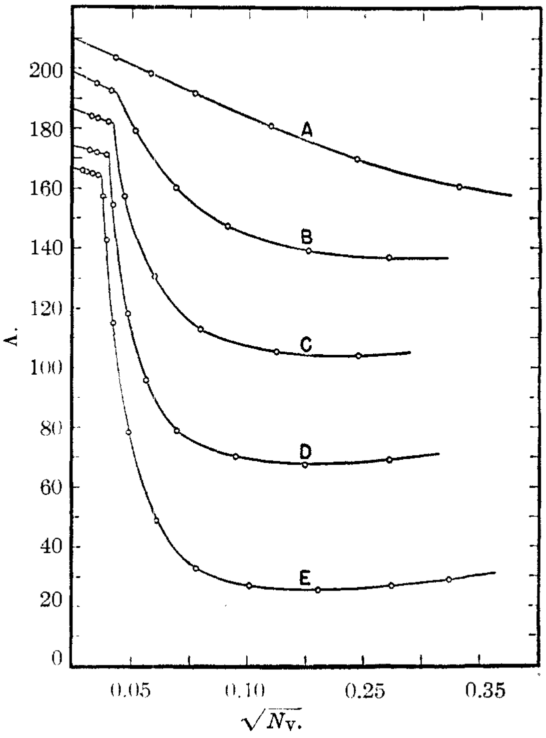

Fig. 2.—Equivalent conductivities of various mixtures of hexyl- and octadecylammonium chlorides in aqueous solution at 60.0°. The curves represent the following: A, pure $C_6H_{13}NH_2\cdot HCl$; B, 75.0 mole % $C_6H_{13}NH_2\cdot HCl$ and 25.0 mole % $C_{18}H_{37}NH_2\cdot HCl$; C, 50.0 mole % $C_6H_{13}NH_2\cdot HCl$ and 50.0 mole % $C_{18}H_{37}NH_2\cdot HCl$; D, 25.0 mole % $C_6H_{13}NH_2\cdot HCl$ and 75.0 mole % $C_{18}H_{37}NH_2\cdot HCl$; E, pure $C_{18}H_{37}NH_2\cdot HCl$.

Figure 2 shows the equivalent conductivities of aqueous solutions of hexylammonium chloride and octadecylammonium chloride and of their mixtures. Although the equivalent conductivities of mixtures of these two electrolytes are intermediate between those of the components, the concentration of octadecylammonium chloride at the critical point is the same for the mixtures as for the pure salt. Since the critical concentration in such systems is a function only of the concentration of the colloidal electrolyte and is independent of that of the non-colloidal electrolyte it is apparent that the latter has not been incorporated into the micelles. The common-ion effect which has been observed in the system sodium dodecylsulfonate–sodium chloride[5] is apparently not pronounced with the salts used in this investigation.

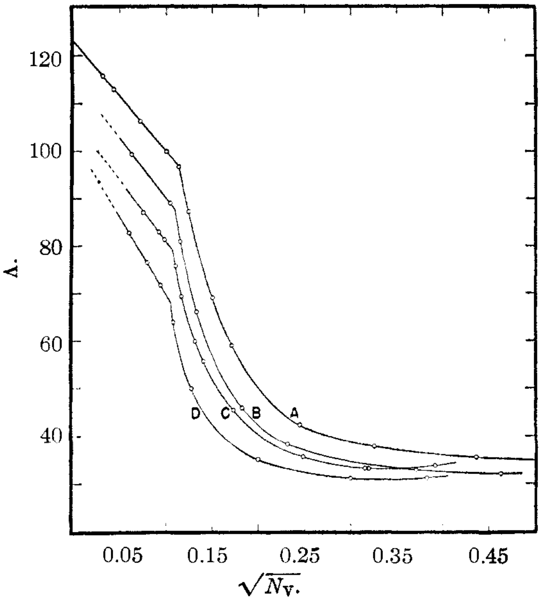

Fig. 3.—The influence of various non-electrolytes upon the equivalent conductivity of dodecylammonium chloride in aqueous solution at 30.0°. The curves represent the following: A, pure $C_{12}H_{25}NH_2\cdot HCl$; B, $C_{12}H_{25}NH_2\cdot HCl$ + 6.7 mole % $C_{11}H_{23}CONHCH_3$; C, $C_{12}H_{25}NH_2\cdot HCl$ + 7.7 mole % $C_{12}H_{26}$, and also $C_{12}H_{25}NH_2\cdot HCl$ + 33.3 mole % $C_{12}H_{26}$; D, $C_{12}H_{25}NH_2\cdot HCl$ + 10 mole % $C_{11}H_{23}CN$, and also $C_{12}H_{25}NH_2\cdot HCl$ + 20 mole % $C_{11}H_{23}CN$.

The influence of non-electrolytes upon the conductivity of aqueous solutions of dodecylammonium chloride is shown in Fig. 3. The concentration values plotted in this figure refer to the molar concentration of the electrolyte. Curve A shows the conductivity of aqueous solutions of dodecylammonium chloride. The addition of 6.7 mole per cent. of methyllauramide, Curve B, materially lowers the conductivity over the entire concentration range. Such an addition also results in a shifting of the critical point toward a lower concentration of electrolyte. The conductivities of two mixtures of dodecylammonium chloride, one containing 7.7 mole per cent. and the other 33.3 mole per cent. of dodecane, are shown in Curve C. The material lowering of the conductivity of the electrolyte and the shifting of the critical point occasioned by the presence of the hydrocarbon is apparent. Since a several-fold increase in the hydrocarbon content of the mixture is without effect upon the conductivity of the electrolyte it follows that the influence of the non-electrolyte is limited by its solubility in the amine salt–water system. Curve D shows the conductivity values obtained for mixtures of dodecylammonium chloride with 10 mole per cent. and 20 mole per cent. of lauronitrile. Lauronitrile materially lowers the conductivity and critical point of aqueous solutions of dodecylammonium chloride, its effect being somewhat greater than that of methyllauramide or dodecane.

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[5] Wright, Abbott, Sivertz and Tartar, THIS JOURNAL, 61, 549 (1939).

The substantial lowering of the conductivity of aqueous solutions of dodecylammonium chloride by the addition of long-chain non-electrolytes indicates that the latter are incorporated into the associated particles formed by the electrolyte. The shift in the critical point toward a lower concentration of electrolyte lends further support to this assumption. The effect of the non-electrolytes upon the conductivity of aqueous solutions of dodecylammonium chloride manifests itself at concentrations much lower than the critical concentration. This supports the contention that associated particles are present in very dilute solutions of this electrolyte.

Summary

The equivalent conductivities of aqueous solutions of mixtures of dodecyl- and octadecylammonium chlorides and of hexyl- and octadecylammonium chlorides have been determined. In the former mixtures the micelles are apparently composed of both components. Although the conductivity values of the latter mixtures are intermediate between those of their components the concentration of octadecylammonium chloride at the critical point is not influenced by the presence of hexylammonium chloride. This indicates that hexylammonium chloride is not included in the micelles.

The presence of long-chain non-electrolytes lowers the conductivity and also the critical concentration of aqueous solutions of dodecylammonium chloride, thus suggesting that such non-electrolytes are included in the micelles.

CHICAGO, ILLINOIS RECEIVED NOVEMBER 25, 1946

The Crystal Structure of Anhydrous Cupric Bromide

BY LINDSAY HELMHOLZ[1]

Introduction

The crystal structure of anhydrous cupric bromide has been determined on part of a program having as its object the correlation of absorption spectra of solids with their structures. The color of this solid resembles that of its solution containing excess bromide ion so closely that a determination of the environment of the metal ion in the solid was undertaken in the hope that this information would aid in the interpretation of both solid and solution spectra. The existence of square coördination about cupric ion has been established in many compounds.[1a–5] It seems likely that the coördination in $CuSO_4{\cdot}5H_2O$ is essentially square covalent also.[6] It was consequently thought of interest to determine whether the preference of bivalent copper for square over tetrahedral coördination would persist if the coordinating ions were larger so that steric interference became important.

It has been found that solid cupric bromide is made up of "strings," with composition $(CuBr_2)_n$ formed by the sharing of edges of the squares of bromine surrounding the copper atoms. The structure is, in this respect, similar to that of palladous chloride[7]; however, a tendency in the case of the copper salt to form fifth and sixth bonds leads to different packing of the "strings." This has the effect of changing the symmetry of the structure from tetragonal (palladous chloride) to monoclinic (cupric bromide).

Experimental

Crystals of cupric bromide were prepared by slow evaporation of a water solution at room temperature. They resembled iodine in luster and color, appearing reddish to brown by transmitted light. The crystals were deposited both as needles and thin plates. Some large crystals were formed but these were found always to be so thoroughly twinned as to be useless for X-ray work and so soft that breaking up the twins without distortion was impossible.

For reasons of convenience the needles were chosen for investigation. Laue photographs were taken in directions normal to the needle axis. Nine out of ten showed twinning of varying degrees of complexity. Three samples, in all cases very small crystals, were found which showed the Laue symmetry C_{2h}, and were apparently untwinned. Series of photographs were taken with *b*- and *c*-axes vertical using a crystal of dimensions 0.03 × 0.015 mm. perpendicular to the needle axis. The Laue photograph showed that the *b*-axis makes an angle of 64° with the needle axis, the $[01\bar{1}]$ direction. This meant that the orientation of the needle with *b* vertical in the X-ray beam was not a favorable one to give an easily calculated absorption correction. The fact that no systematic discrepancies attributable to neglect of absorption are apparent in the agreement between calculated and observed F-values has led me to neglect this effect entirely and to assign rather larger limits of errors to the parameter values than would ordinarily be done.

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(1) Present address: Washington University, St. Louis, Missouri.

(1a) S. B. Hendricks and R. G. Dickinson, THIS JOURNAL, **49**, 2149 (1927); L. Chroback, *Z. Krist.*, **88**, 35 (1935).

(2) G. Tunnel, E. Posnjak and C. J. Ksands, *Z. Krist.*, **90**, 120 (1935).

(3) E. Cr. Cox and K. C. Webster, *J. Chem. Soc.*, 713 (1935).

(4) J. M. Robertson, *ibid.*, 615 (1935).

(5) D. Harker, *Z. Krist.*, **93**, 136 (1936).

(6) C. A. Beevers and G. Lipson, *Proc. Roy. Soc.* (London), **A146**, 570 (1934).

(7) A. F. Wells, *Z. Krist.*, **100**, 189 (1938).