

sured at ten-degree intervals from 25° to 75°.

4. Coefficients of expansion of aqueous solutions of barium chloride and of lanthanum chloride ranging in concentration from 0.06 to 1 molal have been determined at ten-degree intervals from 25° to 55°.

5. The apparent molal expansibilities of potassium chloride, barium chloride and lanthanum chloride in aqueous solutions have been calculated and their significance in relation to Gucker's theoretical equations is discussed.

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Conductivities of Quaternary Ammonium Chlorides Containing Two Long-chain Alkyl Groups

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The concentration of colloidal electrolyte at the critical point for micelle formation has repeatedly been shown to decrease with increase in the chain length of the colloidal electrolyte. That this is true for the cationic colloidal electrolytes has been shown by a comparison of the equivalent conductivities of the alkylammonium chlorides of varying chain length¹ and of several of the alkyltrimethylammonium bromides.² It has recently been observed³ that the position of the critical point is not materially influenced by the substitution of short-chain hydroxyalkyl groups for methyl groups in the higher alkyltrimethylammonium chlorides. The opinion has previously been expressed by Hartley⁴ that the critical concentration is more dependent upon the chain length than upon the nature of the ionized groups. On the other hand, compounds which form two long-chain ions, such as octyltrimethylammonium octanesulfonate⁵ and 1,1-dimethyl-3-hydroxybutylammonium caprylate,⁶ form micelles at much lower concentrations than compounds which yield only one of the single long-chain, component ions. When we consider the long-chain alkyltrimethylammonium chlorides it appears that, although the replacement of methyl groups by other short-chain groups may not decidedly influence the electrical behavior, if a methyl group is replaced by a radical the chain length of which is comparable with that of the original long chain, such a substitution should be attended by a decided change in the conductivity values. We have, therefore, determined the equivalent conductivities of aqueous solutions of dioctyl-, didecyl-, didodecyl-, ditetradecyl-, dihexadecyl- and octyldodecyl-dimethylammonium chlorides and have compared the results with those obtained for several of the higher alkyltrimethylammonium chlorides. The comparisons have shown that significant differences exist between the conductivity behaviors of the higher dialkyldimethylammonium chlorides

and those of the alkyltrimethylammonium chlorides. This comparison suggests that with the former the total number of carbon atoms in the long chains is determinative as regards their conductivity characteristics.

Experimental

Preparation of Dioctyl-, Didecyl-, Didodecyl-, Ditetradecyl- and Dihexadecyldimethylammonium Chlorides.—All the quaternary ammonium chlorides were similarly prepared. The preparation of didodecyldimethylammonium chloride will be described in detail as an example of the procedure employed.

Predistilled dodecylamine was carefully fractionated through a Stedman-packed column. In a two-necked flask fitted with a mercury-sealed stirrer and an air condenser, 212 g. of this distillate (f. p. 28.26°) and 8.5 g. of 50% Raney nickel suspended in dodecylamine were heated with stirring at 200° for two and one-half hours. The resulting product was taken up in ethyl acetate, the Raney nickel removed by filtration, and the didodecylamine crystallized from the solvent.

To 77 g. of the recrystallized didodecylamine dissolved in 200 cc. of ethanol, 49 cc. of 85% formic acid was slowly added, the temperature being maintained at about 40°. After this addition, 46 cc. of a 36% aqueous formaldehyde solution was added and the temperature raised to 60°. After the evolution of carbon dioxide had subsided, the temperature was maintained at the reflux point for one-half hour. The solution was then neutralized with aqueous sodium hydroxide, and the top layer was drawn off, dried over anhydrous potassium carbonate, filtered, and distilled (b. p. 183° at 0.35 mm.). The didodecylmethylamine so obtained (f. p. 10.4°) was dissolved in ethyl acetate, methyl chloride was added, and the mixture was heated in a bomb at 80° for one hour. The didodecyldimethylammonium chloride was recrystallized twice from ethyl acetate to give a white, crystalline, hygroscopic product. Dioctyldimethyl- and didecyldimethylammonium chlorides are extremely hygroscopic. This property was not observed with ditetradecyldimethyl- and dihexadecyldimethylammonium chlorides. The freezing points of the intermediate methylalkylamines are as follows: methyl-dioctyl-, -30.1°; methyl-didecyl-, -7.4°; methyl-ditetradecyl-, 26.0°; and methyl-dihexadecylamine, 36.5-37.5°.

Preparation of Octyldodecyldimethylammonium Chloride.—To 102 g. of dodecyl chloride dissolved in 50 cc. of ethanol was added 38.7 g. of methylamine and the solution was heated in a bomb at 125° for eight hours. The contents of the bomb were neutralized with aqueous sodium hydroxide, the top layer dissolved in Skellysolve F, dried over anhydrous potassium carbonate, filtered, and the methyl-dodecylamine distilled. To 64 g. of distillate was added 56.3 g. of freshly distilled octyl bromide and the mixture was heated at 90° for five hours. One-half of the

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

(2) Scott and Tartar, *ibid.*, **65**, 692 (1942).

(3) Ralston and Eggenberger, *ibid.*, **69**, 2095 (1947).

(4) Hartley, *Kolloid-Z.*, **88**, 22 (1939).

(5) Scott, Tartar and Lingafelter, *THIS JOURNAL*, **65**, 698 (1943).

(6) Gonick, *ibid.*, **68**, 177 (1946).

theoretical amount of aqueous sodium hydroxide required for complete neutralization was added at the end of two and one-half hours and the remainder added slowly during the last two and one-half hours. The top layer was extracted with Skellysolve F, dried over anhydrous potassium carbonate, filtered, and the octyldodecylmethylamine distilled (b. p. 170° at 0.25 mm.). This distillate was converted to the quaternary ammonium chloride by heating with methyl chloride in a bomb at 80° for one hour. The product was recrystallized twice from cold ethyl acetate. Octyldodecyltrimethylammonium chloride is very hygroscopic.

Conductivity Determinations.—Conductivities were determined in the manner and with the equipment previously described.⁷ In order to eliminate errors due to adsorption the cell was brought into equilibrium with the various solutions before the conductance measurements were made.

Results and Discussion

The equivalent conductivities of aqueous solutions of dioctyldimethyl-, didecyldimethyl- and didodecyldimethylammonium chlorides at 30° are shown in Fig. 1. The most significant feature of

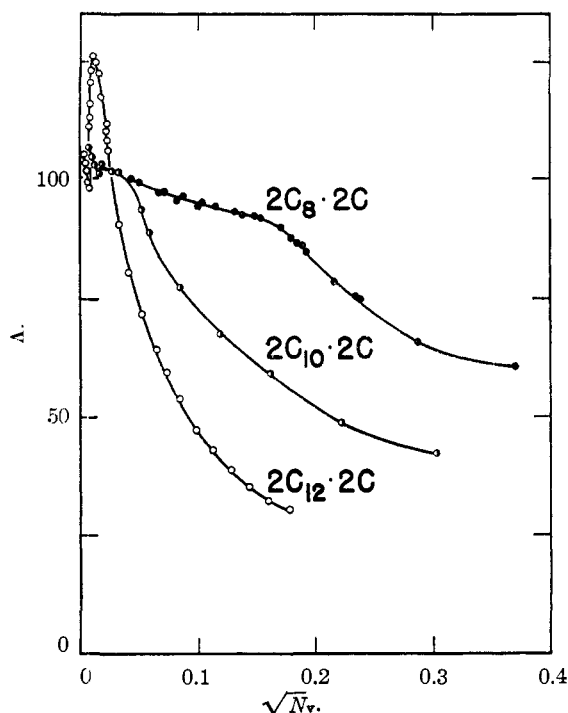


Fig. 1.—Equivalent conductivities of dialkyldimethylammonium chlorides at 30°.

these is the maxima which occur at concentrations between the critical points and infinite dilution. These inflections increase with increasing length of the alkyl chain, and with didodecyldimethylammonium chloride the equivalent conductivity at 0.0001 *N* is materially higher than that at infinite dilution. Similar maxima have been found to occur upon the addition of methanol to aqueous solutions of octadecylpyridinium chloride⁸ and of ethanol to aqueous solutions of dodecylammonium chloride.⁹ The occurrence of a maximum conduc-

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

(8) Evers, Grieger and Kraus, *ibid.*, **68**, 1137 (1946).

(9) Ralston and Hoerr, *ibid.*, **68**, 2460 (1946).

tivity in dilute solutions of colloidal electrolytes was first observed by Hartley and associates,¹⁰ who reported that at dilutions approximating 0.0004 *N* the conductivity of methylene blue is approximately 30% higher than at infinite dilution. A recent communication¹¹ has called attention to the presence of maxima in the conductivity curves of aqueous solutions of hexadecyl- and octadecylpyridinium iodates.

The maxima in the curves shown in Fig. 1 occur at progressively lower concentrations with increase in the number of carbon atoms in the molecule. That the positions of these maxima are a function of the total number of carbon atoms in the two long alkyl chains is shown by a comparison of the equivalent conductivity curves of didecyl- and octyldodecyltrimethylammonium chlorides, Fig. 2, both of which contain twenty carbon atoms in the two long alkyl chains. The close similarity of

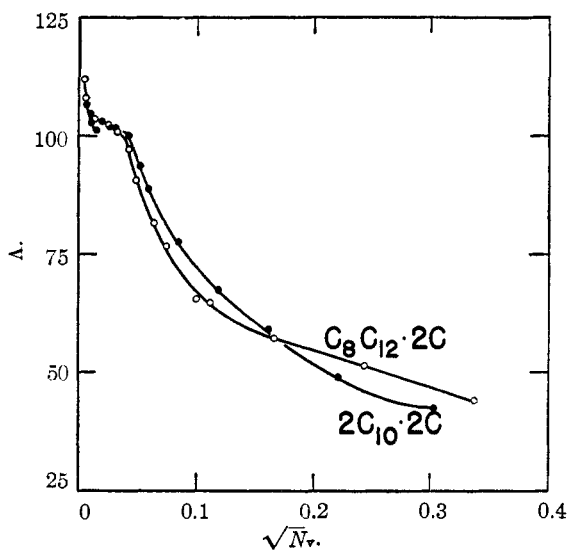


Fig. 2.—Equivalent conductivities of dialkyldimethylammonium chlorides at 30°.

these curves is evident and in contrast to that of didodecyldimethylammonium chloride. Both ditetradecyldimethyl- and dihexadecyldimethylammonium chlorides, Fig. 3, show much larger equivalent conductivities in very dilute solutions than would be anticipated on the basis of their high molecular weights. Since these curves fall very abruptly and since even moderately concentrated solutions of these salts show low values for their equivalent conductivities, we are of the opinion that the high values of the very dilute solutions are evidence of the presence of maxima.

The conductivity behaviors of the above-mentioned compounds are strikingly different from those of the alkyltrimethylammonium chlorides which we have examined. These include do-

(10) Moilliet, Collie, Robinson and Hartley, *Trans. Faraday Soc.*, **31**, 120 (1935).

(11) Brown, Grieger, Evers and Kraus, *THIS JOURNAL*, **69**, 1835 (1947).

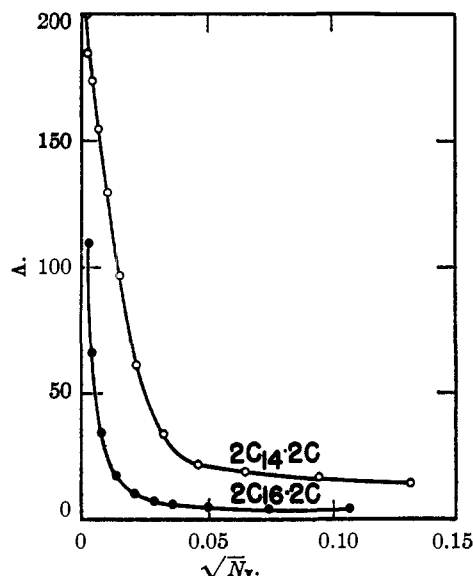


Fig. 3.—Equivalent conductivities of dialkyldimethylammonium chlorides at 30°.

decyl-, tetradecyl-, hexadecyl- and octadecyltrimethylammonium chlorides. Figure 4 shows a comparison of the equivalent conductivity of dodecyltrimethylammonium chloride with that of didodecyltrimethylammonium chloride and also of hexadecyltrimethylammonium chloride with dioctyltrimethylammonium chloride. The latter comparison shows that the critical point occurs at a much lower concentration when the carbon atoms are in a single chain, although the curve for the dioctyltrimethylammonium chloride shows evidence of a maximum which is not apparent with hexadecyltrimethylammonium chloride. None of the alkyltrimethylammonium chlorides which we have investigated has exhibited a maximum in its equivalent conductivity.

It has formerly been customary to consider the equivalent conductivity curves of colloidal electrolytes to be characterized by three ranges. In the first range the conductivity falls linearly with concentration, in the second range an abrupt drop is encountered, and in the third range the values either remain essentially constant or exhibit a slight rise. All workers are in agreement that this characteristic behavior of colloidal electrolytes is occasioned by the formation of associated particles; however, diverse opinions have been expressed as to the nature of these particles and the concentration at which they first appear. McBain¹² has held that associated ions are present in very dilute solutions, well within the first range, although Hartley⁴ has stated that below the critical point for micelle formation the colloidal electrolyte functions as an ordinary strong electrolyte. The occurrence of maxima in the conductivity

(12) McBain, *Nature*, **145**, 702 (1940).

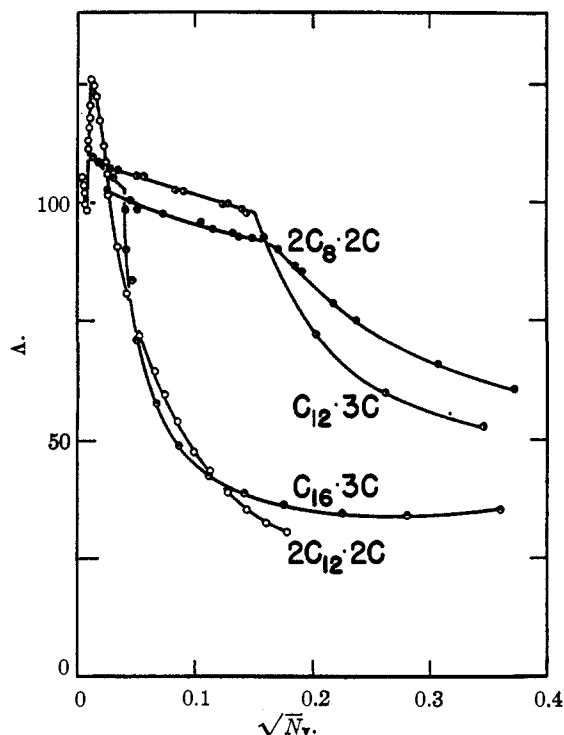


Fig. 4.—Comparison of equivalent conductivities of alkyltrimethylammonium chlorides at 30°.

curves of the higher dialkyl quaternary ammonium chlorides indicates that association into ionic aggregates occurs at low concentrations followed by the formation of less-conducting micelles. This phenomenon can be attributed to the incorporation of undissociated molecules into the ionic aggregates. Since the present study has been confined to a limited number of compounds of a specific type we are not justified in drawing extensive conclusions. High hydrocarbon loading of the molecule apparently favors the formation of maxima, and a number of unpublished observations on long-chain cationic electrolytes lead us to believe that this phenomenon is frequently encountered.

Summary

The equivalent conductivities of dioctyl-, didodecyl-, ditetradecyl-, dihexadecyl- and octyldodecyltrimethylammonium chlorides have been determined. Didodecyltrimethylammonium chloride shows a maximum value at concentrations below the critical point and evidences of maxima are also present with both its lower and its higher homologs.

The conductivity behavior of the dialkyldimethylammonium chlorides has been compared with that of several alkyltrimethylammonium chlorides.