evident that the results fall off in accuracy for values above about 15,000, because the computation then involves a very small difference between the two terms in the denominator of eqn. (4).

TABLE III

DETERMINATION OF MOLECULAR WEIGHTS OF POLYDIMETHYLSILOXANES BY THE SOUND VELOCITY METHOD

$$M = \frac{48.10d}{v^{1/3} - 40.855\left(\frac{n^2 - 1}{n^2 + 2}\right)}$$

| Fluid | Theoretical molecular weight | Found molecular weight | Deviation, % |
|---|---|---|---|
| 0.65 cs. | 162.2 | 141.0 | −13.1 |
| 1.0 | 236.3 | 233.7 | − 1.1 |
| 1.5 | 310.4 | 316.9 | + 2.1 |
| 2.0 | 384.5 | 371.6 | − 3.3 |
| 3.0 | 520 | 554 | + 6.5 |
| 5.0 | 720 | 753 | + 4.6 |
| 10 | 1,160 | 1,208 | + 4.1 |
| 20 | 1,970 | 1,971 | + 0.1 |
| 50 | 3,900 | 4,170 | + 6.9 |
| 100 | 7,100 | 7,680 | + 8.2 |
| 200 | 11,200 | 11,560 | + 3.2 |
| 350 | 15,800 | 15,440 | − 2.3 |
| 500 | 19,000 | 23,100 | +21.5 |
| 1000 | 26,500 | 23,200 | −12.5 |

In a paper that came to attention after this work was completed, Warrick[14] has shown how similar results may be obtained from refractive index and density data alone.

**Molar Sound Velocity Increments.**—Just as in the familiar case of molar refraction, the molar sound velocity $R = v^{1/3}M/d$ of a compound may be calculated by summing the increments[15] for each atom in the molecule, or alternatively for each bond in the molecule. No velocity increment involving silicon has previously been reported. Using the present data on the first four polymers and a value of 95.2 for the C–H bond, the bond increment for silicon–carbon is here determined as 35.4, and that for silicon–oxygen as 61.5. These figures give truly additive molar sound velocities, in which the deviations from experimental values are only a few tenths of a per cent.

Attempts to calculate an atomic increment for silicon gave values of 129, 122, 120 and 117, respectively, for the first four liquids. A corresponding lack of constancy in the atomic *refraction* increments for silicon in these same compounds has been reported[14]; it was necessary to use *bond* refraction increments, again, in order to attain an additive system. This situation was tentatively attributed to wide variations in the ionic character of the bonds in organosilicon compounds.

**Acknowledgment.**—The assistance of Patricia E. Mortell in the measurements of sound velocity is hereby gratefully acknowledged.

## Summary

The variation of sound velocity with molecular weight has been studied in a series of 14 polydimethylsiloxanes, at 30 and 50.7°. These fluids were found to possess remarkably high compressibilities.

Bond increments for the molar sound velocity have been determined for the silicon–carbon and silicon–oxygen bonds.

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[14] Warrick, THIS JOURNAL, **68**, 2455 (1946).

[15] Lagemann and Dunbar, *J. Phys. Chem.*, **49**, 428 (1945).

WASHINGTON, D. C. RECEIVED JULY 2, 1948

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[CONTRIBUTION FROM THE METCALF RESEARCH LABORATORY OF BROWN UNIVERSITY]

# Properties of Electrolytic Solutions. XXXVI. Effect of Addition Agents on the Conductance of Long Chain Salts[1]

BY GEORGE L. BROWN,[2] PHILIP F. GRIEGER[3] AND CHARLES A. KRAUS

## I. Introduction

In previous papers of this series, it has been shown that the addition of methanol to aqueous solutions of long chain salts has marked effect on their properties in the critical region and at higher concentrations.[4]

The present study was undertaken for the purpose of determining the effect of additives in somewhat greater detail in order to ascertain the generality of the phenomena and some of the underlying factors that influence observed results. The present, like the several preceding investigations, has been exploratory in nature. A high precision is not claimed for the results; nevertheless, it is believed that, in the critical region, they are not seriously in error. Precision measurements in the dilute region are now under way in this Laboratory, and the results will be communicated in due course.

The effect of additions of methanol, isopropyl alcohol and *t*-butanol on the conductance of dodecylammonium chloride in water was measured at several concentrations of the additives.

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[1] This paper is based on a portion of a thesis presented by G. L. Brown in partial fulfillment of the requirements for the degree of Doctor of Philosophy in the Graduate School of Brown University, October, 1947.

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[3] Lalor Foundation Fellow, Brown University, 1947–1948. Present address: Department of Chemistry, University of Illinois, Urbana, Illinois.

[4] Evers and Kraus, THIS JOURNAL, **70**, 3049 (1948); Grieger and Kraus, *ibid.*, **70**, 3803 (1948); see also Ward, *J. Chem. Soc.*, I, 522 (1939); *Proc. Roy. Soc.* (*London*), **176A**, 412 (1940).

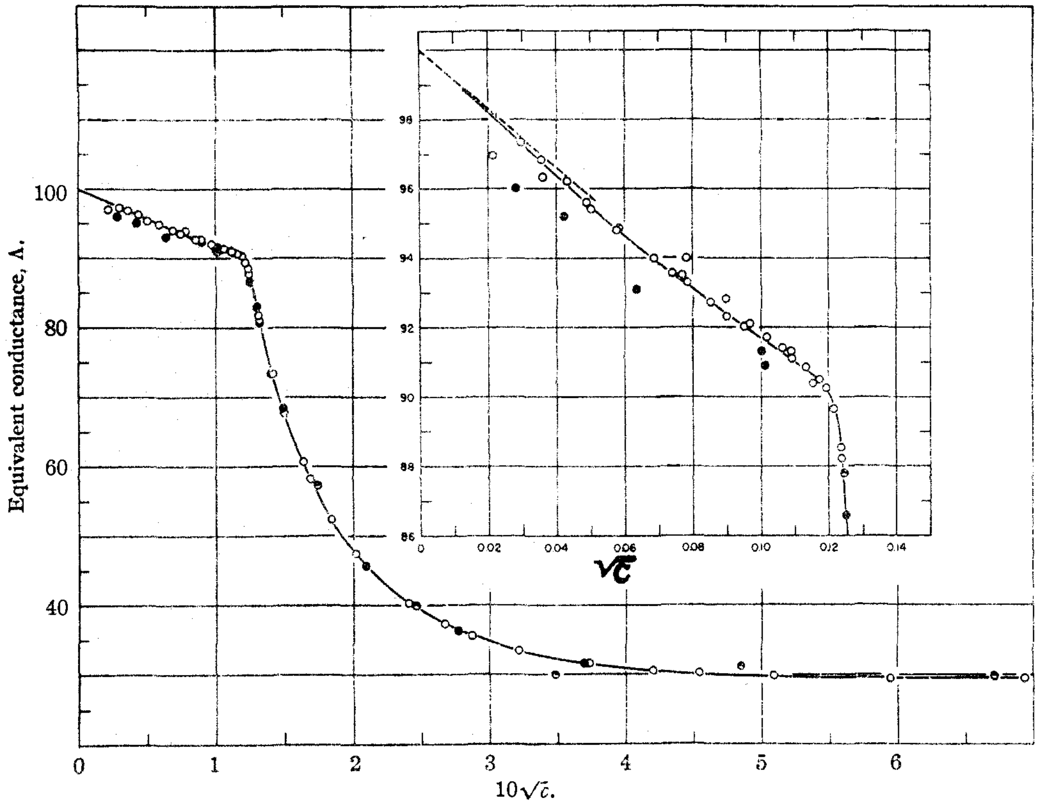

Fig. 1.—Dodecylammonium chloride in water at 25°: ○, this investigation; ●, Ralston and Eggenberger; ◓, Ralston, Hoerr and Hoffman. Dotted line on insert has theoretical slope.

More interesting, perhaps, are the results upon addition of methanol and tertiary butanol to solutions of octadecylpyridonium iodate and hexadecylpyridonium iodate; each of these two salts exhibits a maximum in pure water.[5]

Measurements were also carried out with dodecylammonium chloride in a 24.65% methanol–water mixture to which were added varying proportions of dodecanol: from 0.044 to 0.651 mole of dodecanol per mole of salt. The reason for carrying out the measurements in a methanol–water mixture was to increase the solubility of dodecanol.

The conductance of aqueous solutions of the hydrochlorides of two diamines having ten carbon atoms connecting the ammonium groups was measured for the purpose of determining whether or not they exhibit the usual properties of long chain salts.

## II. Experimental

1. **Apparatus and Procedure.**—These were substantially the same as those described in earlier papers of this series.[4] All measurements were carried out at 25 ± 0.01°.

2. **Solvents.**—Freshly distilled water was employed having a specific conductance of $1 \times 10^{-6}$ mho, or lower.

Methanol, after standing over lime, was decanted onto activated alumina pellets and, after refluxing, was distilled in a packed column. Middle and later fractions, excepting the last, had a conductance varying from $1 \times 10^{-7}$ to $0.3 \times 10^{-7}$.

Isopropyl alcohol, commercial Petrohol, was treated after the manner of methanol. Solvent having a specific conductance of $4 \times 10^{-9}$ was readily obtained. The density at 25° was found to be 0.7856 as against 0.7805 as given in the literature.[6] This may indicate the presence of some higher alcohols as impurities. For the purpose in hand, these could have little effect on the results obtained.

*t*-Butanol was purified by distillation. Its refractive index, $n^{25}_D$, was found to be 1.3865.

Dodecanol was used as supplied by the dealer, without purification; it had a negligible specific conductance.

3. **Salts: Dodecylammonium Chloride.**—Hydrogen chloride was passed through a solution of the amine (purified by distillation, m. p., 27.9–28.2°) in diethyl cellosolve. The product, after filtration, was twice recrystallized from diethylcellosolve. It was finally recrystallized from absolute ethanol and washed with acetone; m. p. (sealed tube) 182.3°; chlorine: found, 15.95 ± 0.02; theory, 15.985%.

Hexadecylpyridonium iodate was prepared by metathesis of the iodide with freshly prepared silver iodate in ethanol. After filtration, the salt was precipitated by addition of acetone and recrystallized four times from an acetone–ethanol mixture; iodate: found, 36.6 and 37.2%; calcd., 36.5%. Difficulty was experienced in the analyses due to absorption of iodine by the hexadecylpyridonium iodide which precipitated upon addition of potassium iodide.

Octadecylpyridonium iodate was prepared like the corresponding hexadecyl compound; iodate: found, 34.31 and 34.68%; calcd., 34.49%.

1-N-Morpholino-10-N′-piperidinodecane dihydrochloride and di-*n*-propylamino-10-N-piperidinodecane dihydrochloride were made from the corresponding amines which were kindly furnished by Dr. N. J. Leonard, of the Univer-

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[5] Brown, Grieger, Evers and Kraus, This Journal, **69**, 1835 (1947).

[6] Brunel, *ibid.*, **45**, 1334 (1923).

sity of Illinois. Preparation and analysis of the amines are described by Price, Guthrie, Herbrandson and Peel.[7] Analyses of the salts are as follows: morpholino salt, chlorine: found, 18.55%; calcd., 18.50%; dipropyl salt, chlorine: found, 17.85%; calcd., 17.85%.

## III. Results

The results of measurements with dodecylammonium chloride in water and mixtures containing varying amounts of tertiary butanol, isopropyl alcohol and methanol, respectively, are presented in Table I. The square root of concentration, in moles per liter of solution, appears in the first column and the corresponding value of the equivalent conductance in the second column. Results are shown graphically in Figs. 1, 2 and 3.

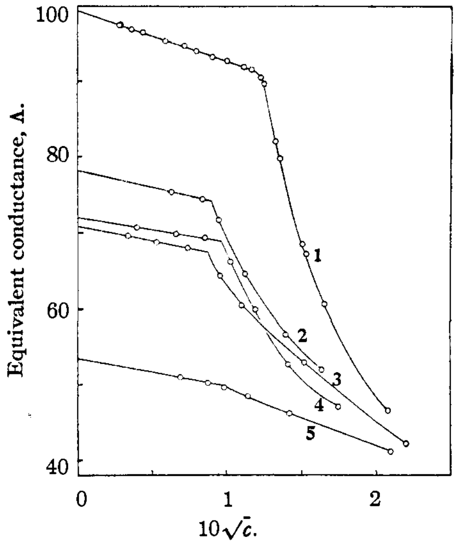

Fig. 2.—Dodecylammonium chloride in alcohol-water mixtures at 25°: (1) water, (2) 5.66% *t*-butanol, (3) 7.88% *t*-butanol, (4) 8.00% isopropanol, (5) 16.19% isopropanol.

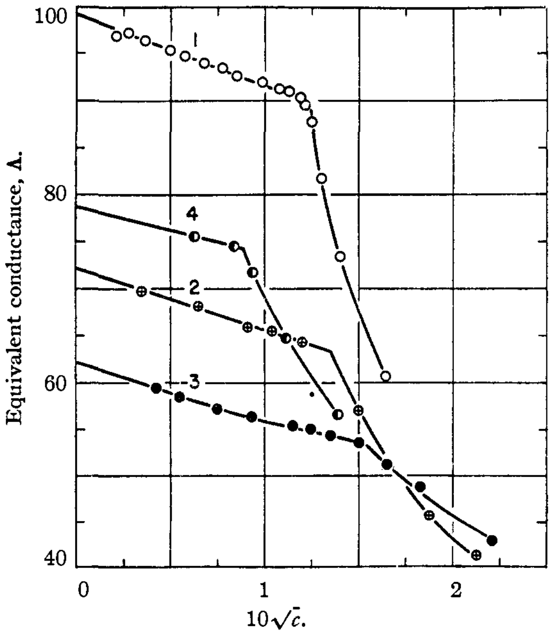

Fig. 3.—Dodecylammonium chloride in methanol-water mixtures at 25°: methanol, %: (1) 0.0, (2) 16.19, (3) 24.65; butanol, %, (4) 5.66.

The results for octadecylpyridonium iodate in pure water and in the presence of methanol and *t*-butanol, and for hexadecylpyridonium iodate in water and in the presence of *t*-butanol, are similarly given in Table II. The results are shown graphically in Fig. 4.

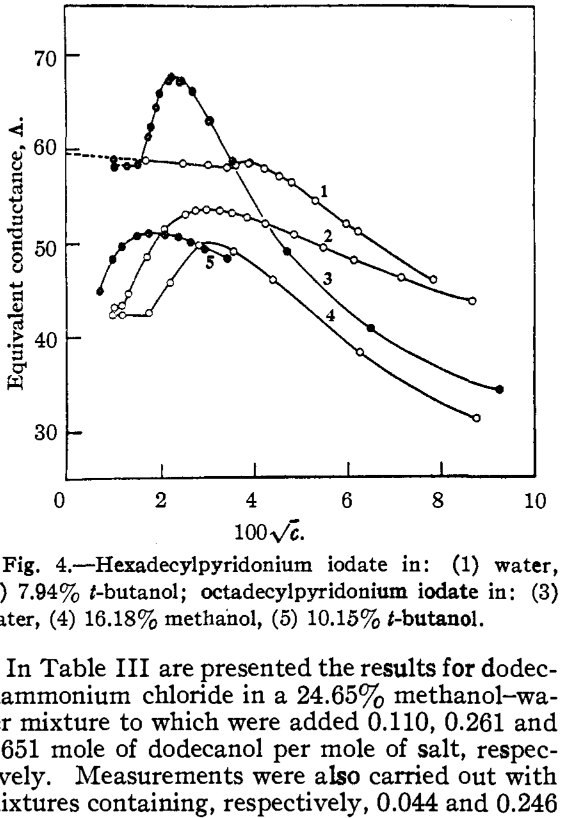

Fig. 4.—Hexadecylpyridonium iodate in: (1) water, (2) 7.94% *t*-butanol; octadecylpyridonium iodate in: (3) water, (4) 16.18% methanol, (5) 10.15% *t*-butanol.

In Table III are presented the results for dodecylammonium chloride in a 24.65% methanol-water mixture to which were added 0.110, 0.261 and 0.651 mole of dodecanol per mole of salt, respectively. Measurements were also carried out with mixtures containing, respectively, 0.044 and 0.246 mole of dodecanol per mole of salt. These values are shown in Fig. 5 along with those for which numerical data are given in the table.

The results for the diammonium salts are shown graphically in Fig. 6.

Except in the case of solutions of dodecylammonium chloride and the diammonium salts in water, solution densities were taken equal to solvent densities. The densities of aqueous solutions of dodecylammonium chloride at 25° were computed from the equation of Ralston and Hoerr.[8]

Values of the specific conductance, $\kappa_0$, the density, *d*, and the dielectric constant, *D*, for the solvent mixture are given at the head of each table. The composition of the solvent mixtures is given in weight per cent. of additive.

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[7] Price, Guthrie, Herbrandson and Peel, *J. Org. Chem.*, **11**, 281 (1946).

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

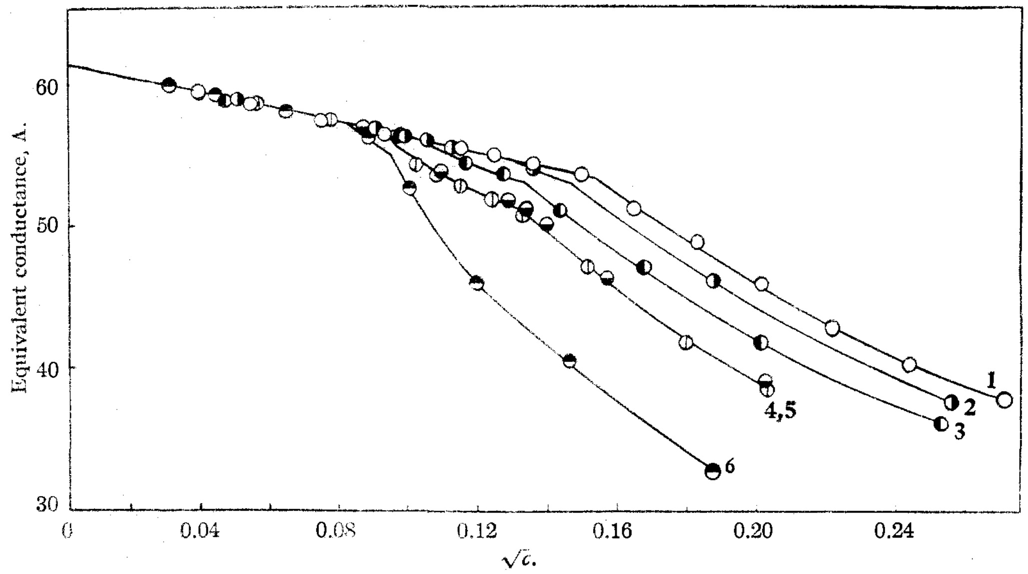

Fig. 5.—Dodecylammonium chloride in 24.65% methanol on addition of following moles of dodecanol per mole salt: (1) 0.0, (2) 0.044, (3) 0.111, (4) 0.246, (5) 0.261, (6) 0.651.

## IV. Discussion

**1. Conductance of Dodecylammonium Chloride in Water at 25°.**—In Fig. 1, the equivalent conductance of dodecylammonium chloride is plotted as a function of the square root of concentration. The results of Ralston and his coworkers are also shown for comparison. As may be seen from inspection of the figure, our results are in excellent agreement with those of Ralston and Eggenberger[9] at concentrations higher than the critical and are in fair agreement at lower concentrations. Our results are also in fair agreement with those of Ralston, Hoerr and Hoffman[10] at concentrations greater than critical.

The results of the present investigations are not sufficiently precise to establish definitely the form of the conductance curve below the break-point. For example, the solvent correction is about 1 and 10% at concentrations of $10^{-3}$ and $10^{-4}$, respectively. They indicate, however, that $\Lambda$ is not a linear function of $\sqrt{c}$ up to the break-point, since an upward curvature is noticeable. Below $3 \times 10^{-3}$, the curve approximates the Onsager slope (*viz.*, 83) within the experimental error.

TABLE I

CONDUCTANCE OF DODECYLAMMONIUM CHLORIDE IN WATER AND IN MIXTURES WITH TERTIARY BUTANOL, ISOPROPANOL AND METHANOL AT 25°

| $10\sqrt{c}$ | Λ | $10\sqrt{c}$ | Λ | $10\sqrt{c}$ | Λ | $10\sqrt{c}$ | Λ | $10\sqrt{c}$ | Λ | $10\sqrt{c}$ | Λ | $10\sqrt{c}$ | Λ |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Water | | 5.66% *t*-Butanol | | 7.88% *t*-Butanol | | 8.00% Isopropyl alcohol | | 16.19% Isopropyl alcohol | | 16.19% Methanol | | 24.65% Methanol | |
| $\eta_0 = 1.0$ to $1.3 \times 10^{-6}$ | | $\kappa_0 = 0.69 \times 10^{-6}$, $d = 0.9881$, $D = 73.8$ | | $\kappa_0 = 0.70 \times 10^{-6}$, $d = 0.9845$, $D = 72.0$ | | $\kappa_0 = 0.80 \times 10^{-6}$, $d = 0.9837$, $D = 72.8$ | | $\kappa_0 = 0.57 \times 10^{-6}$, $d = 0.9724$, $D = 66.8$ | | $\kappa_0 = 0.62 \times 10^{-6}$, $d = 0.9703$, $D = 71.6$ | | $\kappa_0 = 0.50 \times 10^{-6}$, $d = 0.9568$, $D = 68.0$ | |
| 0.4317 | 96.22 | 6.243 | 75.56 | 3.365 | 69.09 | 3.952 | 70.84 | 6.896 | 51.08 | 3.723 | 69.70 | 4.002 | 59.44 |
| .4951 | 95.40 | 8.333 | 74.61 | 5.228 | 68.16 | 6.539 | 70.03 | 8.729 | 50.36 | 6.272 | 68.50 | 5.504 | 58.53 |
| .6846 | 94.01 | 9.403 | 71.82 | 7.345 | 67.56 | 8.409 | 69.46 | 9.785 | 49.73 | 9.121 | 65.98 | 7.500 | 57.28 |
| .9004 | 92.32 | 11.13 | 64.75 | 9.110 | 63.89 | 10.19 | 66.39 | 11.35 | 48.55 | 10.37 | 65.50 | 9.334 | 56.38 |
| 1.193 | 90.25 | 13.90 | 56.61 | 10.89 | 59.92 | 11.81 | 60.04 | 14.15 | 46.24 | 12.02 | 64.35 | 11.52 | 55.38 |
| 1.215 | 89.46 | 16.30 | 52.01 | 15.12 | 52.45 | 14.07 | 52.68 | 20.90 | 41.19 | 14.99 | 57.00 | 12.45 | 54.99 |
| 1.312 | 81.80 | | | 21.97 | 46.00 | 17.38 | 47.23 | | | 18.75 | 45.72 | 13.59 | 54.21 |
| 1.635 | 60.68 | | | 32.33 | 41.74 | | | | | 21.25 | 41.24 | 14.95 | 53.61 |
| 2.018 | 47.46 | | | | | | | | | 25.37 | 36.13 | 16.48 | 51.20 |
| 3.217 | 33.57 | | | | | | | | | | | 18.28 | 48.88 |
| 4.205 | 30.74 | | | | | | | | | | | 20.10 | 45.92 |
| 6.938 | 29.46 | | | | | | | | | | | 22.15 | 42.84 |
| | | | | | | | | | | | | 27.14 | 37.81 |

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[9] Ralston and Eggenberger, THIS JOURNAL, **70**, 436 (1948).

[10] Ralston, Hoerr and Hoffman, *ibid.*, **64**, 97 (1942).

TABLE II

CONDUCTANCE OF HEXADECYLPYRIDONIUM IODATE AND OCTADECYLPYRIDONIUM IODATE IN WATER AND WATER–ALCOHOL MIXTURES AT 25°

| Hexadecylpyridonium iodate in water | | Hexadecylpyridonium iodate in 7.94% *t*-butanol | | Octadecylpyridonium iodate in water | | Octadecylpyridonium iodate in 16.18% methanol | | Octadecylpyridonium iodate in 10.15% *t*-butanol[11] | |
|---|---|---|---|---|---|---|---|---|---|
| $10^2\sqrt{c}$ | $\Lambda$ | $10^2\sqrt{c}$ | $\Lambda$ | $10^2\sqrt{c}$ | $\Lambda$ | $10^2\sqrt{c}$ | $\Lambda$ | $10^2\sqrt{c}$ | $\Lambda$ |
| $\kappa_0 = 1.04 \times 10^{-6}$ | | $\kappa_0 = 0.64 \times 10^{-6}$, $d = 0.9844$, $D = 71.9$ | | $\kappa_0 = 1.01 \times 10^{-6}$ | | $\kappa_0 = 0.60 \times 10^{-6}$, $d = 0.9700$, $D = 71.8$ | | $\kappa_0 = 0.70 \times 10^{-6}$, $d = 0.9815$, $D = 69.8$ | |
| 1.457 | 58.76 | 1.001 | 43.27 | 1.054 | 58.13 | 0.9834 | 42.45 | 0.6977 | 45.0 |
| 1.700 | 58.78 | 1.163 | 43.43 | 1.287 | 59.06 | 1.182 | 42.40 | 0.9777 | 48.4 |
| 2.512 | 58.44 | 1.342 | 44.70 | 1.347 | 58.21 | 1.747 | 42.59 | 1.513 | 50.8 |
| 3.037 | 58.30 | 1.693 | 48.27 | 1.809 | 62.37 | 2.216 | 45.80 | 1.764 | 51.08 |
| 3.452 | 58.00 | 1.716 | 48.62 | 2.008 | 65.87 | 2.841 | 49.77 | 2.134 | 50.94 |
| 3.639 | 58.25 | 2.096 | 51.51 | 2.275 | 67.62 | 3.583 | 49.11 | 2.663 | 50.10 |
| 3.917 | 58.43 | 2.551 | 53.11 | 2.480 | 67.27 | 4.412 | 46.06 | 3.437 | 48.39 |
| 3.952 | 58.59 | 2.773 | 53.48 | 2.707 | 66.09 | 6.272 | 38.29 | | |
| 4.251 | 57.87 | 2.986 | 53.58 | 3.081 | 63.04 | 8.767 | 31.26 | | |
| 4.570 | 57.08 | 3.276 | 53.49 | 3.578 | 58.68 | | | | |
| 4.825 | 56.40 | 3.537 | 53.22 | 4.719 | 49.11 | | | | |
| 5.338 | 54.45 | 3.868 | 52.77 | 6.505 | 40.85 | | | | |
| 6.252 | 51.15 | 4.262 | 52.12 | 9.261 | 34.33 | | | | |
| 7.851 | 45.97 | 4.867 | 50.97 | | | | | | |
| 9.140 | 42.80 | 5.522 | 49.56 | | | | | | |
| 14.16 | 35.75 | 6.149 | 48.21 | | | | | | |
| | | 7.169 | 46.29 | | | | | | |
| | | 8.687 | 43.77 | | | | | | |

TABLE III

CONDUCTANCE OF DODECYLAMMONIUM CHLORIDE IN 24.65% METHANOL WITH DODECANOL ADDED AT 25°

| 0.110 Mole dodecanol per mole salt | | 0.261 Mole dodecanol per mole salt | | 0.651 Mole dodecanol per mole salt | |
|---|---|---|---|---|---|
| $10^2\sqrt{c}$ | $\Lambda$ | $10^2\sqrt{c}$ | $\Lambda$ | $10^2\sqrt{c}$ | $\Lambda$ |
| $\kappa_0 = 0.62 \times 10^{-6}$ | | $\kappa_0 = 0.77 \times 10^{-6}$ | | $\kappa_0 = 0.77 \times 10^{-6}$ | |
| 4.781 | 58.70 | 3.170 | 59.74 | 4.291 | 59.20 |
| 9.797 | 56.28 | 5.629 | 58.58 | 6.495 | 57.97 |
| 11.66 | 54.37 | 7.770 | 57.35 | 8.885 | 56.14 |
| 12.72 | 53.58 | 10.22 | 54.19 | 10.06 | 52.60 |
| 14.34 | 51.02 | 10.81 | 53.51 | 11.92 | 45.92 |
| 16.76 | 47.06 | 11.48 | 52.76 | 14.60 | 40.48 |
| 20.12 | 41.76 | 12.37 | 51.79 | 18.75 | 32.74 |
| 25.28 | 36.17 | 13.27 | 50.66 | | |
| | | 15.11 | 47.03 | | |
| | | 17.94 | 41.76 | | |
| | | 20.29 | 38.49 | | |

The critical concentration lies between 1.42 and 1.44 × $10^{-2}$. Ralston, Hoerr and Hoffman[11] give 1.30 × $10^{-2}$. Corrin and Harkins,[12] using the indicator method, found values ranging between 1.24 and 1.36 × $10^{-2}$, depending upon the dye used.

**2. Effect of Alcohols on Dodecylammonium Chloride in Aqueous Solution.**—As appears from the earlier work of Evers[4] and of Grieger,[4] the hexadecyl and octadecyl quaternary ammonium salts, as used by them, show a marked shift of the breakpoint toward higher concentrations on addition of methanol. The same is true of solutions of dodecylammonium chloride as appears from Fig. 3. Whether or not there is an initial recession of the break point concentration on addition of small amounts of methanol is uncertain, but it may be inferred that, if it occurs at all, it is very small.

The effect of different alcohols on the breakpoint concentration of dodecylammonium chloride is of interest. The effect is shown graphically in Figs. 2 and 3 and the values are given in Table IV.

TABLE IV

EFFECT OF ALCOHOLS ON BREAKPOINT CONCENTRATION, $C_b$, OF DODECYLAMMONIUM CHLORIDE IN WATER

| Alcohol | % Alcohol | $C_b \times 10^2$ |
|---|---|---|
| ...... | 0.0 | 1.4 |
| Methanol | 16.2 | 3.1 |
| Methanol | 24.7 | 5.2 |
| Isopropyl | 8.0 | 0.92 |
| Isopropyl | 16.2 | 1.04 |
| *t*-Butanol | 5.7 | 0.79 |
| *t*-Butanol | 7.9 | 0.74 |

It will be noted that for dodecylammonium chloride, as for quaternary hexadecyl and octadecyl compounds, the addition of methanol causes an increase in the breakpoint concentration. Isopropyl alcohol, on the other hand, causes a marked decrease of the critical concentration. Thus, 16% of methanol raises the breakpoint from 1.4 × $10^{-2}$ to 3.1 × $10^{-2}$, while 16% of isopropyl lowers it to 1.04 × $10^{-2}$. The decrement, in the case of *t*-butanol, is even greater the breakpoint falling to 0.74 × $10^{-2}$ for 8% of this alcohol as against 0.92 × $10^{-2}$ for 8% of isopropyl alcohol.

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(11) Measurements by P. F. Grieger.

(12) Corrin and Harkins, THIS JOURNAL, **69**, 683 (1947).

The breakpoint concentration passes through a minimum on addition of isopropyl alcohol but in the case of *t*-butanol, the concentration is still decreasing as far as the highest content of alcohol measured. Ralston and Hoerr[13] have determined the effect of ethanol on the breakpoint of dodecylammonium chloride. They found little change on initial addition and a marked shift toward higher concentration for larger additions.

It is, thus, evident that the effect of an added alcohol on the breakpoint concentration is markedly dependent on the number of carbon atoms in the alcohol.

**3. Hexadecyl- and Octadecylpyridonium Iodate.**—These two salts are remarkable in that both exhibit a maximum in their conductance curves in pure water.[14] The results are shown graphically in Fig. 4, curves 1 and 3. In curves 2, 4 and 5 are shown the results obtained on adding tertiary butanol and methanol.

For convenience in discussion, numerical values are given in Table V for some of the variables that characterize the curves of Fig. 4. The concentration at which the curve begins to rise above the straight line in dilute solution is termed the "risepoint."

TABLE V

CHARACTERISTIC VALUES FOR CURVES OF FIGURE 4

| Solvent mixture | $\Lambda$ Risepoint | $\Lambda$ Max. | Rise, % | $c \times 10^4$ Risepoint | $c \times 10^4$ Max. |
|---|---|---|---|---|---|
| Hexadecylpyridonium Iodate | | | | | |
| Water | 58.0 | 58.6 | 1 | 9.9 | 16 |
| 7.9% Butanol | 43.3 | 53.5 | 24 | 1.35 | 9 |
| Octadecylpyridonium Iodate | | | | | |
| Water | 57.8 | 67.6 | 17 | 0.9 | 5 |
| 16.2% Methanol | 42.6 | 49.8 | 16 | 2.9 | 8 |

These two salts are of particular interest in that they enable us to study the effect of various factors on the maximum phenomenon in water. The addition of two carbon atoms to the hexadecyl chain decreases the risepoint concentration to one-tenth that of the hexadecyl compound. The rise at the maximum is increased from 1 to 17% and the concentration of the maximum is reduced in the ratio of 3 to 1. It is apparent that the maximum phenomenon is very sensitive to the length of the hydrocarbon chain.

On addition of 16% methanol to the solution of the octadecyl compound, no great change occurs; the conductance increase at the maximum is not appreciably altered, the risepoint and the maximum are shifted toward higher concentrations. In 10% *t*-butanol, the risepoint concentration could not be determined but it appears from curve 5 that it is not far from $0.5 \times 10^{-4}$. The value of $\Lambda$ at the maximum is 51 and the limiting conductance of octadecylpyridonium iodate, based on the conductance of this salt in water and potassium iodate in water and in the butanol-water mixture[15] is 40. Thus, the height of the maximum in water and in the 10% *t*-butanol mixtures is approximately the same. Although the measurements were carried to a concentration of only $10^{-3}$, it is evident that the bow of the maximum is much broader in 10% *t*-butanol than in water.

On addition of *t*-butanol to a solution of the hexadecyl compound, the conductance curve is greatly altered. The increase of $\kappa$ at the maximum rises from 1 to 24% and the bow of the maximum is widened toward both lower and higher concentrations. The risepoint is shifted to lower concentration in the ratio of 7 to 1 and the maximum is shifted in the same direction in the ratio of 2 to 1.

**4. Dodecylammonium Chloride on Addition of Dodecanol.**—Measurements were carried out with five different proportions of dodecanol to salt in a 25.64% methanol-water mixture; the results for three of them are presented in Table III, while all are shown graphically in Fig. 5. Two series were carried out for nearly the same proportion of alcohol to salt; the results are in good agreement as may be seen from curves 4 and 5 of the figure.

With increasing proportion of dodecanol, the breakpoint recedes to lower concentration. Breakpoint values are presented in Table VI.

TABLE VI

BREAKPOINT CONCENTRATIONS FOR DODECYLAMMONIUM CHLORIDE ON ADDITION OF DODECANOL IN 25.64% METHANOL-WATER MIXTURE

| | | | | | |
|---|---|---|---|---|---|
| Moles dodecanol per mole salt | 0.0 | 0.044 | 0.111 | 0.261 | 0.651 |
| Breakpoint concn. $\times 10^2$ | 2.37 | 1.69 | 1.08 | 0.83 | 0.69 |

The breakpoint concentration is markedly lowered (to $^1/_3$) on addition of 0.651 mole of dodecanol per mole of salt. More significant, perhaps, is the fact that at concentrations below the breakpoint, the conductance values are the same as in the pure solvent mixture, regardless of the proportion of dodecanol. This indicates that below the breakpoint, the salt behaves like a normal electrolyte and is unaffected by the dodecanol. This result is at variance with those obtained by Ralston and Hoerr[16] for dodecylammonium chloride in aqueous solutions on addition of methyllauramide, dodecane and lauronitrile. These authors found only a slight depression in the breakpoint concentration on making the additions, while they found the conductance to be strongly (and rather uniformly) depressed at all salt concentrations, even below the breakpoint. For a given addition agent, the conductance was found to be independent of the amount of non-electrolyte added.

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[13] Ralston and Hoerr, THIS JOURNAL, **68**, 2460 (1946).

[14] Recently, Ralston, Eggenberger and Du Brow, *ibid.*, **70**, 977 (1948), found that the equivalent conductance of didodecyldimethylammonium chloride in water passes through a maximum in the neighborhood of $C = 10^{-4}$.

[15] Unreported measurements by P. F. Grieger.

[16] Ralston and Hoerr, THIS JOURNAL, **69**, 883 (1947).

More recently, Ralston and Eggenberger[17] have reported that the equivalent conductance of dodecylammonium chloride in water and in water saturated with a number of sparingly soluble organic non-electrolytes (hydrocarbons, alcohols, etc.) is the same at concentrations less than the critical.

As the concentration of dodecylammonium chloride is increased above that of the breakpoint in the presence of dodecanol, there occurs a change in the character of the curves which may be of the nature of a second breakpoint. This is best shown by curves 4 and 5 for 0.246 and 0.261 mole of dodecanol per mole of salt. The two series are in good agreement, and there is little doubt that, at a certain concentration, the course of the curves undergoes a marked change. At concentrations above the "second breakpoint," the curves are all convex to the concentration axis, and they parallel one another rather closely.

It is of interest to note that for 0.044 and 0.111 mole of dodecanol per mole of salt, the solutions remained homogeneous over the entire range of concentration. For 0.26 mole of dodecanol, the solution became cloudy at the second breakpoint, the cloudiness increasing up to the first breakpoint; thereafter, the cloudiness decreased with dilution. For 0.65 mole of dodecanol, the solution was cloudy, although stable, over the whole range of concentration. The reproducibility of the results leaves little doubt that, in these solutions, we are dealing with a system in equilibrium. The fact that below the breakpoint the curves coincide for all proportions of alcohol to salt is strong evidence that under these conditions the two (alcohol and salt) are not associated.

**5. Salts of Doubly Charged Long Chain Ions.**—It was of interest to determine whether salts with two ions connected by a hydrocarbon chain would exhibit properties similar to those of uni-univalent long chain salts. Measurements were carried out with 1-N-morphine 10-N'-piperidinodecane dihydrochloride and di-N-propyl-10-N-piperidinodecane dihydrochloride. The results are shown graphically in Fig. 6 along with the conductance curve for decylammonium chloride at 20° as determined by Ralston and Hoerr.[18] As may be seen from the figure, the conductance curves for the diammonium salts exhibit no singularities up to 0.25 $N$. It may be concluded that these salts do not exhibit the properties of ordinary long chain electrolytes over the concentration range measured, at least not so far as conductance is concerned.

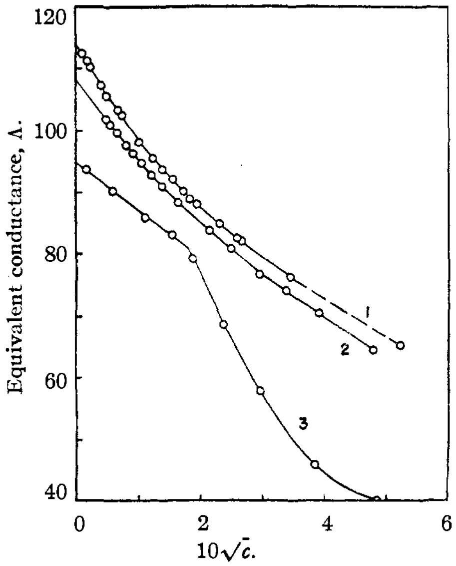

Fig. 6.—Diammonium salts in water at 25°: (1) 1-N-morpholino-10-N'-piperidinodecane dihydrochloride; (2) di-N-propyl-10'N'-piperidinodecane dihydrochloride; (3) decylammonium chloride at 20° (Ralston and Hoerr).

## V. Summary

1. The effect of isopropyl alcohol and *t*-butanol on the conductance of dodecylammonium chloride in aqueous solution has been determined and compared with that of methanol.

2. It has been found that octadecylpyridonium and hexadecylpyridonium iodate exhibit a maximum in their conductance curves in aqueous solution; the maximum is much the more pronounced for the octadecyl compound.

3. The effect of methanol and *t*-butanol on the conductance of the octadecyl compound in aqueous solution has been determined as has also that of *t*-butanol on solutions of the hexadecyl compound. The effect of butanol in the case of the latter compound is very pronounced.

4. The effect of dodecanol on the conductance of solutions of dodecylammonium chloride in a 25.64% methanol–water mixture has been studied. The breakpoint concentration is lowered on addition of dodecanol; at concentrations below the breakpoint, the conductance is unaffected by addition of dodecanol. There are indications of a second break at concentrations above that of the normal breakpoint.

5. The conductance of the two diammonium salts with ten carbon atoms between the ionic groups follows the course of a normal electrolyte as far as measured (0.25 $N$).

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[17] Ralston and Eggenberger, THIS JOURNAL, **70**, 983 (1948).

[18] Ralston and Hoerr, *ibid.*, **64**, 772 (1942).