the resistance change per carbon atom is much less than for the symmetrical ions. As Bair[4] has shown, a break occurs in the resistance curve between the tetradecyl and the hexadecyl ion.

It is of interest to note that the resistance of the hexyltrimethylammonium ion is 15% greater than that of the phenyltrimethylammonium ion which has the same number of carbon atoms. Evidently, ion resistance is markedly dependent on structure.

On substituting a methyl group for one hydrogen of the ammonium ion, there is a large resistance increase. Thereafter, the change is approximately a linear function of the number of methyl groups until the tetramethyl ion is reached. The last substitution causes relatively little change in resistance. The conductance of tetramethylammonium picrate was redetermined. Our present value is 0.1 Λ-unit less than that of Daggett.[5] Our value for potassium bromide is 0.26 Λ-unit higher than that of other recent investigators.[6]

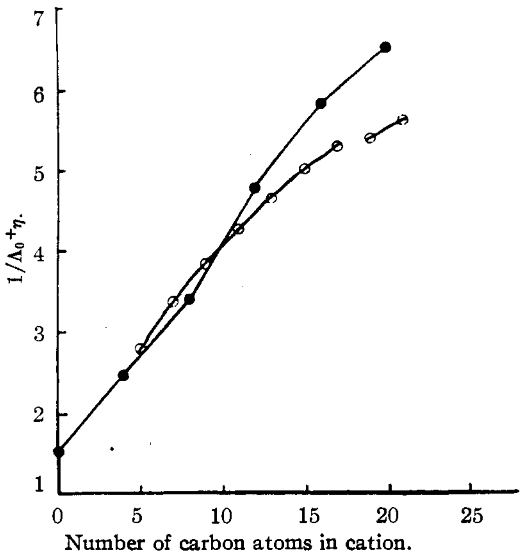

Fig. 1.—Ion resistances as function of number of carbon atoms: ●, symmetrical; O, unsymmetrical trimethyl.

PROVIDENCE, R. I. RECEIVED NOVEMBER 9, 1950

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[6] H. S. Harned and B. B. Owen, "The Physical Chemistry of Electrolytic Solutions," Reinhold Publishing Corp., New York, N. Y., 1950, p. 537.

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[CONTRIBUTION FROM THE METCALF RESEARCH LABORATORY OF BROWN UNIVERSITY]

# Properties of Electrolytic Solutions. L. Effect of Substituent Groups on the Properties of Long Chain Ions[1]

BY MAURICE J. MCDOWELL[2] AND CHARLES A. KRAUS

For solutions of long chain salts at the critical concentration, the derivative of conductance with respect to concentration exhibits a discontinuity; depending on constitutional factors, the conductance may either decrease or increase with increasing concentration. At concentrations below the critical, the slope of the $\Lambda-\sqrt{C}$ plots may conform to the theoretical values of Onsager for a 1–1 electrolyte or the slope may be greater than that of a 1–1 electrolyte. For salts with chains of 16 or more carbon atoms the slope is greater than for 1–1 electrolytes; for chains of 14 carbon atoms or less the slopes are normal. In the present investigation, the conductance of a series of octadecyltrialkylammonium bromates has been measured from the triethyl to the tri-*n*-amyl derivative, inclusive. Results of conductance measurements are presented which show how the properties of these solutions are affected by the sizes of the substituent alkyl groups.

## I. Introduction

With long chain quaternary ammonium electrolytes near the critical concentration and below, we have two types of phenomena to consider, both of which are dependent upon constitutional factors: (1) with increasing concentration at the critical point, the conductance may either decrease below or increase above that of a normal electrolyte; (2) at concentrations below the critical point, the slope of the $\Lambda-\sqrt{C}$ plot may be normal or it may be greater than that of a 1–1 electrolyte.

The constitutional factors that govern these phenomena are: length of the hydrocarbon chains, size of the charged heads of the long chain ions and size of the counter ions. The effect of chain length on the critical phenomenon has been investigated extensively. The effects due to the other two factors mentioned above have thus far received little attention.

In the present investigation we have been primarily concerned with the effect of the size of the charged head of the long chain ion on the properties of its solutions. For this purpose, we have employed salts of quaternary ammonium ions having one long chain, the other three substituents being alkyl groups ranging from ethyl to *n*-amyl, inclusive. As negative ion we have employed the bromate. We have measured the conductance of bromates of octadecyltriethyl-, tri-*n*-propyl-, tri-*n*-butyl- and tri-*n*-amyl-ammonium ions. The corresponding trimethyl salt had already been measured by Bair.[3] We have also measured the conductance of hexadecyltri-*n*-butylammonium bromate.

## II. Experimental

**1. Apparatus, Procedure and Materials.**—The apparatus and the procedure employed in carrying out the measurements have been described in earlier papers.[4,5] All measurements were carried out at 25 ± 0.002°.

The salts were prepared by the reaction of the long chain iodides with the appropriate tertiary amines. The bro-

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[1] This paper is based on a portion of a thesis presented by Maurice J. McDowell in partial fulfillment of the requirements for the degree of Doctor of Philosophy in the Graduate School of Brown University, June, 1950.

[2] Ethyl Corporation Fellow (1947–1948); University Fellow (1948–1949); Metcalf Fellow (1949–1950) in Brown Universtiy.

[3] E. J. Bair and C. A. Kraus, THIS JOURNAL, 73, 1129 (1951).

[4] D. W. Kuhn and C. A. Kraus, *ibid.*, 72, 3676 (1950).

[5] H. M. Daggett, B. J. Bair and C. A. Kraus, *ibid.*, 73, 779 (1951).

mates were prepared by metathesis of the iodides with silver bromate. The silver salt was dissolved in a minimum quantity of hot 10% aqueous ammonia. This solution was poured slowly into a solution of the iodide in ethanol the volume of which was so adjusted that on addition of the aqueous solution the resultant solution contained 96% alcohol.

After separating from the silver iodide, the solution was evaporated under reduced pressure and the product was pumped to dryness. These salts are very soluble in organic solvents; they were recrystallized from absolute ethyl ether or ether to which a small amount of alcohol had been added.

The following salts were prepared: octadecyltriethylammonium bromate, m.p. 107°; octadecyltri-*n*-propylammonium bromate, m.p. 61°; octadecyltri-*n*-butylammonium bromate, m.p. 68°; octadecyltri-*n*-amylammonium bromate, m.p. 64°; hexadecyltri-*n*-butylammonium bromate, m.p. 58°.

2. **Results.**—In Table I are presented values of the equivalent conductance for the salts measured at the concentrations indicated. In computing concentrations, the density of the solutions has been assumed to be equal to that of water, 0.99707 g./ml.; the density of the salts has been assumed to be 1.5 in making buoyancy corrections. The specific conductance of the pure solvent was known to 0.1%, or better, in all cases. It varied between 3.5 and 5.5 × $10^{-7}$ mho; values are omitted from the table.

TABLE I

CONDUCTANCE OF LONG CHAIN TRIALKYLAMMONIUM SALTS AT 25°

| $C \times 10^4$ | Λ |
|---|---|
| A. Octadecyltriethylammonium Bromate | |
| 0.44637 | 72.78 |
| 0.89218 | 72.25 |
| 1.3423 | 72.03 |
| 1.8025 | 71.81 |
| 2.9251 | 69.69 |
| 4.2669 | 64.26 |
| 1.5511 | 72.02 |
| 2.2569 | 71.545 |
| B. Octadecyltri-*n*-propylammonium Bromate | |
| 0.40886 | 71.975 |
| .83470 | 71.45 |
| 1.8556 | 75.695 |
| 3.9139 | 70.56 |
| 0.21489 | 72.54 |
| .65047 | 71.81 |
| 1.0315 | 71.48 |
| 1.4144 | 72.84 |
| 2.1097 | 76.47 |
| C. Octadecyltri-*n*-butylammonium Bromate | |
| 0.23077 | 71.30 |
| .60895 | 74.26 |
| 1.2003 | 86.73 |
| 1.7916 | 86.58 |
| 2.9681 | 80.23 |
| 0.34789 | 72.261 |
| .69793 | 77.145 |
| 1.0283 | 85.104 |

| $C \times 10^4$ | Λ |
|---|---|
| D. Octadecyltri-*n*-amylammonium Bromate | |
| 0.10390 | 68.97 |
| .17926 | 73.21 |
| .36726 | 93.88 |
| .53702 | 99.07 |
| .71585 | 100.01 |
| .90232 | 98.95 |
| E. Hexadecyltri-*n*-butylammonium Bromate | |
| 0.38791 | 71.17 |
| .94823 | 70.41 |
| 1.8971 | 69.60 |
| 2.8388 | 68.80 |
| 4.7569 | 70.29 |
| 0.21552 | 71.66 |
| .63865 | 70.81 |
| 2.7814 | 69.03 |
| 3.4183 | 69.07 |
| 5.9777 | 69.86 |
| 7.0800 | 68.34 |
| 3.0244 | 68.93 |
| 5.0885 | 70.20 |

## III. Discussion

The present investigation has been addressed toward a study of the effect of the size of substituent groups on the properties of solutions of long chain quaternary ammonium ions. We have been concerned with the effect of substituents on: (a) the critical concentration; (b) the maximum; and (c) the slopes of the $\Lambda - \sqrt{C}$ plots at concentrations below the critical.

In Fig. 1, the results of Table I are shown graphically, conductances being plotted as ordinates against values of the square root of concentration as abscissas. In Table II are collected values for the critical concentration (col. 2); the percentage rise in the value of Λ at the maximum over that at the critical concentration (col. 3); the values of $\Lambda_0$ (col. 4); the observed slopes below the critical point (col. 5); the value of the theoretical slope for a 1–1 salt (col. 6) and the value of the slope for a 2–1 salt (col. 7).

TABLE II

SIGNIFICANT VALUES OF VARIABLES AND CONSTANTS FOR OCTADECYLTRIALKYLAMMONIUM BROMATES

| Substituent group | Critical concn. × $10^4$ | Rise of max., % | $\Lambda_0$ | Obsd. slope | Onsager 1–1 slope | Onsager 2–1 slope |
|---|---|---|---|---|---|---|
| Methyl[a] | 3.1 | No max. | 75.6 | 137 | 78 | 144.1 |
| Ethyl | 2.5 | No max. | 73.7 | 139 | 77 | 143.8 |
| Propyl | 1.25 | 7.6 | 73.0 | 150 | 77 | 143.3 |
| Butyl | 0.5 | 22 | .. | ... | .. | ... |
| Amyl | 0.16 | 45 | .. | ... | .. | ... |
| Butyl[b] | 3.3 | 1.6 | 72.4 | 220 | 77 | 216[c] |

[a] Values due to Young, Grieger and Kraus[6] and Bair and Kraus.[3] [b] Hexadecyl derivative. [c] Onsager 3–1 slope.

a. **Critical Concentration.**—As the size of the substituent groups increases, the critical concentration is shifted toward lower concentrations. The shift appears to be greater for larger than for smaller groups. Thus, in going from methyl to ethyl, the concentrations are approximately in the ratio of 3:2; in going from butyl to amyl, the conconcentration ratio is 3:1. While the critical concentration decreases with increasing number of carbon atoms in the substituent groups, the increase is far less than that for a corresponding increase in the number of carbon atoms in the long chain. Thus, on addition of three carbons to the butyl groups of octadecyltributylammonium bromate, the critical concentration decreases in the ratio of 3:1; on adding two carbon atoms to the hexadecyl chain of hexadecyltributylammonium bromate, the critical concentration decreases in the ratio of 6:1. It is clear, however, that carbon atoms in the substituent groups interact with the atoms of other ions in much the same way as do carbon atoms in the long chains. In both cases, these interactions promote the formation of micellar ions and, the larger the number of carbon atoms, the lower the concentration at which micelles appear.

b. **The Maximum.**—The appearance of a maximum in the conductance of certain long chain salts is a striking phenomenon. In pure water, it has been observed, heretofore, only in exceptional cases, such as octadecylpyridonium iodate,[7] salts of ions having two long chains[8a] and certain dyes.[8b] From the foregoing results, however, the maximum appears to be a common phenomenon and

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(6) H. S. Young, P. F. Grieger and C. A. Kraus, THIS JOURNAL, **71**, 309 (1949).

(7) G. L. Brown, P. F. Grieger, E. C. Evers and C. A. Kraus, *ibid.*, **69**, 1835 (1947).

(8) (a) A. W. Ralston, D. N. Eggenberger and P. L. Du Brow, *ibid.*, **70**, 977 (1948); (b) C. Robinson and M. E. Garrett, *Trans. Faraday Soc.*, **35**, 771 (1939).

dependent on the size of the heads of the long chain ions and probably, also, on the size of the counter ions.

The octadecyl-, trimethyl- and triethylammonium bromates exhibit no maxima; in both cases the conductance falls off at the critical point, somewhat more steeply for the methyl than for the ethyl derivative. The propyl derivative already exhibits a pronounced maximum and, as the substituent alkyl groups become larger, the height of the maximum increases. The height of the maximum is also dependent on the number of carbon atoms in the long chain. Thus, the conductance of octadecyltributylammonium bromate at the maximum is 22% greater than that at the critical point; for the corresponding hexadecyl salt the maximum is only 1.6% greater. In attempting to interpret these results, it must be borne in mind that the critical concentration of the hexadecyl salt is six times that of the octadecyl salt.

The sharp decrease in conductance which most long chain electrolytes exhibit in water at the critical point can only be due to a decrease in the number of charges capable of transport under the action of an external field. If present views regarding the nature of solutions of long chain electrolytes are correct, and they seem to be reasonably well founded, then the conductance of a unit of charge on a micellar ion should be greater than that of the same charge on a single long chain ion. If the counter ions did not form non-conducting pairs with ions of the micelles, we should expect a sharp rise in conductance at the critical point in all cases. The falling off of the conductance at the critical point can only be due to the binding of some of the counter ions by ions in the micelles.

From the results presented above, it seems clear that the extent to which the counter ions are bound by the micellar ions depends on the size of the charged heads of the micellar ions. As these heads become larger, fewer counter ions are bound; a maximum appears with the propyl derivative and the magnitude of the maximum steadily increases as we proceed to the butyl and the amyl derivatives.

We should also expect the appearance of a maximum (and its magnitude) to be dependent on the size of the counter ion. Although data are fragmentary, such data as we have are in accord with this view. Thus, octadecylpyridonium chloride exhibits no maximum[9] while the corresponding iodate exhibits a pronounced maximum.[7]

The force acting on a counter ion in the neighborhood of a micellar ion may be divided into two parts: (1) interaction of the counter ion with the over-all charge on the micellar ion; this might be treated as the action of a surface charge on the individual counter ions; (2) interaction of a counter ion with an undivided charge on one of the units of the micellar ion.

It is difficult to arrive at an evaluation of the force that may exist between individual ions on close approach in water. The size of these ions is not known and the macroscopic dielectric constant of the medium ceases to have physical meaning in short range interactions. With quaternary ammonium ions, at least the larger ones, hydration is of secondary importance and we can approximate ion size. The size of the negative ions, however, remains uncertain. The increasing magnitude of the maximum with increasing size of the substituent alkyl groups in the case of the bromates clearly indicates specific interaction of the counter ions with individual ions of the micelle. The larger the heads of the micellar ions, the greater the maximum and, therefore, the smaller the number of counter ions bound by the micelle.

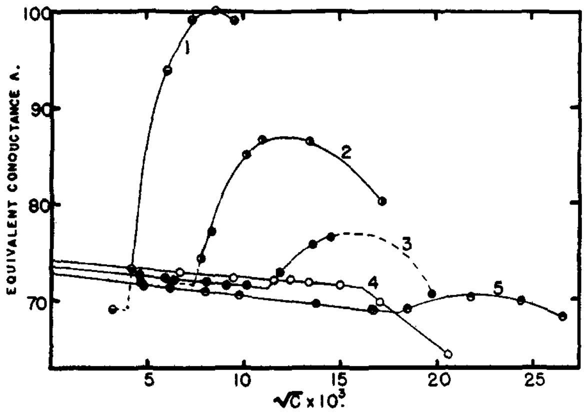

Fig. 1.—Conductance of long chain quaternary ammonium bromates: (1) octadecyltriamylammonium, (2) octadecyltributylammonium, (3) octadecyltripropylammonium, (4) octadecyltriethylammonium, (5) hexadecyltributylammonium bromate.

We can gain some idea of the distances between charges of ions in ion-pairs from the polar moments of salts in benzene. The polar moment of tetra-*n*-butylammonium perchlorate is $14.1 \times 10^{-18}$; the distance between charges then is $2.96 \times 10^{-8}$ cm. In water, the bromate ion is probably hydrated and its effective size is greater than it would be in a solvent such as benzene. Nevertheless, the force acting between a bromate ion and a quaternary ammonium ion might be expected to be appreciable. The greatest uncertainty lies in the dielectric constant. In any case, it seems reasonable to conclude that the energy necessary to separate a bromate ion from a given micellar ion is of significant magnitude.

**c. Concentrations below the Critical.**—Kuhn and Kraus[4] and Bair and Kraus[3] have shown that salts having chains of sixteen or more carbon atoms do not conform to the Onsager limiting equation. While the conductance of these salts varies as a linear function of the square root of concentration, the slope of the lines is much greater than that of 1–1 salts. As may be seen from Table II (cols. 6 and 7), the slopes of the three octadecyl salts, whose slopes could be measured, are all much greater than the theoretical and approximate those of 2–1 salts. Indeed, the slope of the propyl derivative appears to be slightly greater than that of a 2–1 salt.

Because of the low critical concentration of the octadecyl, tributyl and triamyl derivatives, their slopes could not be determined. However, hexadecyltributylammonium bromate has a critical

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[9] E. C. Evers and C. A. Kraus, This Journal, 70, 3049 (1948).

point at 3.3 × $10^{-4}$ $N$ and its slope was readily determined. For this salt, the slope was found to be 220, the theoretical slope for a 1–1 salt is 77, for a 3–1 salt it is 216. Thus, for this salt, the slope is that of a 3–1 salt within the limit of experimental error. As has been pointed out in earlier papers, the greater slope of these salts might be accounted for on the basis of ion-pair formation. However, in view of the fact that similar salts having ions containing chains of 14 carbon atoms, or less, exhibit a normal slope, it is highly improbable that ion-pairs are formed.

It seems more probable that in the case of ions having chains of 16 or more carbon atoms, association of the chains occurs at concentrations below the critical. In this connection, it is important to note that association is markedly dependent on the size of the substituent alkyl groups on the ion head. Thus, the slope of hexadecyltributylammonium bromate is that of a 3–1 salt. Evidently, the van der Waals interaction between the ions is increased due to the presence of the butyl groups.

On the basis of the evidence presently available, we may conclude that if the chains on the ions are of sufficient length, association occurs at concentrations below the critical. The size of the substituent groups on the head of long chain quaternary ammonium ions likewise affects the tendency for such ions to associate. It should not be concluded, however, the the multiple ions in a given case all have the same degree of complexity. Rather, we should expect multiple ions of different degrees of complexity to exist in equilibrium with one another and probably with simple ions. With different salts, the mean value of the association number will differ and may approximate that of a 2–1 or a 3–1 salt, for example. If an equilibrium exists, we should expect it to shift as concentration decreases. Unfortunately, the critical concentrations of these salts are so low and the observable conductance differences are so small that it is difficult, it not impossible, to demonstrate any shift of equilibrium.

**d. Ion Conductances.**—Values for the conductance of the long chain ions have been derived from the $\Lambda_0$ values of Table II. They are based on Daggett's value of 55.66 for the conductance of the bromate ion and are collected in Table III.

TABLE III

ION CONDUCTANCES

| Ion | No. C atoms | $\Lambda_0^+$ |
|---|---|---|
| Octd·$Me_3N^+$ | 21 | 19.9 |
| Octd·$Et_3N^+$ | 24 | 18.0 |
| Octd·$Pr_3N^+$ | 27 | 17.3 |
| Hexd·$Bu_3N^+$ | 28 | 16.9 |

The conductance decrease with increasing number of carbon atoms in the cation is very much less for long chain ions than it is for symmetrical quaternary ammonium ions as Bair has shown. Thus, the conductance of the tetraamylammonium ion, with 20 carbon atoms, is 17.13, while that of the octadecyltripropylammonium ion, with 27 carbon atoms, is 17.3. The ratio of conductances of the octadecyltrimethyl and tripropylammonium is 1.15; for the tetramethyl and the tetrapropylammonium ions, the ratio is 1.92. It is true that in the first instance above only 6 carbon atoms were added while, in the second, 8 were added. However, in going from the tetramethyl- to the tetraethylammonium ion, where only 4 carbon atoms are added, the conductance ratio is 1.38.

The addition of carbon atoms to the alkyl groups on the head of a long chain ion decreases the conductance far less than a similar addition to the substituent groups of symmetrical ions.

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[CONTRIBUTION FROM THE RESEARCH LABORATORIES OF THE SPRAGUE ELECTRIC COMPANY]

# The Rates of Decomposition of Acetyl Peroxide in Acetic Acid and Carbon Tetrachloride

BY SIDNEY D. ROSS AND MORTON A. FINEMAN

The rate of decomposition of a commercial 25% solution of acetyl peroxide in dimethyl phthalate has been studied in acetic acid and carbon tetrachloride. It is shown that the presence of dimethyl phthalate does not appreciably affect the decomposition in these solvents. In acetic acid the decomposition is unimolecular and there is no evidence of either induced decomposition or inhibition. In carbon tetrachloride, individual runs are first-order, but the rate is a function of the initial peroxide concentration. The decomposition is subject to inhibition but not to acid catalysis. It is not possible to decide mathematically between the two rate equations. $-\mathrm{d}P/\mathrm{d}t = k_1P + k_2P^{3/2}$ (1) and $-\mathrm{d}P/\mathrm{d}t = k_1P + k_2P^2$ (2). There are, nevertheless, reasons for preferring the first rate equation.

Our interest in acetyl peroxide was twofold. We were interested in the decomposition characteristics of the acetyl peroxide, which is supplied by the Buffalo Electro-Chemical Company, Inc., as a 25% solution in dimethyl phthalate,[1] since this is the only readily available and easily handled form of this polymerization catalyst. The decomposition of acetyl peroxide was also of interest in connection with an intensive study of the decomposition of lead tetraacetate which is now in progress in these laboratories. The decomposition of lead tetraacetate is characterized by pseudo zero-order kinetics and strong acceleration of the rate of decomposition by both trichloroacetic acid and lead diacetate.[2] The pseudo zero-order kinetics makes Waters[3] suggestion of acetyl peroxide as a possible intermediate in the decomposition of lead tetraacetate an attractive one. Although Kharasch, Friedlander and Urry[4] have recently reported evidence which is contrary to this sugges-

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(1) This corresponds to a dimethyl phthalate concentration 1.82 times that of the peroxide.

(2) Unpublished results from these laboratories.

(3) W. A. Waters, *Ann. Reports of the Chemical Society, London*, **42**, 143 (1945).

(4) M. S. Kharasch, H. N. Friedlander and W. H. Urry, *J. Org. Chem.*, **14**, 91 (1949).