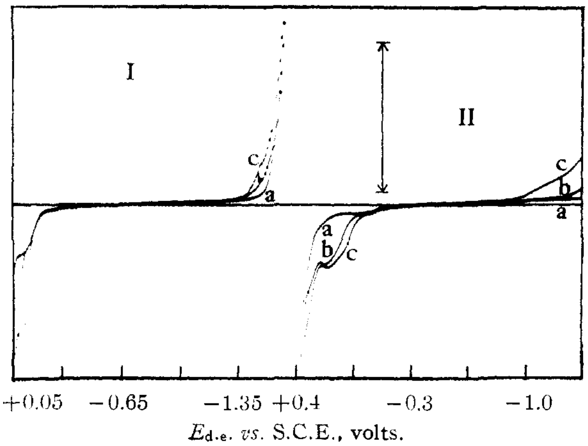

Fig. 13.—Polarograms of (a) 0, (b) 1.83 and (c) 3.44 m*M* +3 vanadium in (I) sodium pyrophosphate saturated at *p*H 5.5, and (II) sodium tetraborate saturated at *p*H 5.1. The height of the arrow corresponds to ten microamperes.

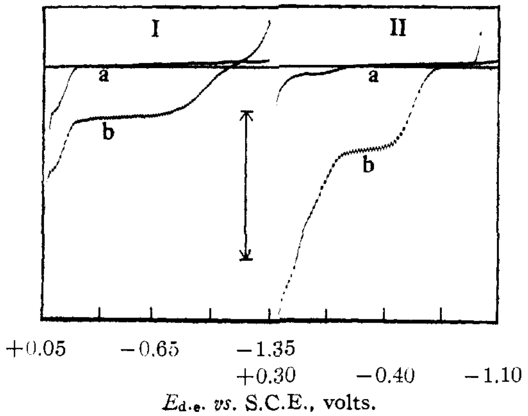

Fig. 14.—Polarograms of (I) (a) 0 and (b) 2.22 m*M* +2 vanadium in saturated sodium pyrophosphate at *p*H 5.5; (II) (a) 0 and (b) 2.24 m*M* +2 vanadium in saturated sodium tetraborate at *p*H 5.1. The height of the arrow corresponds to ten microamperes.

state, while the cathodic wave at about −1.6 v. represents reduction to the +2 state.

The faintly bluish-green solutions of +2 vanadium in this tartrate medium give a single anodic wave at −0.175 v. (curves I, Fig. 6), which has a diffusion current constant of −1.070 ± 0.002. Since this is equal to the value found for a one-electron oxidation of +3 vanadium in this medium, +2 vanadium is oxidized only to the +3 state in tartrate solutions. In view of the easy oxidizability of +3 vanadium, this result is surprising. The alternative is that the +2 vanadium complex is actually oxidized to the +4 state but that its diffusion coefficient is only one-fourth that of the vanadic tartrate complex: this seems very improbable. Apparently the vanadic complex formed at the electrode surface is a metastable form which must rearrange before it can be easily oxidized to the +4 state, and this rearrangement is so slow as to inhibit the further oxidation at the dropping electrode. A similar example of a metastable complex formed at the dropping electrode was recently reported by Pecsok and Lingane.[8]

No indication of reduction below the +2 state was observed in any of the media used.

[8] R. L. Pecsok and J. J. Lingane, THIS JOURNAL, **72**,189 (1950).

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[CONTRIBUTION FROM THE METCALF RESEARCH LABORATORY OF BROWN UNIVERSITY]

Properties of Electrolytic Solutions. XLIX. Conductance of Some Salts in Water at 25°[1]

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

Following up the observations of Bair and Kraus, that the equivalent resistance of long chain quaternary ammonium ions is less than that of corresponding symmetrical ions, the conductance of a series of alkyltrimethylammonium ions has been measured from ethyltrimethyl- to tetradecyltrimethylammonium inclusive, in steps of two carbon atoms. Up to, and including, the hexyltrimethylammonium ion, the equivalent resistance of the unsymmetrical ions is greater than that of corresponding symmetrical ions. For the octyltrimethylammonium ion and ions with longer chains, the resistance of the unsymmetrical ions is less than that of the symmetrical ions. The resistance of the three partially substituted methylammonium ions has been determined as has also that of the phenyltrimethylammonium ion. The conductances of potassium bromide and of tetramethylammonium picrate have also been measured.

I. Introduction

Kuhn and Kraus[3] and Bair and Kraus[4] have measured the conductance of several long chain salts at concentrations below the critical. Dodecyl- and tetradecyltrimethylammonium salts exhibit the normal behavior of 1–1 salts. Hexadecyl- and octadecyltrimethylammonium salts exhibit a behavior that diverges from that of 1–1 salts in that the limiting slopes of the $\Lambda-\sqrt{C}$ plots are much greater than the theoretical for 1–1 salts and approximate that of 2–1 salts. Bair[4] determined the limiting conductance of the long chain ions of the above measured salts and found that the equivalent resistance of these ions is much less than that of symmetrical quaternary ammonium ions[5] having the same number of carbon atoms. It seemed of interest to investigate the conductance of alkyltrimethylammonium ions as influenced by the length of the hydrocarbon chain.

We have measured the conductance of these

[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 University.

[3] D. W. Kuhn and C. A. Kraus, THIS JOURNAL, **72**, 3676 (1950).

[4] E. J. Bair and C. A. Kraus, *ibid.*, **73**, 1129 (1951).

[5] H. M. Daggett, E. J. Bair and C. A. Kraus, *ibid.*, **73**, 799 (1951).

ions from ethyltrimethyl- to tetradecyltrimethylammonium, inclusive, in steps of two carbon atoms. We have also measured the conductance of potassium picrate and potassium bromide for the purpose of obtaining more accurate values for the limiting conductance of the picrate and the bromide ions. In addition, we have measured the conductance of the partially substituted methylammonium picrates as well as of tetramethylammonium picrate.

II. Apparatus, Procedure and Materials

1. **Apparatus.**—The necessary instruments, thermostat, cells, and the like, have been described by Kuhn[3] and Daggett.[5] Temperature was maintained at 25 ± 0.002° and was checked at intervals with a platinum resistance thermometer. The cell was calibrated by means of a 1×10^{-3} *N* solution of potassium chloride using Shedlovsky's value of 146.98×10^{-6} mho for the specific conductance of this solution. The cell was provided with a magnetic stirrer.

2. **Procedure.**—This was the same as that described in earlier papers with one exception. Since the salts to be measured conform to Onsager's equation, we have carried out measurements at concentrations between 1×10^{-4} and 1×10^{-3} *N*. The observed values were substituted in Onsager's equation which was then solved for Λ_0. The values were averaged and the average adopted as the most probable. As Daggett, Bair and Kraus[5] have pointed out, if Onsager's equation holds, more accurate values are obtained in this way than by graphical extrapolation of conductance values at lower concentrations. In the case of salts that do not conform to Onsager's equation, it is necessary to employ graphical extrapolation.

3. **Materials.**—The salts were prepared according to conventional methods and were purified by repeated crystallization from suitable solvents until reproducible conductance values were obtained. The purification of the salts is greatly simplified if reactants and solvents are carefully purified before use. The following salts were prepared and purified: ethyltrimethylammonium bromide, m.p. 338°; *n*-butyltrimethylammonium bromide, m.p. 212°; *n*-hexyltriethylammonium bromide, m.p. 186°; *n*-octyltrimethylammonium bromide, m.p. 215°; *n*-decyltrimethylammonium bromide, m.p. 239–242°; *n*-dodecyltrimethylammonium bromide, m.p. 243°; *n*-tetradecyltrimethylammonium nitrate m.p., 205–207°; phenyltrimethylammonium bromide m.p., 215°. The partially substituted ammonium salts sublime or decompose on heating.

Potassium bromide of reagent grade was recrystallized twice from pure conductivity water and four times from 30% ethanol. Another sample was prepared by decomposing a purified sample of potassium bromate by heating to 380° in a silica tube. The product was recrystallized repeatedly from water and 50% ethanol. It was dried at 400° *in vacuo*. The two preparations gave identical results.

Potassium picrate was prepared by neutralizing the acid with potassium carbonate in aqueous solution. The starting materials were purified before use. The product was recrystallized repeatedly from water and ethanol.

Before using, organic salts were dried *in vacuo* (10 microns) at temperatures from 50–100°.

III. Results

In Table I are presented conductance values for the different salts measured. Concentrations are expressed in equivalents per liter of solution, assuming the density of the solutions to be that of water, 0.99707 g./ml. Buoyancy corrections for the quaternary salts were made on the assumption that their density was 1.5; densities of other salts were taken from the literature. The specific conductance of the water used, which was subtracted from the measured specific conductance of the solution, varied between $3\text{–}5 \times 10^{-7}$; values are omitted from the table. Λ_0 values as computed from Onsager's equation

$$\Lambda_0 = (\Lambda + 60.19\sqrt{C})/(1 - 0.2290\sqrt{C}) \qquad (1)$$

are given in column 3 and differences from mean values are given in column 4.

TABLE I

CONDUCTANCE OF SOME SALTS IN WATER AT 25°

$C \times 10^4$	Λ	Λ_0	Dev., %
A. Tetramethylammonium picrate			
1.8183	74.154	75.198	−0.01
3.6964	73.720	75.208	.00
5.5266	73.402	75.222	+ .02
	Λ_0 = 75.21	Mean Λ_0 75.209	
B. Ethyltrimethylammonium bromide			
3.0215	117.451	118.970	0.00
6.0460	116.832	118.981	+ .01
9.0208	116.319	118.945	− .02
		Mean Λ_0 118.966	
3.1305	117.469	119.016	+0.02
6.1996	116.810	118.987	.00
9.3455	116.288	118.960	− .02
	Λ_0 = 118.98	Mean Λ_0 118.988	
C. *n*-Butyltrimethylammonium bromide			
2.7375	110.333	111.752	0.00
5.4226	109.774	111.771	+ .01
8.1807	109.296	111.749	− .01
		Mean Λ_0 111.757	
2.7436	110.299	111.719	+0.02
5.4618	109.691	111.695	.00
8.2093	109.217	111.674	− .02
	Λ_0 = 111.72	Mean Λ_0 = 111.674	
D. *n*-Hexyltrimethylammonium bromide			
2.3290	106.412	107.707	0.00
4.5911	105.902	107.720	+ .01
6.8266	105.469	107.685	− .02
		Mean Λ_0 107.704	
2.4304	106.386	107.708	+0.02
4.8093	105.831	107.691	.00
7.2191	105.393	107.672	− .02
	Λ_0 = 107.70	Mean Λ_0 107.690	
E. *n*-Octyltrimethylammonium bromide			
2.0638	103.492	104.701	0.00
4.1014	102.999	104.703	.00
6.1691	102.603	104.693	.00
		Mean Λ_0 104.699	
2.0137	103.469	104.663	+0.01
4.1076	102.941	104.646	− .01
6.1120	102.573	104.653	.00
	Λ_0 = 104.68	Mean Λ_0 104.654	
F. *n*-Decyltrimethylammonium bromide			
1.8418	101.355	102.491	+0.01
3.6768	100.876	102.479	.00
5.1485	100.578	102.476	− .01
		Mean Λ_0 102.482	
1.8934	101.384	102.535	+0.02
3.7550	100.872	102.493	− .02
7.4922	100.215	102.505	− .01
	Λ_0 = 102.60	Mean Λ_0 102.511	

TABLE I (*Continued*)

$C \times 10^4$	Λ	Λ_0	Dev., %
G. Dodecyltrimethylammonium bromide			
1.7207	99.705	100.797	+0.05
3.4421	99.179	100.723	− .03
5.1726	98.839	100.732	− .02
Mean Λ_0 100.751			
0.96088	99.856	100.772	+0.01
2.5779	99.431	100.767	.00
4.1632	99.058	100.756	− .01
Λ_0 = 100.76 Mean Λ_0 100.765			
H. Tetradecyltrimethylammonium nitrate			
1.3878	91.527	92.485	−0.01
3.0406	91.113	92.532	+ .03
4.7173	90.727	92.494	− .01
6.7249	90.374	92.484	− .01
Mean Λ_0 92.499			
1.6251	91.505	92.542	+0.04
3.2131	91.030	92.489	− .02
4.8121	90.702	92.487	− .02
Λ_0 = 92.50 Mean Λ_0 92.506			
I. Phenyltrimethylammonium bromide			
2.3466	111.492	112.809	+0.02
4.6813	110.929	112.790	.00
7.0590	110.491	112.776	− .01
Λ_0 = 112.79 Mean Λ_0 112.792			
J. Trimethylammonium bromide			
3.6210	123.430	125.120	+0.02
7.1943	122.725	125.107	.00
9.3253	122.372	125.084	− .02
Λ_0 = 125.10 Mean Λ_0 125.104			
K. Dimethylammonium chloride			
3.5514	126.169	127.854	0.00
9.7567	125.052	127.846	.00
Λ_0 = 127.85 Mean Λ_0 127.850			
L. Methylammonium chloride			
2.9262	132.633	134.188	−0.03
5.8353	132.009	134.205	− .01
10.2845	131.357	134.273	+ .04
Λ_0 = 134.22 Mean Λ_0 134.222			
M. Potassium picrate			
2.1998	102.707	103.953	0.00
4.3697	102.190	103.945	− .01
6.5171	101.799	103.943	− .01
8.6727	101.470	103.943	− .01
9.8223	101.351	103.983	+ .03
Mean Λ_0 103.953			
1.9344	102.812	103.980	0.00
3.8601	102.312	103.962	− .02
5.7894	101.967	103.987	+ .01
7.7942	101.626	103.971	− .01
9.8140	101.368	103.999	+ .02
Λ_0 = 103.97 Mean Λ_0 103.980			
N. Potassium bromide (from decomposed $KBrO_3$)			
0.89720	151.197	152.097	+0.02
1.8071	150.815	152.092	+ .01
3.5543	150.252	152.043	− .02
7.8213	149.411	152.068	.00
1.2985	148.630	152.053	− .01
Mean Λ_0 152.071			
(From reagent grade KBr)			
3.2173	150.347	152.051	0.00
7.4768	149.439	152.036	− .01
15.807	148.281	152.058	+ .01
Λ_0 = 152.06 Mean Λ_0 152.049			

IV. Discussion

1. Consistency of Results.—As may be seen on inspection of Table I, the variation in the computed values of Λ_0 for a given series is of the order of a few hundredths of one per cent. This is particularly true of potassium bromide where the concentration range involved was greater than for other salts. The mean values of Λ_0 for successive series also agree within a few hundredths of one per cent. There is little evidence of structure in the variation of computed values of Λ_0 as concentration increases. So far as present measurements are concerned, Onsager's equation holds within the limit of experimental error. This being so, it would seem that the present method of evaluating Λ_0 is preferable to the commonly used extrapolation method.

2. Ion Conductances.—In Table II are collected Λ_0 values for the different salts together with conductance values for the positive ions. Ion conductances are based on Daggett's value of 149.98 for the limiting conductance of potassium chloride and 73.58 for the conductance of the potassium ion. Values for the bromide and picrate ions are given in the table.

TABLE II

LIMITING CONDUCTANCES AT 25°

Salt	Λ_0	Λ_0^+
$Et\cdot Me_3NBr$	118.98	40.50
$Bu\cdot Me_3NBr$	111.73	33.25
$Hex\cdot Me_3NBr$	107.70	29.22
$Oct\cdot Me_3NBr$	104.68	26.20
$Dec\cdot Me_3NBr$	102.50	24.02
$Dodec\cdot Me_3NBr$	100.76	22.28
$Tetrad\cdot Me_3NNO_3$	92.50	21.12
$Ph\cdot Me_3NBr$	112.79	34.31
Me_4NPi	75.21	44.82
Me_3NHBr	125.10	46.62
$Me_2\cdot NH_2Cl$	127.85	51.45
$MeNH_3Cl$	134.22	57.82
KPi	103.97	30.39[a]
KBr	152.06	78.48[a]

[a] Negative ion.

The manner in which ion conductances vary as a function of the number of carbon atoms in the chain is of interest. In Fig. 1 are plotted values of the reciprocal of the conductance viscosity product, $1/\Lambda_0^+\eta$ as a function of the number of carbon atoms in the ions. In the same figure are shown ion resistances for the symmetrical quaternary ammonium ions as measured by Daggett.[5] The resistances of the ethyl-, butyl- and hexyltrimethylammonium ions are greater than those of corresponding symmetrical ions. Beginning with the octyltriphenylammonium ion, the resistances are less than those of corresponding symmetrical ions. For the longer chain, unsymmetrical ions, 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]

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

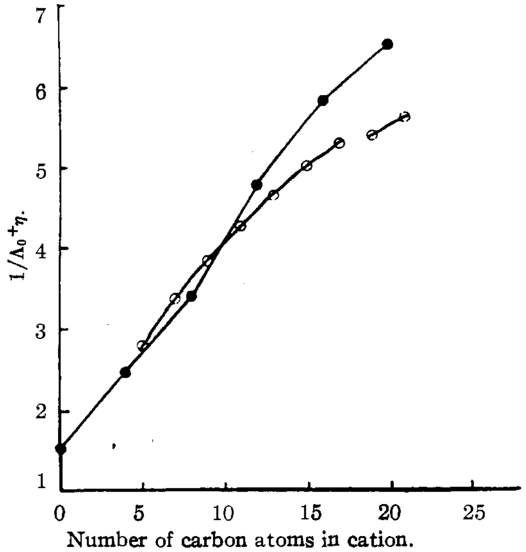

Fig. 1.—Ion resistances as function of number of carbon atoms: ●, symmetrical; ○, unsymmetrical trimethyl.

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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.

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(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).