[CONTRIBUTION FROM THE METCALF RESEARCH LABORATORY OF BROWN UNIVERSITY]

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

BY EDWARD J. BAIR[2] AND CHARLES A. KRAUS

The conductance of dodecyl-, tetradecyl-, hexadecyl- and octadecyl-trimethylammonium salts has been measured to low concentrations. For the dodecyl and the tetradecyl salts, the slopes of the $\Lambda-\sqrt{C}$ plots are normal, conforming to the Onsager equation within the limit of experimental error. For the hexadecyl and the octadecyl salts, the slopes are much greater than the theoretical, approximating that of 2–1 salts. The equivalent ion resistance of the long chain ions is markedly less than that of symmetrical quaternary ammonium ions having the same number of carbon atoms. The curve of equivalent resistance against the number of carbon atoms in the cations exhibits a break between the tetradecyl- and the hexadecyltrimethylammonium ions; the ions of shorter chains have a relatively higher resistance.

I. Introduction

Kuhn and Kraus[3] have measured the conductance of dodecylammonium chloride and octadecyltrimethylammonium chloride and nitrate in aqueous solution at low concentrations. The dodecyl salt is normal in its behavior; the slope of the $\Lambda-\sqrt{C}$ plot follows the Onsager equation within the limit of experimental error. While the conductance of the other two salts varies as a linear function of $\sqrt{C}$, the lines exhibit slopes much greater than those of 1–1 salts. Indeed, the observed slopes are only slightly below that of a 2–1 electrolyte.

It seemed worthwhile to examine this unexpected phenomenon in somewhat greater detail. Accordingly, measurements were carried out with octadecyltrimethylammonium chloride, bromate and nitrate and hexadecyl, tetradecyl- and dodecyltrimethylammonium nitrate. The octadecyl and hexadecyl salts all exhibit slopes much greater than that of 1–1 electrolytes, while the tetradecyl and dodecyl salts conform to the theoretical relation for 1–1 salts.

For the octadecyl and hexadecyl salts, the critical concentration is very low so that it was found necessary to carry the measurements to concentrations well below 1×10^{-4} N. Since these salts do not follow the theoretical relation of Onsager, it was necessary to evaluate Λ_0 by graphical extrapolation. The improved technique of Daggett, Bair and Kraus[4] made it possible to carry out precise measurements to the lowest concentration (0.16×10^{-4}) with comparative ease.

II. Apparatus, Procedure and Materials

The apparatus and procedure employed were much the same as those of Daggett[4] and need not be described here. The cell, similar to that of Daggett, was provided with a magnetic stirrer. In measuring solutions of long chain salts, this stirrer is essential, since the properties of these solutions are such that any bubbles formed in mixing the solutions are very stable and tend to adhere tenaciously to the electrode surfaces.

Possible sources of error in the procedure were studied. On allowing the equilibrated cell to stand open in the conditioned box overnight, the conductance change was of the order of 0.5%; on allowing the capped cell to stand overnight, the maximum change observed was 0.05%. This change may well have been due to the solution of impurities. In practice, the cell, after filling with water, was allowed to stand for an hour or more in the thermostat after temperature equilibrium was established; if the conductance changed appreciably, the cell was recleaned.

On introducing the cups containing the salts, the cell was open to the box atmosphere for not more than ten seconds. The maximum change observed in the specific conductance of water on introducing an empty cup amounted to 0.07%. The maximum error introduced at concentrations as low as 0.16×10^{-4} N, due to uncertainty of solvent correction, amounted to about 0.02%.

Salts were prepared by conventional methods and purified by recrystallization from suitable solvents.

N-Octadecyltrimethylammonium nitrate was recrystallized four times from acetone (Series I) and then from hexane with 3% alcohol added (Series II); m.p. 200–210°.

N-Octadecyltrimethylammonium bromate was recrystallized from acetone four times for Series I and six times for Series II; m.p. 210° dec.

N-Octadecyltrimethylammonium chloride was recrystallized from acetone with a few drops of ethanol added to increase its solubility; m.p. 220° dec.

N-Hexadecyltrimethylammonium nitrate was recrystallized from acetone with a few drops of ethanol added, three times for Series I and six times for Series II; m.p. 190–200°.

N-Dodecyltrimethylammonium nitrate was recrystallized twice from absolute ethanol and once from acetone with a few drops of ethanol added (Series I), then twice from acetone–ethanol (Series II); m.p. 200–210°.

Melting points are not sharp and do not serve as satisfactory indicators of purity in the case of salts of the type here employed. Check conductance measurements with recrystallization between series is a more reliable criterion.

III. Results

In Table I are recorded conductance values for the salts as measured for two independent series in each case. Concentrations are expressed in equivalents per liter of solution, assuming the density of the solution to be equal to that of water at 25°, namely, 0.99707 g./ml. In computing concentrations, the density of the long chain salts has been assumed to be equal to that of water. The error so introduced would be of the order of a few hundredths of one per cent. and within the limit of absolute error of these measurements. The purity of these salts is the limiting factor. Conductances are given to three places of decimals; relative values are reliable to the order of 0.01%. The specific conductance of the water used is given at the head of each series of measurements. All measurements were carried out at 25 ± 0.002°.

IV. Discussion

In Fig. 1, conductances are shown graphically as a function of the square root of concentration for

---

[1] This paper is based on a portion of a thesis presented by Edward J. Bair in partial fulfillment of the requirements for the Degree of Doctor of Philosophy in the Graduate School of Brown University, October, 1949.

[2] Graduate Fellow of the Stanolind Oil and Gas Company, Brown University, 1948–1949.

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

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

TABLE I

CONDUCTANCE OF LONG CHAIN SALTS IN WATER AT 25°

$C \times 10^4$	Λ	$C \times 10^4$	Λ
A. Octadecyltrimethylammonium nitrate			
$\kappa_0 = 5.218 \times 10^{-7}$		$\kappa_0 = 4.305 \times 10^{-7}$	
0.15904	90.790	0.19361	90.754
.32501	90.512	.38647	90.485
.60332	90.174	.70859	90.112
1.0882	89.784	1.2446	89.696
1.9244	88.867	2.0912	86.407
$\kappa_0 = 4.429 \times 10^{-7}$			
0.20742	90.660		
B. Octadecyltrimethylammonium bromate			
$\kappa_0 = 4.219 \times 10^{-7}$		$\kappa_0 = 5.065 \times 10^{-7}$	
0.16246	74.978	0.19843	75.180
.28745	74.754	.43143	74.568
.55918	74.470	.80570	74.273
1.0331	74.088	1.4976	73.825
2.0712	73.552	2.7004	73.326
C. Octadecyltrimethylammonium chloride			
$\kappa_0 = 4.971 \times 10^{-7}$		$\kappa_0 = 5.467 \times 10^{-7}$	
0.22323	95.583	0.18396	95.711
.43248	95.348	.44409	95.375
.82853	94.984	.80096	94.944
1.5977	94.461	1.5471	94.540
2.6956	93.930		
D. Hexadecyltrimethylammonium nitrate			
$\kappa_0 = 4.432 \times 10^{-7}$		$\kappa_0 = 5.146 \times 10^{-7}$	
0.17047	91.658	0.19195	91.591
0.51785	91.182	0.54116	91.117
1.2292	90.650	1.1064	90.690
2.6150	89.934		
E. Dodecyltrimethylammonium nitrate			
$\kappa_0 = 5.242 \times 10^{-7}$		$\kappa_0 = 6.475 \times 10^{-7}$	
0.46015	93.261	0.33960	93.360
0.89999	93.073	3.4961	92.357
1.8492	92.765		
3.6364	92.333		
		$\kappa_0 = 3.780 \times 10^{-7}$	
		0.23607	93.465
		.45184	93.234
		.87100	93.099
		1.6810	92.800

several salts. The diameter of the circles on the plots corresponds to 0.1% of the conductance value.

All the salts measured yield linear plots. The deviation of the measured values from the lines as drawn average 0.03% for all salts and the maximum is 0.037% for one salt.

1. **Slope.**—In Table II are given values of the slope for the five salts measured as well as that for tetradecyltrimethylammonium nitrate which was measured by Dr. M. J. McDowell.[5] The experimental slopes (col. 2) are compared with theoretical values[6] in columns 3, 4 and 5.

TABLE II

LIMITING SLOPES OF LONG CHAIN SALTS

Salt	Exp. slope	Onsager slope	Ratio exp. theor.	Onsager 2-1 slope
Octd Me_3NNO_3	152	81.1	1.88	151.6
Octd Me_3NBrO_3	137	77.5	1.76	143.3
Octd Me_3NCl	144	84.0	1.72	153.6
Hexd Me_3NNO_3	142	81.3	1.75	152.1
Tetd Me_3NNO_3	81.4	81.4	1.00	...
Dod Me_3NNO_3	81.7	81.7	1.00	...

For the dodecyl- and the tetradecyl-trimethylammonium salts, the limiting slopes are equal to the theoretical of Onsager within the limit of experimental error. It is of interest to note that for the dodecyl salt, Λ_0 values computed by means of the Onsager equation for 10 points in 3 series yield an average value of 93.86 with an average deviation of 0.024 Λ unit. The concentration range is from 0.236×10^{-4} to 3.636×10^{-4} *N*.

For the hexadecyl and octadecyl salts, the slopes are approximately 75% greater than that predicted for a 1–1 salt. The slope of octadecyltrimethylammonium nitrate is that of a 2–1 salt; the slopes of the other octadecyl and hexadecyl salts are approximately 5% less than that of a 2–1 salt. The broken lines of Fig. 1 indicate the slopes for 1–1 salts.

The steeper slope might be accounted for on the basis of ion-pair formation. However, in view of the fact that the tetradecyl and dodecyl salts behave normally, it seems unlikely that ion-pairs are formed in the case of salts with longer chains. It is more probable that association occurs between the long chain ions. If two long chain ions were to associate, the behavior of the resultant ion would simulate that of a 2–1 electrolyte. Whatever view we may take, it is a fact that interaction of some sort occurs in the case of ions having chains of 16 or more carbon atoms; such interaction does not occur in the case of ions having shorter chains.

2. **Ion Conductances.**—In Table III are presented Λ_0 values based on the results of Table I. Ion conductances for the positive ions are given in the last column of the table. These values are based on Daggett's value, 149.98, for the limiting conductance of potassium chloride and 73.58 for the potassium ion. We have used Daggett's value[4] for the bromate ion and Shedlovsky's value for the nitrate ion.

TABLE III

ION CONDUCTANCES

Salt	Λ_0	Λ_0^-	Λ_0^+
Octd Me_3NNO_3	91.40	71.38	20.02
Octd Me_3NBrO_3	75.50	55.66	19.94
Octd Me_3NCl	96.29	76.40	19.89
Hexd Me_3NNO_3	92.20	...	20.82
Tedt Me_3NNO_3	92.50	...	21.12
Dod Me_3NNO_3	93.86	...	22.48

The three values obtained for the conductance of the octadecyltrimethylammonium ion are in reasonably good agreement, considering the difficulty with which these salts are purified. An average value of 19.95 ± 0.05 is most probable.

The manner in which ion conductances or, better, ion resistances, vary with chain length is of inter-

---

(5) M. J. McDowell, Thesis, Brown University, 1950.

(6) In computing constants of the Onsager equation, the dielectric constant of water at 25° was taken to be 79.54 and the viscosity 8.949×10^{-3} poise.

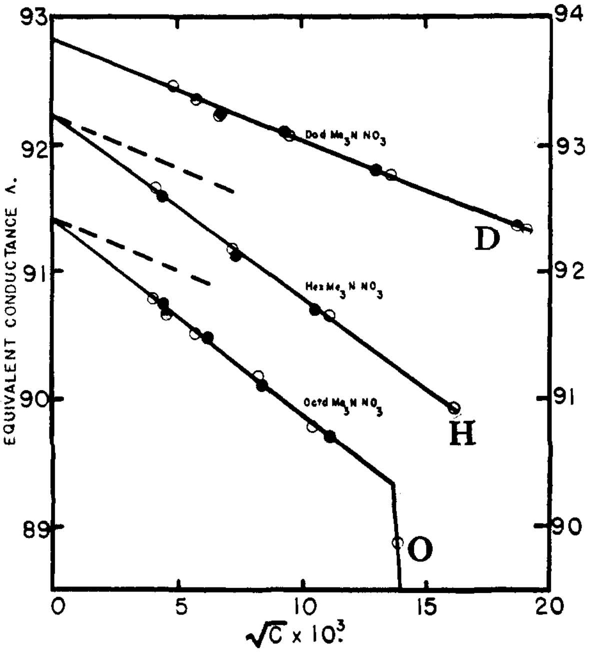

Fig. 1.—Λ-$\sqrt{C}$ plots for salts in water (broken lines, Onsager slope).

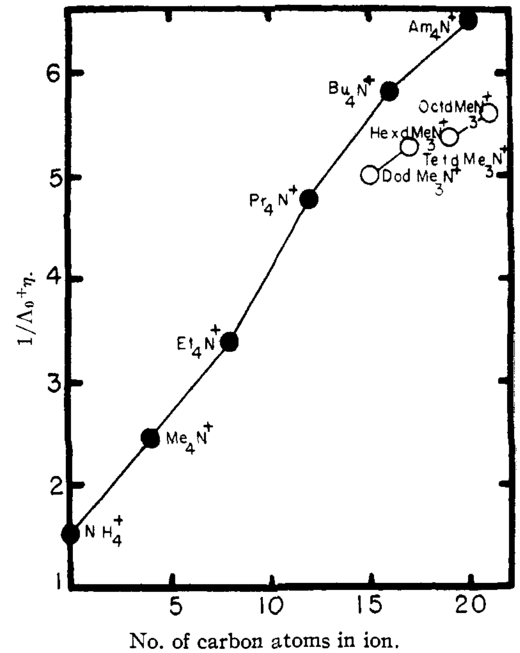

Fig. 2.—Resistance plots for quaternary ammonium ions in water.

est. In Fig. 2 are plotted values of the reciprocal of the ion resistance–viscosity product, $1/\Lambda_0{}^+\eta$, as a function of the number of carbon atoms in the ions. On the same plot are shown resistance values for the symmetrical quaternary ammonium ions as determined by Daggett.[4] For the same number of carbon atoms, the resistance of the long chain ions is markedly lower than that of corresponding symmetrical quaternary ammonium ions. It will be noted, too, that there is a break in the resistance curve between the tetradecyl- and the hexadecyltrimethylammonium ions. Such a break is not unexpected in view of the differences in the slopes which appear in the Λ–$\sqrt{C}$ plots for the same salts.

Providence 12, R. I. Received September 15, 1950

[Contribution from the Institute of Polymer Research, Polytechnic Institute of Brooklyn]

Effect of Ultraviolet Light on the Specific Activity of Chymotrypsin and Trypsin[1]

By Harry Goldenberg[2,3] and A. D. McLaren

Introduction

It has been shown that the quantum yield for inactivation of pepsin at 2537 Å. is the same with either casein or hemoglobin as a substrate for assay of enzymatic activity.[4] Verbrugge[5] reported, however, that trypsin gave a higher quantum yield with Anson's colorimetric hemoglobin method[6] for estimating tryptic activity than was obtained with titrimetric methods for following the digestion of hemoglobin, casein and benzoyl-L-argininamide (BAA). This finding has been questioned for reasons cited elsewhere.[7] Consequently we have repeated the work of Verbrugge to redetermine the effect of ultraviolet light (2537 Å.) on the specific activity of trypsin. In addition we have determined the quantum yield for the inactivation of chymotrypsin as calculated from its loss in ability to hydrolyze casein, L-phenylalaninamide (PA), glycyl-L-phenylalaninamide (GPA), L-phenylalanine ethyl ester (PEE) and chloroacetyl-DL-phenylalanine ethyl ester (CAPEE).

Experimental

Enzymes.—Three samples of crystalline chymotrypsin were used: six-times crystallized enzyme, salt free, supplied

---

(1) Photochemistry of Proteins. XIII.

(2) From the Ph.D. Thesis of H. Goldenberg, Polytechnic Institute of Brooklyn, 1950. Predoctoral Fellow of the National Institutes of Health, 1947–1949.

(3) The Department of Biochemistry, Jewish Hospital of Brooklyn, N. Y.

(4) A. D. McLaren and S. Pearson, *J. Polymer Sci.*, **4**, 45 (1949).

(5) F. Verbrugge, *J. Biol. Chem.*, **149**, 405 (1943).

(6) M. L. Anson, *J. Gen. Physiol.*, **22**, 79 (1938).

(7) A. D. McLaren, *Advances in Enzymology*, **9**, 75 (1949).