Acknowledgment.—The guidance and advice of Dr. D. C. Smith are gratefully acknowledged.

Summary

The reaction of benzaldehyde and certain substituted derivatives with ethanolamine gives compounds with the Schiff base structure rather than the oxazolidine ring structure previously assigned to these compounds.

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[CONTRIBUTION FROM THE METCALF RESEARCH LABORATORY OF BROWN UNIVERSITY]

Properties of Electrolytic Solutions. XLVI. Conductance of Long Chain Salts at Low Concentration in Water[1]

BY DONALD W. KUHN[2] AND CHARLES A. KRAUS

I. Introduction

In the limit, the conductance of ordinary salts in aqueous solution changes with concentration in accordance with Onsager's theory, in that the conductance is a linear function of the square root of concentration. The slope of this line is predetermined by the limiting conductance, Λ_0, the charges on the ions and the dielectric constant and the viscosity of the solvent.

It has commonly been assumed that solutions of long chain salts conform to this relation from the lowest concentrations up to the critical point where the course of the conductance curve changes abruptly. If the critical concentration is high, deviation occurs as in the case of ordinary salts. In brief, it has commonly been assumed that long chain salts behave like normal electrolytes at concentrations below the critical.

It should be noted, however, that up to now, there have been no measurements with long chain salts of sufficient precision to warrant any definite conclusion as to the course of the conductance curve at low concentrations. While the indications are that the conductance varies linearly as a function of the square root of concentration, the measurements have been carried out at relatively high concentrations and the experimental data are not sufficiently precise to fix the slope of the straight line with certainty. Chance observations in this laboratory have led us to suspect that the slope of the $\Lambda-\sqrt{C}$ curve might be greater than the theoretical, particularly in the case of salts with very long chains. Accordingly, it was thought worth while to investigate the precise course of the conductance curve of long chain salts at concentrations below the critical.

Since the critical concentration of salts with very long chains is often quite low (2.0×10^{-4} N), it was necessary to devise suitable techniques for carrying out conductance measurements at very low concentrations. The specific conductance of ordinary distilled water is of the order of 1×10^{-6} mho. The equivalent conductance of long chain salts is in the neighborhood of 100. The specific conductance of a 5×10^{-5} N solution is, therefore, 5×10^{-6}, or 5000×10^{-9} mho. It is obvious that if the conductance of the salt is to be determined with precision, the conductance of water must be known to a few units in the ninth place of decimals.

Shedlovsky and his co-workers have elaborated a technique that has proved quite successful with solutions of ordinary salts in water. This technique, however, is not readily applicable to solutions of long chain salts, chiefly because bubbles formed in stirring are very stable and cling tenaciously to the electrodes and the walls of the cell. It appeared desirable, therefore, to devise a technique adapted to solutions of long chain salts.

The method, as finally employed, consists in carrying out all manipulations with the conductance cell in a closed chamber similar to the well-known "dry box." The carbon dioxide content of the atmosphere within this chamber is controlled and manipulations are carried out within the box by means of long-sleeved rubber gloves. An attempt was first made to absorb all the carbon dioxide but this did not prove successful. It was found, however, that by passing the air from the atmosphere through an aspirator pump and then through the box, water in equilibrium with this air had a specific conductance of approximately 0.4×10^{-6} which was very constant. The pH of the tap water was 9, which accounts for the low value of the specific conductance of water in equilibrium with air from the aspirator pump.

II. Apparatus and Procedure

1. **The Conditioning Box.**—As a chamber within which to carry out manipulations, a stainless steel "dry box" was employed; the top of the box consisted of a sheet of lucite. The box was provided with an air-lock which was provided with a movable platform and closures to the box and to the external atmosphere. These devices could be conveniently manipulated from without the box. Air from without the laboratory was passed through three aspirator pumps, the air and water being discharged into a chamber of about 5 gallons capacity. From this chamber the air was piped into the box as well as into the air-lock. From the chamber the air passed out through three cylindrical metal guard chambers each of about 2 gallons capacity. The purpose of the guard chambers was to ensure that no air from without was introduced into the box during manipulations with the rubber gloves.

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(1) This paper is based on a portion of a thesis presented by Donald W. Kuhn in partial fulfillment of the requirements for the Degree of Doctor of Philosophy in the Graduate School of Brown University, May, 1949.

(2) Du Pont Postgraduate Fellow in Chemistry, Brown University, 1947–1948.

2. **Conductance Cell.**—Several cells of the erlenmeyer type and of 500-cc. capacity were employed. They were provided with ground glass caps which were lubricated with silicone lubricant. The electrodes of the cells were lightly platinized and the constants were determined by intercomparison with a standard cell whose constant was based on the conductance values of Jones and Bradshaw.

3. **Weight Buret.**—The buret used for introducing a known solution into the conductance cell consisted of a cylindrical tube of approximately 60-cc. capacity. Attached to the tube near the top and parallel to it was a graduated tube of 16 cc. capacity carrying a stopcock at the bottom. A 10-cm. length of smaller tubing was attached to the stopcock and bent at an angle of 105°. This tube was provided with a cap. To introduce solution into the cell, the buret was tilted and the desired amount of solution was run into the graduated chamber. The delivery tube was introduced into the cell which was positioned at an angle of about 30° with the horizontal. The stopcock was then opened and the solution allowed to run into the cell. Thereafter the stopcock was closed and the delivery tube capped. The stopcock was lubricated with silicone grease; it was shown that this grease does not affect the conductance of water.

4. **Measuring Apparatus.**—Resistances were measured with a Jones bridge. In the case of high resistances, a 30,000 ohm shunt was employed. This shunt was shown to give reliable results by checking with a precision, parallel arm bridge especially designed for high resistances. The cell was placed in an oil thermostat whose temperature was maintained at 25 ± 0.005°.

5. **Materials.**—Water was prepared by the method of Kraus and Dexter.[3] Since the water was later saturated with carbon dioxide at the concentration of the atmosphere in the box, no attempt was made to obtain ultrapure water. In general, its specific conductance varied between 0.1 and 0.2 × 10^{-6}. The water was collected and stored in a 3-liter vitreosil flask which was kept in the box.

Octadecyltrimethylammonium chloride was prepared by refluxing the iodide with silver chloride in methanol. It was recrystallized from an ethyl acetate–methanol mixture and four times from acetone to which a few drops of methanol had been added; m.p. 220°.

Octadecyltrimethylammonium nitrate was prepared by treating the iodide with silver nitrate in ethanol solution. It was recrystallized from acetone, m.p. 210°.

Dodecylammonium chloride was prepared by treating the amine with hydrochloric acid. It was recrystallized from ethanol and from acetone, m.p. 182–183°.

All salts were dried *in vacuo* and were recrystallized between series of measurements.

6. **Procedure.**—The cell, after cleaning, drying and weighing, was introduced into the box. Air from the box was drawn through the cell to eliminate carbon dioxide; thereafter, it was washed several times with water from the stock flask and, finally, filled with several hundred cc. of water. Air from the box was now drawn through the water to bring it into equilibrium with the box atmosphere. The cell was then removed from the box and the resistance of the water determined. It was allowed to stand for an hour or more to ensure constancy. The cell was then returned to the box.

A flask containing the desired weight of salt was introduced into the box, the air was replaced and the required amount of water was added. After weighing, solution was introduced into the weight buret. After weighing the buret, the desired amount of solution was introduced into the cell. It required about one minute to carry out this operation. Thereafter, the buret was reweighed and the conductance of the solution in the cell measured. It might be noted at this point that it was necessary to exercise care not to produce bubbles in the process of mixing the solution. The above operations were repeated until the desired concentration was reached.

III. Results

In Table I are presented the measured equivalent conductance values for dodecylammonium chloride and octadecyltrimethylammonium nitrate and chloride. Concentrations are expressed in moles of salt per liter of solution, the density of the solution being taken to be the same as that of water, 0.99709 g./ml. The density of the salts was taken to be the same as that of water, at the low concentration of the solutions, the error so introduced is negligible. The specific conductance of the water as measured in the cell is given at the head of each series of measurements.

TABLE I

CONDUCTANCE OF SALTS IN WATER AT 25°

A. *n*-Dodecylammonium Chloride

$k_0 = 0.430 \times 10^{-6}$		$k_0 = 0.332 \times 10^{-6}$		$k_0 = 0.372 \times 10^{-6}$	
$C \times 10^4$	Λ	$C \times 10^4$	Λ	$C \times 10^4$	Λ
2.0348	99.11	2.1030	99.06	2.2004	98.99
3.9436	98.60	3.7624	98.63	4.3429	98.48
7.5356	97.96	7.1317	98.02	8.4330	97.78
13.303	97.21	12.417	97.29	15.635	96.89

B. *n*-Octadecyltrimethylammonium Nitrate

$k_0 = 0.3296 \times 10^{-6}$		$k_0 = 0.3160 \times 10^{-6}$	
$C \times 10^4$	Λ	$C \times 10^4$	Λ
0.65063	90.20	0.66301	90.07
1.0558	89.75	1.0132	89.70
1.3820	89.52	1.2967	89.53
1.7410	89.25	1.7747	89.19
$k_0 = 0.3450 \times 10^{-6}$		$k_0 = 0.3282 \times 10^{-6}$	
0.22297	90.67	0.73982	90.11
		1.2353	89.65

C. *n*-Octadecyltrimethylammonium Chloride

$k_0 = 0.3187 \times 10^{-6}$		$k_0 = 0.3533 \times 10^{-6}$		$k_0 = 0.3379 \times 10^{-6}$	
$C \times 10^4$	Λ	$C \times 10^4$	Λ	$C \times 10^4$	Λ
0.89525	94.91	0.89964	94.93	0.71670	95.02
1.5085	94.54	1.3317	94.63	1.2472	94.63
2.2712	94.23	1.8020	94.40	1.7058	94.42
3.2296	93.55	2.2482	94.22	2.2599	94.19

IV. Discussion

The experimental results of Table I are shown graphically in Figs. 1 and 2, equivalent conductances being plotted as ordinates against the square root of concentration as abscissas. The diameter of the circles corresponds to one-tenth per cent. of the observed conductance values.

The measured conductance values are evidently a linear function of the square root of concentration within the limit of experimental error. The straight lines have been extrapolated to the axis of ordinates and values of Λ_0 have been obtained. These are collected in column 2 of Table II and ion conductances are given in column 3.

TABLE II

CONSTANTS OF SALTS IN WATER AT 25°

Salt	Λ_0	Λ_0^+	Slope obs.	Slope theoret.
$DodNH_3Cl$	100.25	23.83	83.3	83.3
$OctdMe_3NNO_3$	91.50	20.06	141.2	81.1
$OctdMe_3NCl$	96.30	19.88	142.8	82.4

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[3] Kraus and Dexter, THIS JOURNAL, **44**, 2468 (1922).

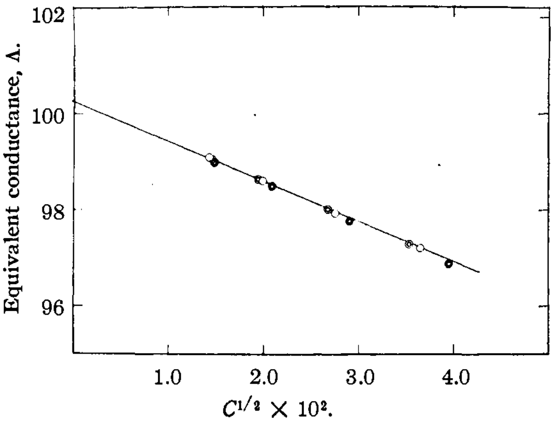

Fig. 1.—Conductance of dodecylammonium chloride in water at 25°.

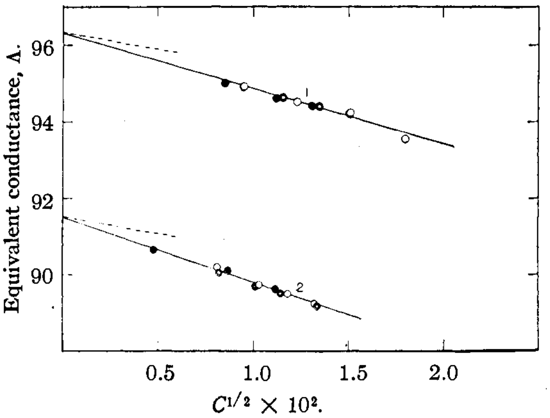

Fig. 2.—Conductance of salts in water at 25°; plot (1), octadecyltrimethylammonium chloride; plot (2), octadecyltrimethylammonium nitrate; broken lines indicate theoretical slope for 1–1 salt.

Assuming 76.42 and 71.44 for the conductance of the chloride and the nitrate ion, respectively, we obtained 19.88 and 20.06 for the conductance of the octadecyltrimethylammonium ion from the measurements with the chloride and the nitrate, respectively. We thus obtain a mean value of 20.0 ± 0.1. The variation is within the limit of experimental error.

As may be seen from Figs. 1 and 2, the experimental conductance values vary as a linear function of the square root of concentration within the limit of experimental error. The slope of the dodecylammonium chloride curve is 83.3 which is the theoretical value. However, as may be seen from Table II, columns 4 and 5, the slope for octadecyltrimethylammonium nitrate and chloride is much greater than the theoretical value. Indeed, the slopes for these two salts approximate that of a 2–1 salt.

It might be suggested that the greater slope is due to ion-pair formation. Not only is such an hypothesis improbable on the basis of the high dielectric constant of water, observations in this Laboratory[4] with corresponding salts of shorter chain length show that such salts behave like normal 1–1 electrolytes. As noted above, dodecylammonium chloride has a normal slope. It might be suggested that in the case of the hexadecyl and octadecyl salts, the long chain ions pair up and thus exhibit the behavior of 2–1 salts.

V. Summary

1. An improved technique is described for the measurement of the conductance of aqueous salt solutions at low concentration.

2. The conductance of dodecylammonium chloride and of octadecyltrimethylammonium chloride and nitrate has been measured at low concentrations.

3. Limiting conductances and ion conductances have been derived from the measured values.

4. Dodecylammonium chloride conforms to the Onsager relation within the limit of experimental error. For octadecyltrimethylammonium chloride and nitrate, the slope of the Λ *vs.* $\sqrt{C}$ plots is much greater than that of a 1–1 salt and approximates that of a 2–1 salt.

PROVIDENCE, R. I. RECEIVED FEBRUARY 4, 1950

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[4] Harry M. Daggett, Thesis, Brown University, June, 1949, Edward J. Bair, Thesis, Brown University, September, 1949.