Electrical Conductance, Density, and Viscosity of Aqueous Solutions of Hydroxylammonium Chloride at 25° C.

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Data for electrical conductance, density, and viscosity have been obtained for aqueous solutions of hydroxylammonium chloride at 25° C. for the concentration range, 0.0505*M* to 3.507*M*. A comparison of conductance data for this salt with similar data for potassium chloride, another strong electrolyte, suggests that associated ionic species, involving hydroxylammonium ion, may be present in aqueous solutions of the former salt. For the concentration range, 0.0505*M* to 1.872*M*, first-order equations for viscosity as functions of concentration are $\eta = 3.667 \times 10^{-2}C + 0.8903$ and $\eta = 5.599 \times 10^{-2}C^{1/2} + 0.8761$. Standard deviations are 8.0774×10^{-4} and 4.8875×10^{-3}, respectively.

IN PRELIMINARY studies of the properties of aqueous solutions of hydroxylammonium chloride, measurements were made of the conductance, viscosity, and density of the salt solutions for concentrations ranging up to 3.507*M*. Data for these properties do not appear to have been reported previously for aqueous solutions of the salt.

EXPERIMENTAL

Solutions. Conductance water was the solvent in all solutions of this investigation. The minimum measured resistance of this water was 7.7×10^6 ohms in a conductance cell of cell constant 1.0753 cm.$^{-1}$ Stock solutions of approximately 0.1*M* and 3.5*M* hydroxylammonium chloride were prepared by using the requisite amounts of the analytical reagent grade of the salt. The solutions were standardized by the ferric salt method (*1*). Solutions of other concentrations were prepared quantitatively by diluting precise volumes of the stock solutions with conductance water in volumetric flasks. Spot standardizations of these solutions revealed that the concentrations were the same as those expected from the dilution procedure.

Conductance Measurements. Resistances of all solutions were measured by means of the precision Jones Conductivity Bridge (Leeds & Northrup Co. No. 4666) and other high-quality companion accessories at a frequency of 2000 cycles. Conductance cells, with lightly platinized electrodes, were of the Jones-type (Leeds & Northrup Co. Nos. 4944 and 4947). The cell constant in each case was calculated as the product of the accepted literature value of the specific conductance of 0.01 demal KCl at 25.0° C. and the measured resistance of that solution in the cell at the same temperature.

The resistances of the hydroxylamine solutions decreased with time and were accompanied by a slight decrease in concentration. This change in concentration was due to catalytic decomposition of the salt in the presence of the platinized electrodes. Moews and Audrieth (*3*) report that the autoxidation of aqueous hydroxylamine solutions is catalyzed by metals. In the present report, the decomposition was of the order of 4% for some of the solutions at the end of 25 hours. However, the change of resistance with time is linear for a period of at least 2 minutes. Because of this fact, it was possible, for resistance-time data taken over this interval and for all concentrations, to obtain the desired resistance at zero time by extrapolation. Thus, the conductance data of Table I are, in effect, values for the solutions at a time when no measurable change had occurred in the concentrations of the active components.

Table I. Conductances and Densities of Aqueous Solutions of Hydroxylammonium Chloride at 25° C.

Salt Concn., *C*, Mole Liter^{-1}	Spec. Cond., κ, Mho Cm.$^{-1}$	Density, ρ, Gram Cm.$^{-3}$	Equiv. Cond., Λ, Mhos Cm.^{2} Equiv.$^{-1}$
0.000535	0.0000772		144.3
	0.0000777		145.2
0.00102	0.000146	0.9971	143.0
	0.000146		143.0
0.00475	0.0006459	0.9973	135.8
	0.0006455		135.9
	0.0006452		135.9
0.0100	0.001286	0.9974	128.6
	0.001286		128.6
0.0152	0.001860		122.7
	0.001868		123.2
0.02067	0.002395	0.9977	115.85
	0.002396		115.90
0.03032	0.003496	0.9982	115.3
	0.003496		115.3
0.03046	0.003494		114.7
0.04023	0.004602	0.9984	114.4
	0.004603		114.4
0.0505	0.005650	0.9988	111.9
	0.005640		111.7
0.05955	0.006670	0.9991	112.0
	0.006675		112.1
0.07071	0.007708	0.9995	109.0
	0.007701		108.9
0.07937	0.008719	0.9998	109.9
	0.008726		110.1
0.0919	0.009711	0.9999	105.7
	0.009705		105.6
	0.009705		105.6
0.1051	0.01077	1.0003	106.1
	0.01079		106.3
	0.01078		106.2
0.5280	0.05058	1.0177	95.8
	0.05061		95.9
1.078	0.09026	1.0291	83.7
	0.09028		83.8
1.445	0.1157		80.1
	0.1157		80.1
1.872	0.1387	1.0502	74.1
	0.1387		74.1
3.507	0.2142	1.0921	61.1
	0.2141		61.1
	0.2141		61.1

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Viscosity and Density Measurements. Specific gravity bottles (Fisher No. 3-230) of 25-ml. capacity and with thermometers of an accuracy within ±0.2° C. were used for measuring the densities of the solutions.

Calibrated viscometers of the Cannon-Fenske-Ostwald-type (Cannon Nos. 25-J-288 and 25-J-328) were used to measure the viscosities of the solutions. Efflux times, of the order of 600 seconds, were determined to 0.1 second with a calibrated stopwatch.

The temperatures of all solutions employed in measurements of the three properties were maintained at 25.00 ± 0.01° C. in an aquarium-type constant temperature bath (Central Scientific Co. No. 97300-1). Data for the solutions are found in Tables I and II.

Table II. Viscosities[a] of Aqueous Solutions of Hydroxylammonium Chloride at 25° C.

Salt Concn., C, Mole Liter^{-1}	Viscosity	
	Centistoke	Centipoise[b] (η)
0.0505	0.8941	0.8915
0.0707	0.8954	0.8928
0.1015	0.8970	0.8944
0.5280	0.9136	0.9109
1.078	0.9316	0.9289
1.445	0.9458	0.9430
1.872	0.9622	0.9594
3.507	1.0427	1.0396

[a] Based on NBS value for pure water at 25° C.: 0.89294 centistoke or 0.89031 centipoise. [b] Centistokes × density of pure water at 25° C., where D_{H_2O} is 0.997050 gram cm.$^{-3}$.

DISCUSSION

Conductance Data. Up to the present time, no theory of conductance has been developed that will yield, for purposes of testing, a conductance equation for the range of concentrations reported in Table I. Analysis of the data by means of the theoretical equations of Onsager and/or Fuoss in the extremely dilute concentration region, for which such equations are valid, is not feasible because conductance data are reported for only three concentrations lower than 0.01*M*. However, some qualitative information on the conductances of aqueous solutions of hydroxylammonium chloride can be obtained by comparing these data with those given by Harned and Owen (*2*) for a uni-univalent salt such as potassium chloride. If the equivalent conductances of Table I are plotted *vs.* the square roots of the concentrations, the conductances decrease sharply (slope is −260.5 by the method of least squares) as $C^{1/2}$ changes from 0 to 0.15 (moles liter^{-1})$^{1/2}$. Extrapolation to infinite dilution yields the value, Λ_∞ = 153.15 mhos cm.^{2} equiv.$^{-1}$ for hydroxylammonium chloride. For aqueous KCl solutions in the same concentration range, the slope and Λ_∞ are −93.84 and 149.86 mhos cm.^{2} equiv.$^{-1}$ (*2*), respectively. Thus, both salts are strong electrolytes. The more pronounced negative slope for the hydroxylammonium chloride plot over this concentration range may be attributed to association of hydroxylammonium ions. This effect is in addition to the normal decrease in ionic mobilities. Structures suggested for possible dimers and trimers, with hydrogen bonding represented by broken lines, are illustrated in Figure 1. For salt concentrations of this report ranging from 0.0225*M* to approximately 0.1*M*, the decrease in conductance with increase in concentration is much less pronounced than for the more dilute range. Over this range, the conductances for hydroxylammonium chloride solutions are about 20 mhos lower than those for KCl solutions of the same concentration.

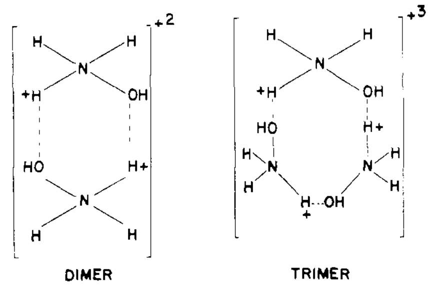

Figure 1. Associated species suggested for hydroxylamine solutions

Viscosity Data. The method of least squares has been used to obtain first-order equations for viscosity (η) as functions of concentration (C). For the concentration range, 0.0505*M* to 1.872*M*, the equations are $\eta = 3.667 \times 10^{-2} C + 0.8903$ and $\eta = 5.599 \times 10^{-2} C^{1/2} + 0.8761$. Standard deviations are 8.0774×10^{-4} and 4.8875×10^{-3}, respectively.

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