Electrical Conductances of Aqueous Potassium Nitrate and Tetramethylammonium Bromide Solutions to 800° C and 4000 Bars

ARVIN S. QUIST and WILLIAM L. MARSHALL
Reactor Chemistry Division, Oak Ridge National Laboratory, Oak Ridge, Tenn. 37830

The electrical conductances of 0.01 *m* solutions of potassium nitrate and tetramethylammonium bromide were measured to 800° C and 4000 bars. Specific conductances of potassium nitrate are reported as a function of pressure at the temperatures of the experimental measurements. Comparison of the conductances of potassium nitrate solutions with those of potassium chloride solutions of equal molality indicates that the mobility of the nitrate ion is less than that of the chloride ion at all temperatures and pressures. No evidence of significant hydrolysis or decomposition was observed with the potassium nitrate solutions. Comparison of specific conductances of tetramethylammonium bromide solutions with those of ammonium bromide solutions of equal molality indicates that the tetramethylammonium bromide solutions are unstable above 300° C.

IN CONNECTION with experimental studies of the behavior of aqueous electrolyte solutions at high temperatures and pressures, it was of interest to measure the electrical conductances of dilute solutions of potassium nitrate and tetramethylammonium bromide to 800° C and 4000 bars. A comparison of the behavior of KNO_3 with that previously observed for several potassium halides *(5)* would indicate whether or not extensive hydrolysis or decomposition of the nitrate ion occurred under these conditions. For example, if hydrolysis of the nitrate ion resulted in its displacement by the more mobile hydroxide ion, the resulting hydrolyzed solution would have a specific conductance significantly higher than the unhydrolyzed solution. Therefore, an approximate constancy in the relative conductance of a KNO_3 solution compared with a KCl solution of the same molality over a range of temperature (KCl does not appear to hydrolyze to 800° C) would suggest no significant hydrolysis of KNO_3. Similarly, by comparing the behavior of $(CH_3)_4NBr$ with that of NH_4Br *(3)*, information could be obtained on the stability of the tetramethylammonium ion in aqueous solutions at high temperatures and pressures.

The general experimental methods and details of the apparatus have been presented *(4)*. A 0.01000 *m* KNO_3 solution was prepared gravimetrically from reagent grade salt (J. T. Baker Chemical Co., Phillipsburg, N.J., 99.2% assay for KNO_3) and conductivity water. Tetramethylammonium bromide of 99.7% (or better) purity was prepared by methods described previously *(1)*, and a 0.01000 *m* solution was prepared from this material. The inner electrodes used for the conductance measurements had cell constants of 0.525 and 0.531 cm^{-1} as determined with 0.01 and 0.1 demal KCl solutions (defined as containing 0.745263 and 7.41913 grams of KCl per 1000 grams of solution, respectively) at 25.00° ± 0.01° C. At high pressures, the over-all accuracy of the measured specific conductances of the KNO_3 solutions was estimated to be better than ±2%. However, at low pressures, above the critical temperature of water of 374° C where relatively low solution densities were obtained, the conductance values approached zero and their uncertainties increased significantly. Decomposition of the tetramethylammonium bromide solutions above 300° C increased the uncertainty of the measured conductance values of this solution.

The results of the measurements on the KNO_3 solutions are shown in Figure 1, where specific conductances are plotted as a function of pressure at the various temperatures of the experimental measurements. Figure 2 compares the specific conductance of 0.01 *m* KNO_3 and KCl *(5)* solutions as a function of temperature at a pressure of 4000 bars. The results presented in Figure 2 indicate that although the mobility of the nitrate ion is less than that of the chloride ion at all temperatures, the behavior of these two electrolytes is qualitatively alike. Similar relative behavior is observed at lower pressures. The fact that KCl does not undergo appreciable hydrolysis under the same conditions probably indicates no unusual behavior (hydrolysis or decomposition) in these KNO_3 solutions.

Noyes and coworkers *(2)* measured the electrical conductances of dilute aqueous $AgNO_3$, $Ba(NO_3)_2$, and HNO_3 solutions to 306° C at saturation vapor pressures. Although under certain conditions decomposition and/or hydrolysis were reported to occur in these solutions, in general they were relatively stable to 306° C. The present results indicate that dilute KNO_3 solutions are stable to 800° C. Extensive studies were not performed to determine the stability of these solutions over long periods of time. However, during several experimental runs, conductances at elevated temperatures and at a constant pressure were monitored over periods of approximately one hour, with no significant change in conductance. The reproducibility of the data under conditions of increasing and decreasing pressures also furnished evidence of the stability of these solutions, at least over periods of time up to one hour. Possible instability over longer periods of time was indicated by low conductances of some solutions which had remained in the cell overnight while the cell cooled down from the high temperatures of the measurements.

Tetramethylammonium bromide solutions were found to be unstable at temperatures above 300° C. This behavior is shown in Figure 3, where the specific conductances of $(CH_3)_4NBr$ and NH_4Br are compared as a function of temperature at a constant pressure of 4000 bars. Below 300° C

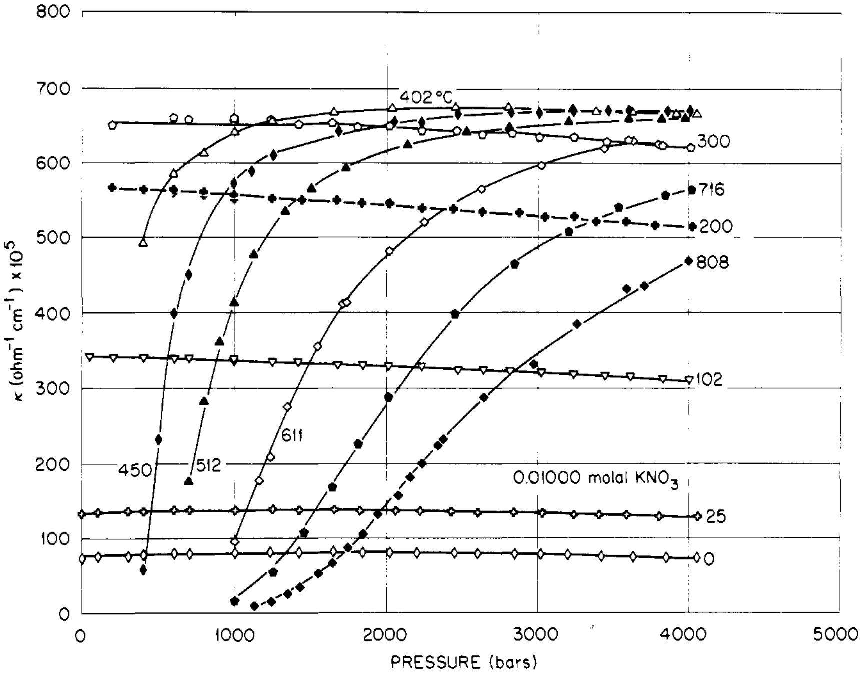

Figure 1. Specific conductances of 0.01000 *m* KNO_3 solutions as a function of pressure at several temperatures

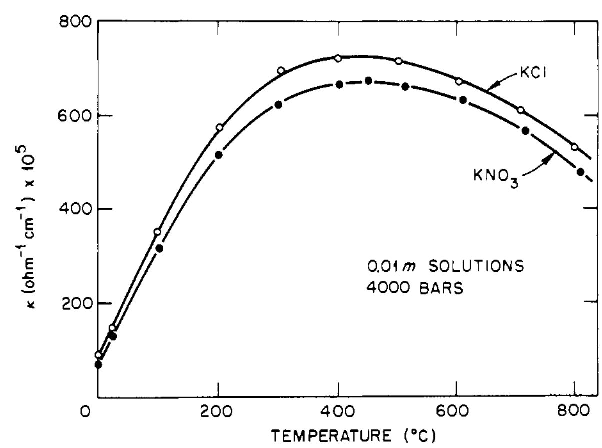

Figure 2. Comparison of specific conductances of 0.01 *m* KCl and KNO_3 solutions as a function of temperature at 4000 bars

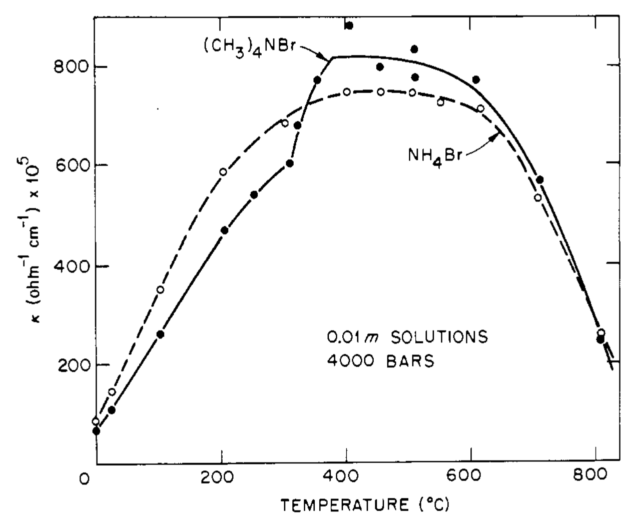

Figure 3. Comparison of specific conductances of 0.01 *m* NH_4Br and $(CH_3)_4NBr$ solutions as a function of temperature at 4000 bars

the conductance of $(CH_3)_4NBr$ is considerably less than that of NH_4Br, primarily because of the larger size of the tetramethylammonium ion as compared to the ammonium ion. Above approximately 300° C the conductance of the tetramethylammonium salt increases rapidly, indicating extensive decomposition or hydrolysis of this ion. Although the results are somewhat erratic in the temperature range 400° to 500° C, the conductance of the $(CH_3)_4NBr$ solution is essentially the same as that of the NH_4Br solution at higher temperatures. This behavior indicates that the final products of the hydrolysis of the tetramethylammonium ion probably include the NH_4^+ ion and some un-ionized carbon-containing molecules.

ACKNOWLEDGMENT

The authors acknowledge the technical assistance of Wiley Jennings in making the conductance measurements. They also express their thanks to Siegfried Lindenbaum for supplying the purified tetramethylammonium bromide.

LITERATURE CITED

(1) Lindenbaum, S., Boyd, G.E., *J. Phys. Chem.* **68**, 911 (1964).
(2) Noyes, A.A., Coolidge, W.D., Melcher, A.C., Cooper, H.C., Kato, Yogoro, Sosman, R.B., Eastman, G.W., Kanolt, C.W., Böttger, W., "Electrical Conductivity of Aqueous Solutions," Carnegie Institution of Washington, Washington, D. C., Pub. **63** (1907).
(3) Quist, A.S., Jennings, W., Jr., Marshall, W.L., "Reactor Chemistry Division Annual Progress Report for the Period Ending December 31, 1968," Oak Ridge National Laboratory, Rept. **ORNL-4400**, 74 (1969).
(4) Quist, A.S., Marshall, W.L., *J. Phys. Chem.* **72**, 684 (1968).
(5) *Ibid.*, **73**, 978 (1969).

RECEIVED for review August 13, 1969. Accepted March 13, 1970. Research sponsored by the U.S. Atomic Energy Commission under contract with the Union Carbide Corp.