

Electrical Conductances of Aqueous Sodium Iodide and the Comparative Thermodynamic Behavior of Aqueous Sodium Halide Solutions to 800° and 4000 Bars¹

by Lawrence A. Dunn² and William L. Marshall

Reactor Chemistry Division, Oak Ridge National Laboratory, Oak Ridge, Tennessee 37830 (Received September 9, 1968)

From electrical conductance measurements on dilute (0.001–0.10 *m*) aqueous solutions, the ionization behavior of NaI was studied in the temperature range 0–800° and at pressures to 4000 bars. Both the conventional (*K*) and complete (*K*⁰) ionization constants were calculated for comparison with published values for NaCl and NaBr. As expected, NaI ionized to a greater extent than either NaBr or NaCl, the order being directly proportional to the anion size. The net change (*k*) in waters of solvation on ionization decreased from 10.2 for NaCl to 9.7 for NaI. For the temperature range 400–800°, the van't Hoff isochore yielded standard thermodynamic functions for the complete equilibrium, NaX(solvated) + *k*H₂O ⇌ Na⁺(solvated) + X⁻(solvated). The Δ*H*⁰ obtained, approximately constant with temperature, was essentially the same as found for NaBr and NaCl. With the calculated values of Δ*G*⁰ and an average value for Δ*H*⁰ of -7.0 kcal mol⁻¹, standard entropy changes of -88.3, -86.2, and -82.9 cal mol⁻¹ deg⁻¹ for the complete reactions were obtained for NaCl, NaBr, and NaI, respectively. The negative values of Δ*S*⁰ show that order is increased by additional solvation on ionization of the electrolyte. Thus, at high temperatures, inclusion of the solvent as a reactant provides a simple description whereby each equilibrium can be described by only three values (*k*, Δ*H*⁰, and Δ*S*⁰) which are essentially independent both of temperature and pressure. The closeness in values of *k* and Δ*S*⁰ for the three halides suggests that averaged values from these salts may be used to estimate the equilibrium properties of most 1-1 salts between 400 and 800°.

Introduction

The properties of aqueous electrolyte solutions at high temperatures and pressures, particularly in the supercritical region, are amenable to investigation by conductance techniques. This method has been applied in several recent publications from this laboratory to the study of the behavior of dilute aqueous solutions of KHSO₄,³ NaCl,⁴ NaBr,⁵ and HBr⁶ to 800° and to pressures of 4000 bars. The results from these studies have indicated that, at high temperatures and pressures, aqueous electrolyte solutions exhibit a simplified be-

havior not evident at lower temperatures. It was found that the isothermal limiting equivalent conductances of these salts in the temperature range 100–800°

(1) Research sponsored by the U. S. Atomic Energy Commission under contract with Union Carbide Corp. Presented before the Division of Physical Chemistry at the 156th National Meeting of the American Chemical Society, Atlantic City, N. J., Sept 8–13, 1968.

(2) Mellon Institute, Carnegie-Mellon University, Pittsburgh, Pa. 15213.

(3) A. S. Quist and W. L. Marshall, *J. Phys. Chem.*, **70**, 3714 (1966).

(4) A. S. Quist and W. L. Marshall, *ibid.*, **72**, 684 (1968).

(5) A. S. Quist and W. L. Marshall, *ibid.*, **72**, 2100 (1968).

(6) A. S. Quist and W. L. Marshall, *ibid.*, **72**, 1545 (1968).

are linear functions of the solvent density.³⁻⁶ Moreover, at temperatures from 400 to 800°, the limiting equivalent conductances for a particular electrolyte were found to be independent of the temperature at constant solvent density.³⁻⁶

This paper presents conductance measurements of dilute (0.001–0.10 *m*) aqueous NaI solutions at temperatures from 0 to 800° and at pressures to 4000 bars. From these measurements limiting equivalent conductances of NaI were obtained at integral temperatures and densities. Ionization constants (*K*) for the conventional equilibrium, $\text{NaI} \rightleftharpoons \text{Na}^+ + \text{I}^-$, were also obtained where NaI behaves as a weak electrolyte. From these values the complete ionization constants (*K*⁰) for NaI were calculated at each temperature.^{7,8} These results were used for calculation of thermodynamic quantities for NaI for comparison with the previously published results for NaCl and NaBr.

For NaCl, NaBr, and NaI a unified behavior has been observed between 400 and 800° in the attainment of an essentially constant value of ΔH° , independent both of pressure and temperature, that describes the behavior of all three electrolytes. Similarly constant values of ΔS° and of the net change in waters of solvation (*k*) for each electrolyte have also been calculated.

Experimental Section

A detailed description of the high-pressure conductance equipment and procedures used has been given previously.⁴ The conductance cell with no pressure seals in the high-temperature region was used exclusively in this work. All solutions were prepared by weight from reagent grade NaI (Mallinckrodt Chemical Works) and conductivity water. The salt was dried for 24 hr at 120° before use. The conductivity water was obtained by passing distilled water through an ion-exchange column and then redistilling it twice from a fused quartz distillation unit. Conductivity measurements were made to 800° and 4000 bars on four solutions of NaI: 0.0009996, 0.005001, 0.05000, and 0.1000 *m*. Previous data of Quist and Marshall⁹ for 0.01000 *m* NaI solutions under the same conditions have been included in the calculations. Four different inner electrodes were used for the conductance measurements. Their cell constants ranged from 0.495 to 2.104 cm^{-1} , as determined from 0.01 and 0.10 demal KCl solutions at $25.00 \pm 0.01^\circ$.

Results and Discussion

Specific conductances and equivalent conductances were calculated from the experimental data in the manner described previously.⁴ An example of isothermal specific conductances of NaI solutions as a function of pressure at the temperatures of the measurements is shown in Figure 1. From comparable figures for all five molalities of NaI, specific conductances at integral pressures were obtained by interpolation. Isobaric

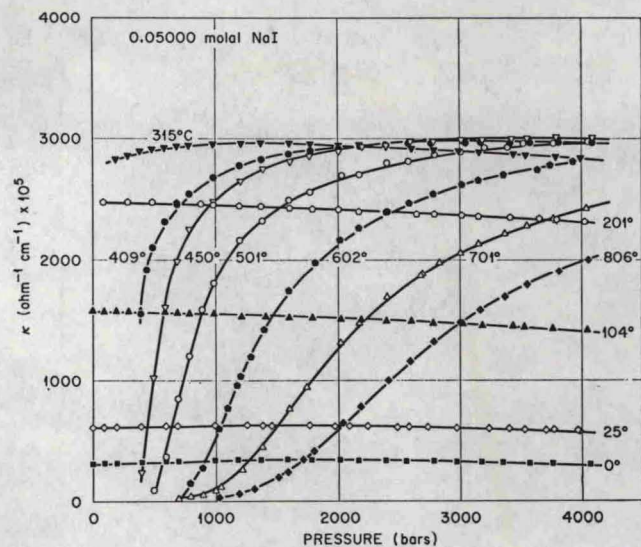


Figure 1. Specific conductances of 0.05000 *m* NaI solutions as a function of pressure at several temperatures.

specific conductances for 0.05000 *m* NaI solutions *vs.* temperature are shown in Figure 2, and isothermal equivalent conductances *vs.* solvent density in Figure 3. The other solutions of NaI exhibit similar behavior except that the density at which the equivalent conductance maximum occurs increases with increasing electrolyte molality. For 0.0009996 *m* NaI the maximum occurs near 0.50 g cm^{-3} , while it occurs at about 0.70 g cm^{-3} for 0.1000 *m* NaI solutions. Similar behavior has been observed for NaCl⁴ and NaBr⁵ solutions.

From plots like Figure 3 equivalent conductances at integral densities were obtained for each molality of NaI at the experimental temperatures. These values were then plotted against temperature at constant solvent density, and from smoothed curves through the data, equivalent conductances at various temperatures and densities were obtained. These are presented in Table I for temperatures from 100 to 800°, and include equivalent conductances for 0.01000 *m* NaI calculated from the specific conductances given elsewhere.⁹ Data obtained at 0 and 25° have been used only for comparative purposes as shown in Figures 1–3, and have not been included in Table I. The values in parentheses represent equivalent conductances at saturation vapor pressure at that temperature.

Calculation of Limiting Equivalent Conductances. From the conductance values in Table I limiting equivalent conductances were calculated by the several methods described previously,⁴ and with the computer programs developed earlier.³⁻⁶ At low temperatures and high densities the Robinson–Stokes equation,¹⁰ the

(7) W. L. Marshall and A. S. Quist, *Proc. Natl. Acad. Sci., U. S.*, **58**, 901 (1967).

(8) A. S. Quist and W. L. Marshall, *J. Phys. Chem.*, **72**, 1536 (1968).

(9) A. S. Quist and W. L. Marshall, *ibid.*, in press.

(10) R. A. Robinson and R. H. Stokes, *J. Amer. Chem. Soc.*, **76**, 1991 (1954).