Conductance of Aqueous Electrolyte Solutions at High Pressures

Data for Eleven 1,1 Electrolyte Systems

ALAN B. GANCY[1] and S. BARRY BRUMMER
Tyco Laboratories, Inc., Waltham, Mass. 02154

Electrical conductivity measurements accurate to 0.1% were made as a function of temperature, pressure, and solution concentration for the following dilute aqueous electrolyte systems: LiCl, NH$_4$Cl, KCl, NaCl, RbCl, CsCl, (Et)$_4$NCl, KF, KBr, KI, and KNO$_3$. Studies were made with solutions of concentrations from 3–15 mM, pressures from 1–2300 atm, and temperatures from 3–55°C. Concentration-dependent pressure ratios of conductance (κ_p/κ_1) were extrapolated to infinite dilution with the aid of the Debye-Hückel-Onsager conductance equation, modified for variation of pressure. The infinite dilution ratios, internally consistent to 0.05% and accurate to <0.2%, are fitted to a third-order polynomial in pressure. These polynomial coefficients are presented, as well as representative original electrical resistance data.

The earliest measurements on the pressure coefficient of electrical conductance of aqueous solutions were concerned more with the magnitude and direction of the pressure effect than with its theoretical significance. Zisman (31) applied the Debye-Hückel equation to his dilute aqueous solution data and purported to show that a large compressibility of the ions was necessary to account for the results. Other investigators studied the chemical effects of pressure on weak electrolyte ionization (4–6, 11, 12, 29). Horne et al. (14–22) made a number of investigations of the pressure coefficient of the conductance of dilute as well as seawater concentrations of aqueous solutions.

Impetus for accurate and systematic determination of conductivities under pressure was provided by the work of Jobling and Lawrence (25) who showed the importance of the density in helping to determine the viscosities of liquids. Following this line, Brummer and Hills (3, 4) determined pressure coefficients of electrolytic conductance in the context of the Stearn and Eyring model for ion conduction (28) and derived certain activation parameters of interest. Ovenden (27) was the first to attempt careful extrapolation of dilute aqueous solution data to zero concentration to eliminate ion-ion interactions from consideration.

None of the prior studies was either sufficiently detailed in scope or experimentally well characterized for the purposes of a detailed analysis of the conduction process. Consequently, we conducted a systematic investigation of several aqueous 1,1 electrolyte systems over ranges of temperature and pressure. This work differs from previous investigations in terms of its higher accuracy, extrapolation to infinite dilution, and the scope of both the temperature and the pressure variable. Literally hundreds of experimental measurements were made over a two-year period. In some cases reproducibility was tested with a year's time intervening and was better than 0.1%.

EXPERIMENTAL

Brief Review of Earlier Methods. A detailed review of the experimental methods of previous investigators was made in an earlier paper (8). Early workers (10) used Pt-in-glass cells for which corrections were not made for the variation

[1] Present address, Industrial Chemicals Division, Allied Chemical Corp., Solvay, N. Y. 13209. To whom correspondence should be addressed.

of cell constant with pressure. The high precision required for extrapolation to infinite dilution was not required for those higher concentration studies. Only one investigator appeared to have considered the criticality of the Pt-in-glass electrode seal (26). In some cases mercury was used to isolate the study solution from the pressure-transmitting fluid. In other cases an organic liquid was used (7, 14–22).

At pressures above 3000 atm the Pt-in-glass seal was no longer reliable, and a Teflon-bodied cell employing a tight-fitting Teflon piston was employed (24). Because of reports of several phase changes in Teflon occurring over the temperature and pressure ranges of interest (30), a Teflon-bodied cell with an internally supported electrode system was devised. The cell constant in this case varies as the pressure coefficient of the borosilicate glass support (7).

The first careful investigation of dilute solutions employed slightly modified conventional Pt-in-glass cells satisfactory to about 2000 atm (27). The rod-ring electrode configuration used in this work was later used to show the unsatisfactory nature of the parallel plate design with respect to the pressure coefficient of its cell constant (23).

In the present investigation Pt-in-glass cells were satisfactory but only after considerable modification of the electrode-to-glass seal. Close attention was also paid to the effect of mercury as an isolation medium, the effect of weak electrolyte impurities, and the pressure coefficient of the cell constant (8).

The Pt electrode connection to the borosilicate glass pressure cell electrode, for example, is effected through a graded glass seal formed around a thin Pt ribbon. This seal was reliable over the entire range of temperature and pressure employed here. Mercury was the preferred medium for solution isolation. To obviate mercury corrosion reactions, solutions were carefully deaerated. The high-pressure conductance cells were filled by manipulating the solutions with helium gas in a closed glass apparatus (8). Weak electrolyte contamination from all sources was negligible in our "clean" experiments simply by deliberately doping test solutions with known amounts of weak electrolyte impurity.

To obtain suitable values of the measured cell resistance, two types of electrode configuration were used: the rod-ring design for dilute solutions and a capillary design for the more concentrated ones. The interrelationship between pressure coefficients of cell constants for the two were exhaustively studied by employing both types simultaneously in one and the same cell. All results were converted to the rod-ring equivalent. The pressure coefficient of the cell constant for the latter was