

IONIC SOLUTIONS UNDER HIGH PRESSURES V

Pressure Effects on the Walden Products and Hydration of
 Et_4N^+ and ClO_4^- Ions in Water

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The electrical conductivities of aqueous solutions at high pressures up to 5,000 atm have been measured in the concentration range from 10^{-4} to 10^{-3}N for tetraethylammonium chloride, Et_4NCl at 25 and 40°C and for tetraethylammonium perchlorate, Et_4NClO_4 at 25°C. The equivalent conductances of the electrolytes at infinite dilution have been determined by means of the Onsager equation which was verified to be valid in the dilute solutions at high pressures in the previous papers^{1,2}. The limiting equivalent conductances determined at high pressures were separated into the single-ion ones on the basis of the same assumption as used in the previous paper². Although the limiting equivalent conductance of Et_4N^+ has a maximum against pressure at 25°C like other tetraalkylammonium ions, that of ClO_4^- , surprisingly and exceptionally, has no maximum even at 25°C where the viscosity of solvent water has a minimum at about 650 atm³. The Walden product of Et_4N^+ decreases slightly with increasing pressure at 25°C and, probably, so at 40°C like that of Me_4N^+ . On the other hand, the Walden product of ClO_4^- at 25°C dramatically decreases with increasing pressure. Thus, it is considered that the pressure dependence of the limiting equivalent conductance of the ion in water can not be explained merely in terms of such bulk properties of water as the viscosity and dielectric constant. These differences in the pressure coefficients of the Walden products were ascribed to the differences between the density of the hydration shell and that of the bulk water.

Introduction

Colladon and Sturm⁴) are the first persons to attempt to examine the effect of pressure on the electrical conductivities of electrolyte solutions, when it was not yet known what carries electricity in solution. In 1885, first of all, Fink⁵) established that pressure (up to 500 atm) does decrease the electrical resistances of electrolyte solutions; it was two years before the appearance of the Arrhenius

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theory for the behavior of electrolyte solutions. In the 1890's, Röntgen⁶⁾, Fanjung⁷⁾ and Tammann⁸⁾ first found a parallelism between the pressure dependence of the electrical conductivities of aqueous solutions and that of the solvent fluidity measured by Cohen⁹⁾. Strictly speaking, however, those early works were not so much accurate but only phenomenological, even after the eminent Debye-Hückel theory¹⁰⁾ for the strong electrolyte solution was developed in 1923. It seems to the authors that first great efforts to determine accurately the limiting equivalent conductances at high pressures were made in the 1950's by Hamann and his coworkers in particular for the purpose of examining the pressure effect on the ionization of weak electrolytes. In the 1960's, the accurately determined limiting equivalent conductances at high pressures began to be analyzed in terms of the transition state theory¹³⁾ by Brummer and Hills^{14, 15)}, Osugi, Shimizu and Takizawa¹⁶⁾, and Adams and Laidler¹⁷⁾, and also in terms of the dielectric relaxation effect by Skinner and Fuoss¹⁸⁾ and Cussler and Fuoss¹⁹⁾.

When we deal with a transport property in solution, there is one fundamental question as to how much the transport property might reflect the equilibrium property of ions in solution. In the case of ionic conductance, however, there would be fairly good correspondence between them for the following reasons. The ions in solution are originally moving very rapidly in a random way colliding with the solvent molecules or with each other, as well-known as Brownian motion. When an external electric field is applied to the system, the ions begin to move preferentially in the direction of the applied field. At this time, if the external perturbation is so weak, as often in the conductance measurement, that it may not disturb the internal field exerted by the ions themselves and polar solvent molecules, the limiting ionic equivalent conductance would minutely reflect the ion-solvent interaction in the equilibrium state. In consequence, the limiting ionic equivalent conductance could be used as a useful probe to study ionic hydration. As a matter of fact, it was previously reported²⁰⁾ that there are linear correlations between the hydration number calculated from the limiting ionic equivalent conductance and the hydration enthalpy for the alkali metal ions and for the halogen ions at normal pressure.

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