

The Effect of Solution Concentration on the High-Pressure Coefficient of Ionic Conductance

by A. B. Gancy and S. B. Brummer

Tyco Laboratories, Inc., Waltham, Massachusetts 02154 (Received November 21, 1968)

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The effect of solution concentration on the pressure coefficient of dilute aqueous solutions has been investigated. Experimental results for LiCl, KCl, RbCl, and NH₄Cl solutions at 25° in the ranges 1–2000 atm and 3–20 mM are presented. NaCl solutions have been investigated up to 120 mM. It is shown that the Debye-Hückel-Onsager limiting law predicts that the pressure coefficient (Λ_p/Λ_1 , Λ = equivalent conductance) should increase with solution concentration, c . This is unexpected since both Λ_p and Λ_1 decrease with c . Experimental data do show the expected increase of Λ_p/Λ_1 with c up to 20 mM. Reasons why this effect has not been found by other workers are suggested. The results fit the limiting law even at 20 mM within 0.1%, *i.e.*, surprisingly well, although the deviations are invariably negative. The reason for this good fit is cancellation in the Λ_p/Λ_1 ratio of nonlimiting-law terms in the concentration dependence of Λ . Deviations from limiting law at higher concentrations were explored with NaCl solutions. The data fit the Robinson and Stokes equation with the distance of closest ion approach, a , taken to be 6.1 Å at all pressures. This value of a derives from an analysis of precise 1 atm NaCl conductance data assuming ion-pair formation. It is shown that no further consideration need be given to the effects of ion association even up to 100 mM (where NaCl is ~8% associated). This is because of cancellation of the effects of association in the Robinson and Stokes expression for Λ_p/Λ_1 . It is suggested that the best method to extrapolate Λ_p/Λ_1 to infinite dilution is to use data at ~3 mM and the limiting-law slope. In typical cases, this approach is valid to 0.1% at 2000 atm, providing the salt association constant at 1 atm is less than about 50 l./mol.

Introduction

The pressure coefficient of ionic conductance of solutions has been suggested to be useful in the construction of a physical theory of the conduction process.^{1,2} From this coefficient, two interesting experimental quantities can be derived: the volume of activation for the ion migration process and the isochoric activation energy. That approach was used in the study of nonaqueous solutions²⁻⁵ and melts.⁶ Preliminary data showed that aqueous solutions are anomalous,² no doubt due to their unusual structural properties.⁷ Because of their central position in physical chemistry and in life processes, a further detailed study of the properties of these solutions is of considerable interest, and this is the intention of our present work. There have been a number of recent studies on the high-pressure conductances of aqueous solutions,⁸⁻¹¹ but none has been either sufficiently detailed in scope or experimentally well characterized for the purposes of our detailed analysis.¹⁻³

Consequently, we have begun a systematic investigation of the effects of temperature (3–55°) and pressure (1–2300 atm) on the conductance of aqueous solutions. Previously,¹² we have developed and validated experimental methods of measuring the conductance at high pressures to within 0.1%. In the present instance, we consider the effect of concentration on the pressure coefficient of ionic conductance. It is well known that the conductance of strong electrolytes is strongly concentration dependent. Indeed, the exact description of this dependence has been a main preoccupation in

studies of solution conductance. We have not attempted to detail the description of this concentration dependence under pressure in very concentrated solutions. Rather, the aim has been to examine how to extrapolate high-pressure data to infinite dilution with high accuracy (0.1%), working at concentrations which are readily and accurately experimentally accessible.

Experimental Section

Experiments were carried out as described recently.¹² An accuracy of 0.1% is claimed and the precision was usually better than 0.05%.

Results were determined and are expressed as ratios κ_p/κ_1 (κ = specific conductance), as in earlier work.^{2,3}

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- (2) S. B. Brummer and G. J. Hills, *ibid.*, **57**, 1823 (1961).
- (3) S. B. Brummer, *J. Chem. Phys.*, **42**, 1636 (1965).
- (4) F. Barreira and G. J. Hills, *Trans. Faraday Soc.*, **64**, 1359 (1968).
- (5) W. A. Adams and K. J. Laidler, *Can. J. Chem.*, **46**, 1977, 1989, 2005 (1968).
- (6) A. F. M. Barton, B. Cleaver, and G. J. Hills, *Trans. Faraday Soc.*, **64**, 208 (1968).
- (7) For an excellent recent review, see J. Lee Kavanau, "Water and Solute-Water Interactions," Holden-Day, San Francisco, Calif., 1964.
- (8) S. D. Hamann and W. Strauss, *Discussions Faraday Soc.*, **22**, 70 (1956).
- (9) A. J. Ellis, *J. Chem. Soc.*, 3689 (1959).
- (10) R. A. Horne and R. P. Young, *J. Phys. Chem.*, **71**, 3824 (1967).
- (11) P. J. Ovenden, Thesis, University of Southampton, 1965.
- (12) A. B. Gancy and S. B. Brummer, *J. Electrochem. Soc.*, **115**, 804 (1968).

There are two important reasons for using these ratios rather than the absolute values of κ (and hence the equivalent conductance Λ). First, use of such ratios prevents the accumulation in the results of residual errors ($\sim 0.05\%$ per pressure cycle) in the absolute values of κ_p and κ_1 in an extended experiment. The ratio itself is of experimental interest, and this procedure prevents cumulative errors in κ_p and κ_1 of up to 0.3% from affecting the ratio by as much as 0.1% in an extended experiment. In the second place, the effect of concentration on the ratio κ_p/κ_1 (or Λ_p/Λ_1) is much less than on the individual conductances. Extrapolation to infinite dilution is therefore shorter and more certain.

Results and Discussion

Quantitative Expression of the Concentration Dependence of the Pressure Coefficient of Conductance. One of the earliest extensive studies of the high-pressure conductance of aqueous solutions was by Körber.¹³ He reported that for KCl solutions κ_p/κ_1 decreased monotonically with increase in concentration in the range 10^{-4} to $3 N$. No quantitative or theoretical analysis was made.

Ellis⁹ reported that in the range 10^{-3} to $10^{-1} N$ for KCl and HCl, the effect of concentration was negligible. He recognized that the Debye-Hückel-Onsager theory predicts a large concentration effect and postulated its absence to result from an important artifact. This was that the ions modify the structure of the water, following the Frank and Evans^{14,15} description. Hence the variation of viscosity with pressure to be used with the Debye-Hückel-Onsager theory was not that of pure water but should reflect the "structural temperature" of the water near the ion. The Debye-Hückel terms below $0.1 N$ should, Ellis argued, lead to a drop in pressure coefficient as the concentration increases. This effect was opposed by a decrease in the structural temperature of the water as the salt concentration increased; (hence, we presume he argues, there is an increase in pressure-destructible order in the solution and an increase in the pressure coefficient at higher concentrations). The two effects appeared approximately to cancel up to $0.1 N$. We will show that Ellis incorrectly interpreted the direction of the Debye-Hückel-Onsager prediction and that in fact the pressure coefficient of conductance should increase with concentration. This alone is enough to vitiate his conclusion, but we will also show that the argument about structural temperatures is not necessary to explain the results,¹⁶ *i.e.*, that data fit the limiting-law predictions made with normal water properties surprisingly well.

Hamann¹⁷ and Fuoss, *et al.*,¹⁸ have also discussed the concentration dependence of the pressure coefficient of conductance. Hamann considered the applicability of the Debye-Hückel-Onsager limiting law to conductance data at high pressure. Large deviations were found even after modifying the equation for the variation of

solvent properties with pressure. Fuoss, *et al.*,¹⁸ have been much concerned with the effect of concentration on solution conductances under pressure. Usually, however, they have worked with low dielectric constant solvents and have mainly been concerned with effects of ion association.

No explicit treatment of the effect of concentration on the pressure coefficient of solution conductance for unassociated salt solutions has been given. Yet the reasons for using pressure coefficients rather than absolute conductances are compelling and this practice is widely followed. It is apparent from the above discussion that there is some uncertainty even as to the direction of the concentration effect on this coefficient. This poses difficulties about extrapolation to infinite dilution. Some explicit treatment of the problem seems needed therefore. Since it will appear that the previous experimental work which has considered this dependence (Körber¹³ and Ellis⁹) is not in agreement with theory (or our data), there is additional *a posteriori* reason for this treatment.

The method of treating the pressure coefficient is formally simple. We consider the equation to describe the concentration dependence at pressure P and divide it by the equation at 1 atm, *i.e.*

$$\Lambda_p = \Lambda_p^0 - f(c_p) \quad (1)$$

and

$$\frac{\Lambda_p}{\Lambda_1} = \frac{\Lambda_p^0 - f(c_p)}{\Lambda_1^0 - f(c_1)} \quad (2)$$

The problem is in the choice of $f(c_p)$. In principle, this is not a large difficulty. Thus, in the concentration range where the Debye-Hückel-Onsager limiting law applies, $f(c_p)$ is given by

$$f(c_p) = (\alpha_p \Lambda_p^0 + \beta_p) \sqrt{c_p} = S_p \sqrt{c_p} \quad (3)$$

Here, α_p and β_p are the usual constants¹⁹ comprising solvent physical and universal constants.

(13) F. Körber, *Z. Phys. Chem.*, **67**, 212 (1909).

(14) H. S. Frank and M. W. Evans, *J. Chem. Phys.*, **13**, 507 (1945).

(15) See also R. W. Gurney, "Ionic Processes in Solution," McGraw-Hill Book Co., Inc., New York, N. Y., 1953, and ref 7.

(16) We should say in addition that if Ellis' view about structural temperature were correct, it would have its greatest effect on the concentration dependence of conductance at 1 atm. Deviations from ideal equations attributable to this cause have not been reported in the range up to $0.1 M$. In this range of concentration, it does appear appropriate to use the normal viscosity of water in the extended Debye-Hückel-Onsager equations. We do not argue that pressure does not destroy the water structures around the ions—it certainly does; what we say is that at these concentrations, this effect is purely ion-solvent and that the ion-solvent cospheres of the individual ions are essentially independent. Hence the effects would be concentration independent.

(17) S. D. Hamann, "Physico-Chemical Effects of Pressure," Butterworth and Co. Ltd., London, 1957.

(18) J. F. Skinner and R. M. Fuoss, *J. Phys. Chem.*, **70**, 1426 (1966).

(19) H. S. Harned and B. B. Owen, "Physical Chemistry of Electrolyte Solutions," 3rd ed, Reinhold Publishing Corp., New York, N. Y., 1957, p 179.