

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

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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 NH<sub>4</sub>Cl 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 ( $\Lambda_p/\Lambda_1$ ,  $\Lambda$  = equivalent conductance) should increase with solution concentration,  $c$ . This is unexpected since both  $\Lambda_p$  and  $\Lambda_1$  decrease with  $c$ . Experimental data do show the expected increase of  $\Lambda_p/\Lambda_1$  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  $\Lambda_p/\Lambda_1$  ratio of nonlimiting-law terms in the concentration dependence of  $\Lambda$ . 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  $\Lambda_p/\Lambda_1$ . It is suggested that the best method to extrapolate  $\Lambda_p/\Lambda_1$  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.<sup>1,2</sup> 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 solutions<sup>2–5</sup> and melts.<sup>6</sup> Preliminary data showed that aqueous solutions are anomalous,<sup>2</sup> no doubt due to their unusual structural properties.<sup>7</sup> 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,<sup>8–11</sup> but none has been either sufficiently detailed in scope or experimentally well characterized for the purposes of our detailed analysis.<sup>1–3</sup>

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,<sup>12</sup> 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.<sup>12</sup> An accuracy of 0.1% is claimed and the precision was usually better than 0.05%.

Results were determined and are expressed as ratios  $\kappa_p/\kappa_1$  ( $\kappa$  = specific conductance), as in earlier work.<sup>2,3</sup>

- (1) S. B. Brummer and G. J. Hills, *Trans. Faraday Soc.*, **57**, 1816 (1961).
- (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  $\kappa$  (and hence the equivalent conductance  $\Lambda$ ). 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  $\kappa_p$  and  $\kappa_1$  in an extended experiment. The ratio itself is of experimental interest, and this procedure prevents cumulative errors in  $\kappa_p$  and  $\kappa_1$  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  $\kappa_p/\kappa_1$  (or  $\Lambda_p/\Lambda_1$ ) 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.<sup>13</sup> He reported that for KCl solutions  $\kappa_p/\kappa_1$  decreased monotonically with increase in concentration in the range  $10^{-4}$  to  $3 N$ . No quantitative or theoretical analysis was made.

Ellis<sup>9</sup> 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<sup>14,15</sup> 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,<sup>16</sup> *i.e.*, that data fit the limiting-law predictions made with normal water properties surprisingly well.

Hamann<sup>17</sup> and Fuoss, *et al.*,<sup>18</sup> 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.*,<sup>18</sup> 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 (Körber<sup>13</sup> and Ellis<sup>9</sup>) 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,  $\alpha_p$  and  $\beta_p$  are the usual constants<sup>19</sup> 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.

Normally, deviations from eq 3 occur at concentrations above about 2 mM in most aqueous solutions. Hence a different form of  $f(c_p)$  is required at higher concentrations. The most elaborate and sophisticated of such formulations is that due to Fuoss and Onsager.<sup>20,21</sup> Here, the simplified form suitable for use to  $\sim 10$  mM for an unassociated salt<sup>22</sup> is

$$f(c_p) = S_p \sqrt{c_p} - E_p' c_p \ln c_p + J_p c_p \quad (4)$$

An alternative equation, variously attributed but mostly propounded by Robinson and Stokes,<sup>23</sup> is perhaps less accurate ( $\sim 0.05\%$  at 50 mM) but is easier to handle analytically, *viz.*

$$f(c_p) = \frac{S_p \sqrt{c_p}}{(1 + a_p \chi_p \sqrt{c_p})} \quad (5)$$

Here  $\chi_p$  is a collection of universal constants and solvent parameters and  $a_p$  is the distance of closest approach of the ions.

Our approach has been to explore the predictions of the limiting-law equation (3). It will appear that for simple 1:1 electrolytes the data to 20 mM never depart from this formulation by more than 0.1%. Data at higher concentrations, where significant deviations occur, are then treated according to eq 5.

*Comparison of Experimental Data with the Debye-Hückel-Onsager Limiting Law.* Combining eq 2 and 3, and recalling that  $\Lambda_p/\Lambda_1 = (\kappa_p/\kappa_1)(\rho_1/\rho_p)$ , where  $\rho$  = density, yields

$$\frac{\kappa_p}{\kappa_1} = \left(\frac{\kappa_p}{\kappa_1}\right)_{c \rightarrow 0} \left[ 1 + \left\{ \frac{S_1}{\Lambda_1^0} - \frac{S_p}{\Lambda_p^0} \left(\frac{\rho_p}{\rho_1}\right)^{1/2} \right\} \sqrt{c_1} + \text{higher terms in } (\sqrt{c_1})^n \right] \quad (6)$$

The variation of water viscosity,<sup>24</sup>  $\eta$ , of dielectric constant,<sup>25</sup>  $\epsilon$ , and of density<sup>26</sup> with pressure is known.  $\Lambda_1^0$  is also known, and if  $\Lambda_p^0$  can be determined, the variation of  $\kappa_p/\kappa_1$  with  $c$  can be predicted. The method of determining  $\Lambda_p^0$  was as follows:  $\kappa_p/\kappa_1$  varies approximately as  $\sqrt{c}$  (see below). Data were graphically extrapolated to  $\sqrt{c} = 0$  and the value of  $\Lambda_p^0$  so derived was used to determine the predicted slope  $d(\kappa_p/\kappa_1)/d\sqrt{c_1}$ . This new slope was then used with the data to yield a new value of  $\Lambda_p^0$ , which could be used to recalculate the slope, and so on. In practice, the original graphically extrapolated value of  $\Lambda_p^0$  was always adequate for slope prediction.

The important result from eq 6 is that  $\kappa_p/\kappa_1$  (unlike  $\Lambda$  itself) should *increase with increase in concentration*.

Typical results are shown in Figures 1-5 for LiCl, NaCl, KCl, RbCl, and  $\text{NH}_4\text{Cl}$  at 1000 and 2000 atm and 25°. Similar data were obtained between 3 and 55°. Data were taken above 3 mM. This was to ensure that an accuracy of 0.1% could be achieved,

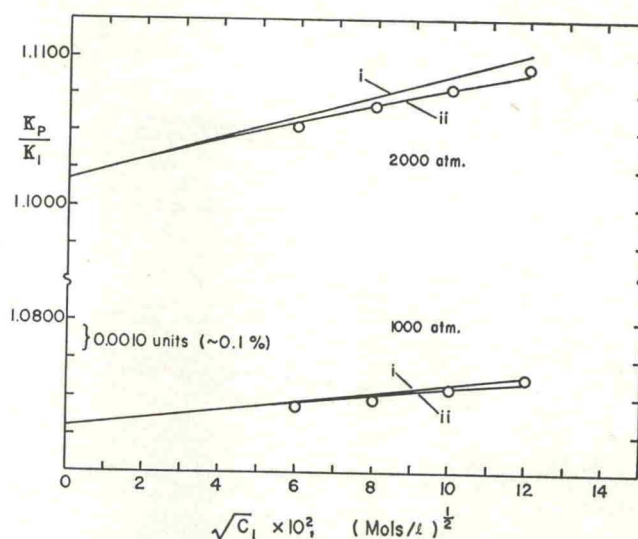


Figure 1. Concentration dependence of the pressure coefficient of conductance for LiCl solutions at 25°: i, limiting law; ii, eq 8 with  $a_1 = 5.75 \text{ \AA}$  and  $a_p/a_1 = 1.00$ .

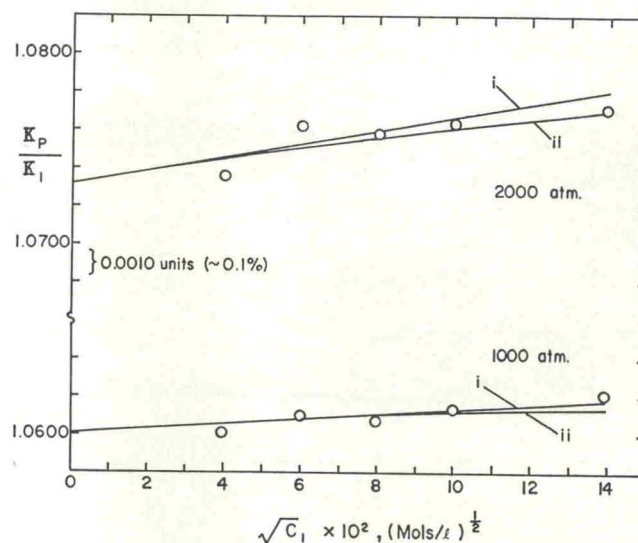


Figure 2. Concentration dependence of the pressure coefficient of conductance for KCl solutions at 25°: i, limiting law; ii, eq 8 with  $a_1 = 5.65 \text{ \AA}$  and  $a_p/a_1 = 1.00$ .

using the procedures described previously.<sup>12</sup> We were not able to obtain results consistently this accuracy below 3 mM. Despite this high concentration range, above the normal expectation of limiting law behavior,  $\kappa_p/\kappa_1$  is found to increase approximately with  $\sqrt{c_1}$  in the

(20) R. M. Fuoss, *J. Amer. Chem. Soc.*, **80**, 5059 (1958).

(21) R. M. Fuoss and L. Onsager, *J. Phys. Chem.*, **61**, 668 (1957).

(22) R. M. Fuoss and K. L. Hsia, *Proc. Nat. Acad. Sci. U. S.*, **57**, 1550 (1967).

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

(24) K. E. Bett and J. B. Cappi, *Nature*, **207**, 620 (1965).

(25) B. B. Owen, *et al.*, *J. Phys. Chem.*, **65**, 2065 (1961).

(26) G. S. Kell and E. Whalley, *Phil. Trans. Roy. Soc. London*, **258**(1094), 565 (1965).

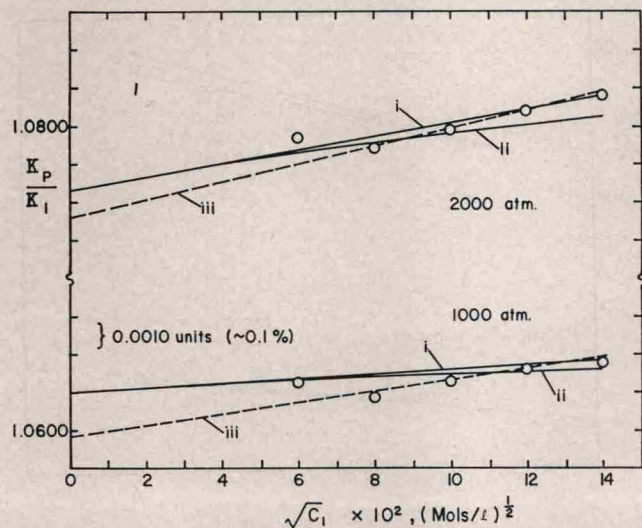


Figure 3. Concentration dependence of the pressure coefficient of conductance for  $\text{NH}_4\text{Cl}$  solutions at  $25^\circ$ : i, limiting law; ii, eq 8 with  $a_1 = 5.75 \text{ \AA}$  and  $a_p/a_1 = 1.00$ ; iii, preliminary slopes.

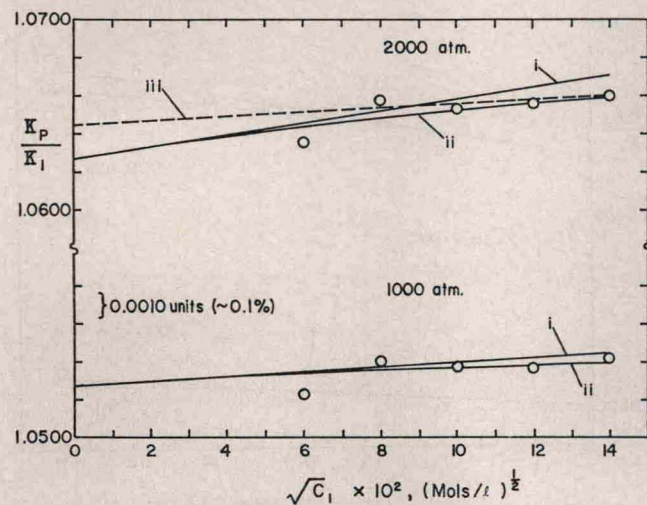


Figure 4. Concentration dependence of the pressure coefficient of conductance for  $\text{RbCl}$  solutions at  $25^\circ$ : i, limiting law; ii, eq 8 with  $a_1 = 5.55 \text{ \AA}$  and  $a_p/a_1 = 1.00$ ; iii, preliminary slope.

concentration range explored, 3–20 mM. We have noted that the limiting-law prediction is that  $\kappa_p/\kappa_1$  should increase with  $\sqrt{c_1}$ . We see that the deviations from limiting law are small ( $\sim 0.1\%$ ) even at 20 mM. In addition, the preliminary hand-drawn slopes of the  $\kappa_p/\kappa_1$  vs.  $\sqrt{c_1}$  plots (constructed without benefit of limiting-law predictions) are more often than not somewhat lower than required by limiting law.

Our results are in contrast to those reported by Körber<sup>13</sup> and Ellis.<sup>9</sup> The good agreement below 10 mM with the predictions of limiting law, which itself predicts the  $\kappa_p/\kappa_1$  should increase with  $c$ , speaks in favor of our findings. We believe that the previous workers did not find this dependence for the following reasons.

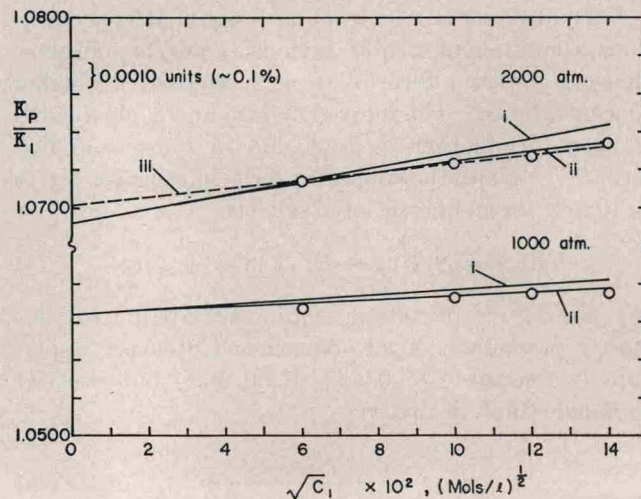


Figure 5. Concentration dependence of the pressure coefficient of conductance for  $\text{NaCl}$  solutions at  $25^\circ$ : i, limiting law; ii, eq 8 with  $a_1 = 6.1 \text{ \AA}$  and  $a_p/a_1 = 1.00$ ; iii, preliminary slope.

Körber found that  $\kappa_p/\kappa_1$  decreased as  $c$  increased from very low to high concentrations. The trend at the highest concentrations is certainly correct. The results at low concentrations were too high, almost certainly because of impurities. Our previous results<sup>12</sup> show that impurities, which affect the results most at low solution concentrations, invariably lead to high  $\kappa_p/\kappa_1$  findings. Ellis' data showed much scatter, after large solvent corrections, and this concealed the concentration effect at high dilutions. At higher concentrations ( $\sim 0.1 N$ ),  $\kappa_p/\kappa_1$  deviates considerably below the limiting-law behavior (see later) and takes on values approximately the same as at lower concentrations. This, combined with his scatter, accounts for Ellis' results.

*Deviations from Limiting-Law Behavior.* We have noted that the data fit limiting-law predictions to within 0.1% out to 20 mM. This is well outside the normal expectation of this theory. Thus at  $25^\circ$  and 1 atm, 10 mM  $\text{NaCl}$  solutions have a conductance 0.8% greater than the limiting-law predicted value. The fact that the  $\kappa_p/\kappa_1$  data follow the limiting law so well at these higher concentrations is due to the cancellation of deviations in the ratio. Thus at 10 mM in eq 2  $f(c_1) \sim 0.8\%$ , and  $f(c_{2000}) \sim 0.75\%$ ; what we see is their difference, *i.e.*, 0.05% at 2000 atm.

Despite this tendency to cancel deviations, it is evident that data at higher concentrations do deviate systematically below limiting-law behavior. It is of some interest to attempt to describe these deviations. The most sophisticated approach is that of eq 4. However, this is not suitable above 10 mM. A semiempirical modification of this equation which has been proposed is<sup>22</sup>

$$f(c_p) = S_p \sqrt{c_p} - E_p c_p \log c_p - A_p c_p - B_p c_p^{3/2} \quad (7)$$

Aside from difficulties of analytic treatment with this

equation, the variation of  $A_p$  and  $B_p$  with  $P$  has to be determined empirically.<sup>27</sup> This makes eq 7 unsuitable for data interpretation.

A less rigorous but experimentally reasonably justifiable equation is the Robinson-Stokes form, eq 5. This equation can be handled analytically and since we were concerned to examine only small deviations from limiting law ( $\sim 0.5\%$  even at 100 mM) its use seems allowable. Then we obtain, after ignoring all terms of higher power than  $c$

$$\kappa_p/\kappa_1 = (\kappa_p/\kappa_1)^0 \left[ 1 + \left\{ \frac{S_1}{\Lambda_1^0} - \frac{S_p}{\Lambda_p^0} \left( \frac{\rho_p}{\rho_1} \right)^{1/2} \right\} \sqrt{c_1} + \frac{S_1}{\Lambda_1^0} \left\{ \left\{ \frac{S_1}{\Lambda_1^0} - \frac{S_p}{\Lambda_p^0} \left( \frac{\rho_p}{\rho_1} \right)^{1/2} \right\} c_1 + a_1 \chi_1 \left\{ \frac{a_p}{a_1} \left( \frac{\epsilon_1 \right)^{1/2} \left( \frac{\rho_p}{\rho_1} \right) - \frac{S_1}{\Lambda_1^0} \right\} c_1 \right\} \right] \quad (8)$$

Here, the coefficient of  $\sqrt{c_1}$  is the limiting-law term, as before. It is dominant at low  $c$  and causes an increase in  $\kappa_p/\kappa_1$  with  $c_1$ . The second term, within the double braces, is the  $c_1$  term in the power expansion of the limiting law (see eq 6). It also causes an increase in  $(\kappa_p/\kappa_1)$  with  $c_1$ . This term is always small ( $\sim 0.04\%$  at 10 mM and 2000 atm). The third term, in  $c_1$ , arises from the Robinson and Stokes modification of the limiting law. It should cause a decrease in  $\kappa_p/\kappa_1$  with increasing  $c_1$ .

To test the application of eq 8, measurements for NaCl solutions were extended to over 100 mM. Results at 25° are shown in Figure 6. Deviations from the  $\kappa_p/\kappa_1$  vs.  $\sqrt{c_1}$  limiting law are found to be proportional to  $c_1$ , as required, under all conditions.

To determine whether these data fit eq 8, we need a value for  $a_1$  and for  $a_p/a_1$ . *A priori* we do not know  $a_p/a_1$  but  $a_1$  is available from 1-atm conductance and activity data. We chose to select  $a_1$  and to determine  $a_p/a_1$ . The usual value for  $a_1$  from activity coefficient data<sup>28</sup> for NaCl is 4.4 Å.

Using this value of  $a_1$ , we obtained the  $a_p/a_1$  data shown in Figure 7 as a function of pressure. Also shown in the figure is the variation with pressure of the cube root of the relative specific volume of water.<sup>26</sup> Presumably  $a_p/a_1$  should not decrease with  $p$  more rapidly than does  $(V_p/V_1)^{1/3}$ . Indeed there are two reasons why  $a_p/a_1$  should vary less rapidly with  $p$  than  $(V_p/V_1)^{1/3}$ . (1) Most of the distance represented by the  $a$  values comprises the ions themselves and not liquid H<sub>2</sub>O; the ions themselves are much less compressible than liquid water. (2) It is generally believed that H<sub>2</sub>O close to ions is much less compressible than is pure liquid H<sub>2</sub>O.<sup>29</sup> Indeed, the assumption of zero compressibility is the basis of a method for determining hydration numbers, which are in reasonable agreement with those obtained by other techniques.<sup>30</sup> In Figure 7, the  $a_p/a_1$  values form a curve which is concave toward the

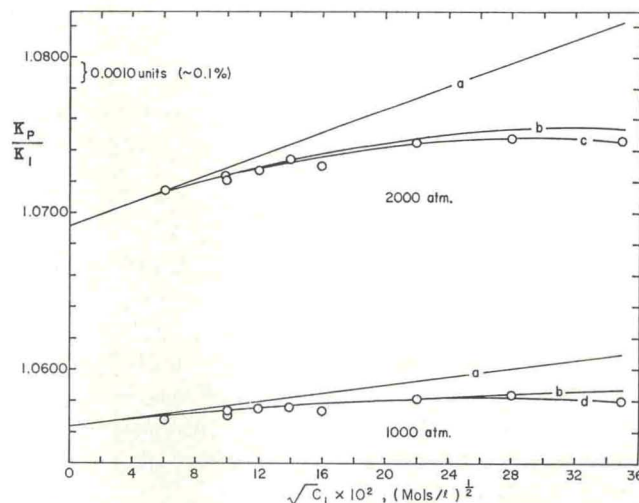


Figure 6. Higher concentration dependence of the pressure coefficient of conductance—NaCl solutions at 25°: a, Debye-Hückel-Onsager limiting law; b, eq 8 with  $a_1 = 6.1 \text{ \AA}$  and  $a_p/a_1 = 1.00$ ; c, eq 8 with  $a_1 = 4.4 \text{ \AA}$  and  $a_p/a_1 = 0.975$ ; d, eq 8 with  $a_1 = 4.4 \text{ \AA}$  and  $a_p/a_1 = 0.994$ .

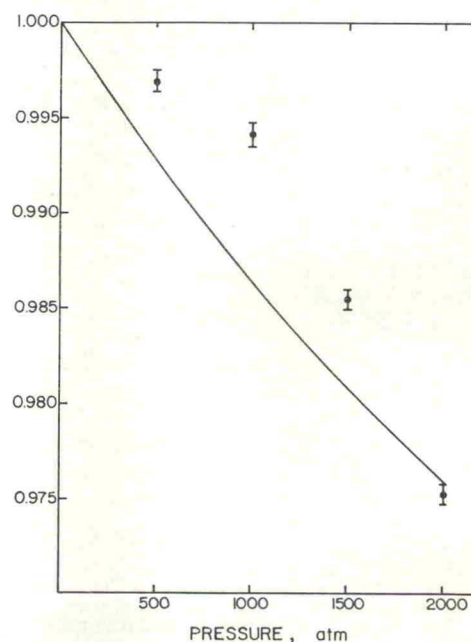


Figure 7. Variation of  $a_p/a_1$  with pressure for NaCl solutions at 25°. Experimental data fitted to eq 8 with  $a_1$  set equal to 4.4 Å.  $\blacksquare$ ,  $a_p/a_1$ ; —,  $(V_p/V_1)^{1/3} \text{H}_2\text{O}$ .

$p$  axis, and the value at 2000 atm actually falls below the  $(V_p/V_1)_{\text{H}_2\text{O}}^{1/3}$  curve. Such behavior is not physically meaningful.

To explore this matter further, we varied  $a_1$  and computed  $a_p/a_1$  values from the data. Results at 500, 1000,

(27) R. M. Fuoss, private communication, Aug 1968.

(28) Reference 19, p 509. Values of  $a_1$  which satisfy an extended Debye-Hückel limiting law are 4.4 Å for  $c = 0.005\text{--}0.1 \text{ M}$ , 4.0 Å for  $c = 0.1\text{--}1 \text{ M}$ , and 3.6 Å for  $c = 0.1\text{--}3 \text{ M}$ .

(29) T. J. Webb, *J. Amer. Chem. Soc.*, **48**, 2589 (1926).

(30) A. Passynski, *Acta Physicochim. USSR*, **8**, 835 (1938).

1500, and 2000 atm are shown in Figure 8. We note that as the chosen  $a_1$  value is increased, the predicted  $a_p/a_1$  value also increases. The curves approach  $a_p/a_1 = 1$  for high  $a_1$ . They intersect one another in the ranges  $a_1 = 6.0\text{--}6.4 \text{ \AA}$  and  $a_p/a_1 = 1.000\text{--}1.002$ . Several features of these results are interesting. First, the tendency of the  $a_p/a_1$  vs.  $a_1$  curves at different pressures to intersect at a common  $a_1$  value is encouraging. This is so because if eq 8 is to have any validity at all it requires that data at different pressures be fitted with the same  $a_1$  value. Secondly, this  $a_1$  value itself is provocative. Fuoss and Hsia<sup>22</sup> have recently suggested that simple 1:1 electrolytes like NaCl may be appreciably associated. When this is taken into account, they obtain an  $a_1$  value not of  $4.4 \text{ \AA}$ , as above, but of  $6.1 \text{ \AA}$ . The third feature of the results shown in Figure 4 which we may comment on is that the convergence of the  $a_p/a_1$  vs.  $a_1$  curves is at  $a_p/a_1 \rightarrow 1$ . This implies that inter-ion hydrated  $\text{H}_2\text{O}$  is not compressible, as is generally accepted.<sup>29</sup>

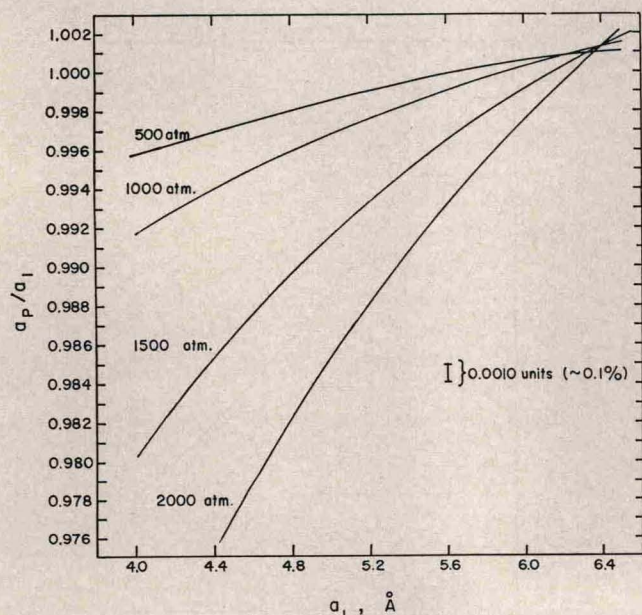


Figure 8. Relationship between  $a_p/a_1$  and  $a_1$  for NaCl solutions at  $25^\circ$  derived by fitting experimental data to eq 8.

We would say then that eq 8 fits the data very well—unexpectedly well indeed—with reasonable values for  $a_1$  and  $a_p/a_1$ . However, there is a problem. The Fuoss and Hsia<sup>22</sup> value for  $a_1$  of  $6.1 \text{ \AA}$  assumes that the salt is associated. In practice an association constant at 1 atm,  $K_1$ , of  $0.92 \text{ l./mol}$  was determined. On this basis, NaCl is  $\sim 1\%$  associated at  $10 \text{ mM}$  and  $\sim 8\%$  associated at  $100 \text{ mM}$ . Yet we have taken no account of this effect in fitting eq 8 using  $a_1 = 6.1 \text{ \AA}$ . We note that the deviations of the data ( $\sim 0.1\%$  at  $100 \text{ mM}$ ) from eq 8 are nowhere near as large as implied by these associations. To examine this matter, eq 8 was rewritten to include the effect of association.

$$\frac{\kappa_p}{\kappa_1} = \left(\frac{\kappa_p}{\kappa_1}\right)^0 \frac{\alpha_p}{\alpha_1} \left[ 1 + \left( \frac{S_1}{\Lambda_1^0} \alpha_1^{1/2} - \frac{S_p}{\Lambda_p^0} \left( \frac{\alpha_p \rho_p}{\rho_1} \right)^{1/2} \right) \sqrt{c_1} + \frac{S_1}{\Lambda_1^0} \left( \frac{S_1 \alpha_1}{\Lambda_1^0} - \frac{S_p \alpha_p}{\Lambda_p^0} \left( \frac{\rho_p}{\rho_1} \right)^{1/2} \right) c_1 + a_1 \chi_1 \left\{ \frac{a_p}{a_1} \left( \frac{\epsilon_1}{\epsilon_p} \right)^{1/2} \left( \frac{\rho_p}{\rho_1} \right) \alpha_p - \frac{S_1 \alpha_1}{\Lambda_1^0} \right\} c_1 \right] \quad (9)$$

Here  $\alpha_1$  is the degree of dissociation at 1 atm and  $\alpha_p$  is the degree of dissociation of the salt at  $p$  atm.  $a_1$  was set equal to  $6.1 \text{ \AA}$ , the precise value according to Fuoss, in preference to a value lying in the range  $6.0\text{--}6.4 \text{ \AA}$  which we determined (Figure 8) from pressure data.  $a_p/a_1$  was set equal to unity. The following cases were investigated:  $\alpha_1 = \alpha_{2000} = 1$ , as before;  $\alpha_1$  from ref 22;  $\alpha_{2000}$  from  $K_{2000} = wK_1$ , where  $w$  is 2, 1, 0.4, and 0.0.

In Figure 9 we show results for NaCl at  $25^\circ$  and 2000 atm. It is seen that the application of hydrostatic pressure, if anything, tends to promote dissociation. Although we are limited by experimental uncertainty ( $\pm 0.05\%$ ), we can conclude that the best fit is for  $K_{2000}/K_1 \sim 0.4$ . This is in line with the known behavior of weak electrolytes which dissociate under pressure.<sup>31</sup> Typical  $K_{2000}/K_1$  values are 0.43 for HAc<sup>32</sup> and 0.17 for  $\text{NH}_4\text{OH}$ .<sup>33</sup>  $K_{1000}/K_1$  is 0.42 for  $\text{H}_2\text{O}$ .<sup>34</sup> The association constants for  $\text{MgSO}_4$  and  $\text{MnSO}_4$  in water decrease approximately one-half on going to 2000 atm.<sup>35</sup>

The important feature of the results shown in Figure 9 is that ignoring ion association completely ( $\alpha_p = \alpha_1 = 1$ ) makes a negligible difference to the ability of the data to fit eq 8. They do fit eq 9 noticeably better than eq 8, when the "best" value of  $w$  is picked. However, the deviation from eq 8 at  $100 \text{ mM}$  is only  $0.1\%$ , the experimental accuracy. It is evident that ion-association effects tend to cancel in the ratio  $\kappa_p/\kappa_1$ . This can be more fully appreciated by calculating the individual terms in eq 9; there is appreciable net cancellation of terms even though the  $\alpha$  values differ widely (e.g.,  $\alpha_1 = 0.922$  and  $\alpha_{2000} = 0.958$  at  $100 \text{ mM}$  for  $w = 0.5$ <sup>36</sup>).

The results of our study indicate then that the Robinson and Stokes equation is adequate to fit the  $25^\circ$  data out to  $100 \text{ mM}$ . To do this, we must take account of ion association to the extent that we use the  $a_1$  values computed by Fuoss, *et al.* If we do this, the same  $a_1$  and  $a_p/a_1$  values will fit results at all pressures.

(31) J. Buchanan and S. D. Hamann, *Trans. Faraday Soc.*, **49**, 1425 (1953).

(32) S. D. Hamann and W. Strauss, *Discussions Faraday Soc.*, **22**, 70 (1956).

(33) S. D. Hamann and W. Strauss, *Trans. Faraday Soc.*, **51**, 1684 (1955).

(34) B. B. Owen and S. R. Brinkley, *Chem. Rev.*, **29**, 461 (1941).

(35) F. H. Fisher, *J. Phys. Chem.*, **66**, 1607 (1962).

(36) Activity coefficients are assumed to be unity in the expression  $1 - \alpha = \alpha^2 \gamma_{\pm}^2 c K_A$  even though the Debye-Hückel values had been used in the Fuoss treatment. One reason for doing this is the anticipated partial cancellation of  $\gamma_{\pm}$  in the pressure ratio. The other is that, even had the  $\gamma_{\pm}$  values at 1 atm been used, the values at  $P$  could not have been derived explicitly from our data.

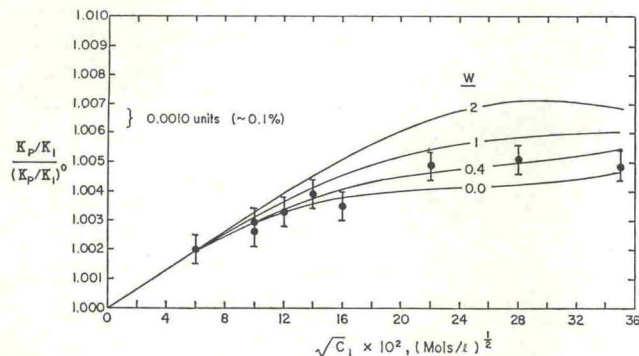


Figure 9. Consideration of association in the pressure coefficient of conductance for NaCl solutions at 25° and 2000 atm. Curves represent eq 9 for various values of  $W$ , where  $K_{2000} = WK_1$ ;  $K_1 = 0.92$  l./mol.<sup>22</sup> Curve for  $W = 1$  is practically identical with that for eq 8, *i.e.*, where  $\alpha_{2000} = \alpha_1 = 1.00$ .

Whether the excellent fit of the 100 mM data to eq 8 or even to eq 9, is physically meaningful, or merely fortuitous, must rest upon a detailed study of results over a wider range of the variables. As a first step in this direction, we compared the 25° dilute solution data for four other salts with the predictions of the Stokes-Robinson equation in Figures 1-4. In each case  $a_p/a_1$  was set equal to 1.00. The  $a_1$  values given in the figure captions were arbitrarily assigned, based upon a comparison among the sums of the known crystallographic radii and the  $a_1$  values determined by Fuoss.<sup>22</sup> At any rate, the calculation is not very sensitive to the  $a_1$  value over this short concentration range. Indeed, this range is actually too narrow for an adequate testing of eq 8. Nevertheless, it is seen in Figures 1-4 that the equation accounts for the direction of the deviations. More importantly, the use of the extended equation results in a more confident extrapolation to infinite dilution, even when used over this limited concentration range.

**Extrapolation to Infinite Dilution.** Our prime concern is to be able to extrapolate confidently to infinite dilution the data taken at concentrations readily and accurately accessible experimentally. One possibility, occasionally followed in the literature, would be to disregard the relatively small concentration dependence and to take the results at one concentration, say 10 mM.<sup>37</sup> This procedure introduces a systematic pressure- and temperature-dependent error. At 25°, it typically (NaCl) produces an error of 0.35% at 2000 atm and 0.15% at 1000 atm. One can readily work at 3 mM and similar treatment of these data yield typical errors of 0.25 and 0.07%. These errors are higher at higher temperatures and with smaller ions.

An alternative would be to extrapolate the approximately linear relation between  $\kappa_p/\kappa_1$  and  $\sqrt{c_1}$  in the range 3-10 mM. This would yield a typical error (NaCl at 25°) of only 0.10% at 2000 atm. In the worst cases we have examined, the extrapolation error with

this procedure would not exceed 0.2%. In cases where the physical constants of the solvent are known, this method would be adequate.

The best method, however, would be to fit the data to a theoretical equation. Since deviations from limiting law, at least insofar as the observed  $\kappa_p/\kappa_1$  vs.  $\sqrt{c_1}$  slopes are concerned, are appreciable in the accessible concentration range, this is not easy. Consequently, we suggest that data at relatively low concentrations be extrapolated using the calculated limiting-law slope. For aqueous solutions of 1:1 electrolytes, no appreciable error (<0.1%) would be typically incurred if data at 2000 atm were extrapolated in this way from as high as 10 mM. However, extrapolation can easily be made from 3 mM.

The effects of possible salt association need not be considered in any such procedure. We have seen that associations as high as 8% are not sufficient to show up in  $\kappa_p/\kappa_1$  ratios. For this degree of association to occur at 3 mM, the association constant would have to be > 50 l./mol. For strong electrolytes, this is probable only in solvents for which the dielectric constant is much lower than that of water. Fuoss' treatment of ion association suggests that this method would then be appropriate for solvents with dielectric constants as low as 20.<sup>38</sup>

### Summary and Conclusions

(1) The Debye-Hückel-Onsager limiting law predicts that the pressure coefficient of conductance should increase approximately as  $\sqrt{c_1}$ . This is found in practice up to 20 mM. Data fit the limiting-law behavior surprisingly well at high concentrations due to cancellation of deviations.

(2) Noncancelling deviations from the limiting law at even higher concentrations may be described by the Robinson and Stokes equation. To do this, we may select an ion approach parameter of  $\sim 6.1$  Å for NaCl invariant with pressure. Such an  $a_1$  value is only obtained in 1-atm concentration dependence work by assuming appreciable ion-pair formation ( $\sim 1\%$  at 10 mM). No further account of the effects of ion association are required to fit our 25° pressure data, however, due to the cancellation of deviations in the conductance ratio equation.

(3) The best method to extrapolate to infinite dilution is to use ratio data at  $\sim 3$  mM with the limiting-law slope. This extrapolation is valid to within 0.1% unless the association constant exceeds 50 l./mol. For NaCl, this restricts the method to solvents with dielectric constants above  $\sim 20$ .

(4) Ratios of conductance,  $\kappa_p/\kappa_1$  or  $\kappa_{T_2}/\kappa_{T_1}$ , are to be

(37) R. A. Horne, B. R. Myers, and G. R. Frysinger, *J. Chem. Phys.*, **39**, 2666 (1963).

(38) This estimate of the dielectric constant was made using the equation of Fuoss and Hsia<sup>22</sup> which relates the association constant to the dielectric constant of the solvent and to the ion-size parameter,

preferred to absolute values where the coefficient itself is required, since they prevent error accumulation and are much less sensitive to concentration and to ion association.

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