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.[20,21] Here, the simplified form suitable for use to ~ 10 mM for an unassociated salt[22] is

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

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

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

Here χ_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

$$\frac{\kappa_p}{\kappa_1} = \left(\frac{\kappa_p}{\kappa_1}\right)_{c\to 0}\left[1 + \left\{\frac{S_1}{\Lambda_1{}^0} - \frac{S_p}{\Lambda_p{}^0}\left(\frac{\rho_p}{\rho_1}\right)^{1/2}\right\}\sqrt{c_1} + \right.$$

$$\left. \text{higher terms in } (\sqrt{c_1})^n\right] \qquad (6)$$

The variation of water viscosity,[24] η, of dielectric constant,[25] ϵ, and of density[26] with pressure is known. $\Lambda_1{}^0$ is also known, and if $\Lambda_p{}^0$ can be determined, the variation of κ_p/κ_1 with c can be predicted. The method of determining $\Lambda_p{}^0$ was as follows: κ_p/κ_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 κ_p/κ_1 (unlike Λ itself) should *increase with increase in concentration.*

Typical results are shown in Figures 1–5 for LiCl, NaCl, KCl, RbCl, and NH_4Cl 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,
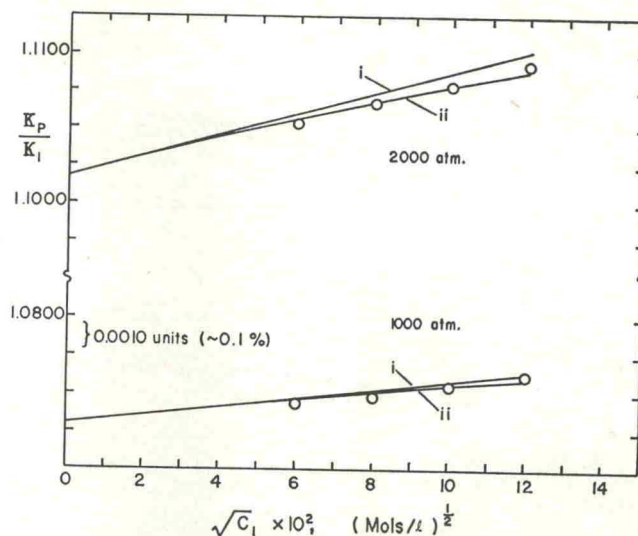

Figure 1. Concentration dependence of the pressure coefficient of conductance for LiCl solutions at 25°: i, limiting law; ii, eq 8 with $a_1 = 5.75$ Å and $a_p/a_1 = 1.00$.
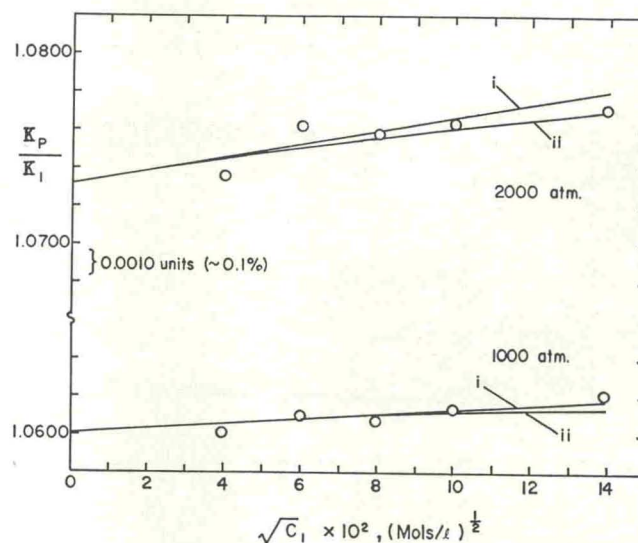

Figure 2. Concentration dependence of the pressure coefficient of conductance for KCl solutions at 25°: i, limiting law; ii, eq 8 with $a_1 = 5.65$ Å and $a_p/a_1 = 1.00$.

using the procedures described previously.[12] 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, κ_p/κ_1 is found to increase approximately with $\sqrt{c_1}$ in the

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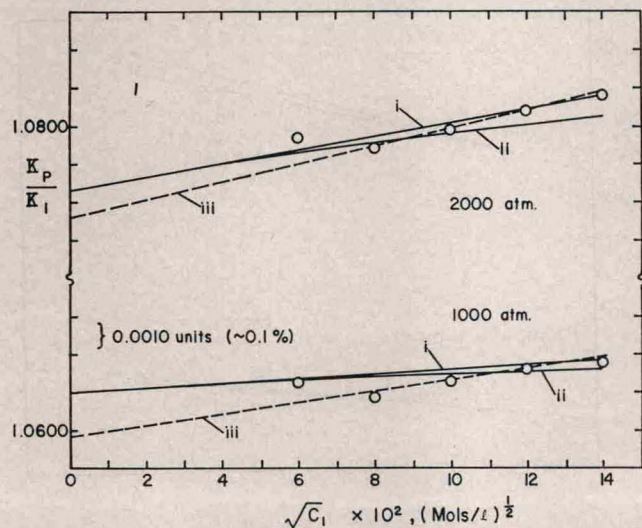
Figure 3. Concentration dependence of the pressure coefficient of conductance for NH$_4$Cl solutions at 25°: i, limiting law; ii, eq 8 with $a_1 = 5.75$ Å and $a_p/a_1 = 1.00$; iii, preliminary slopes.
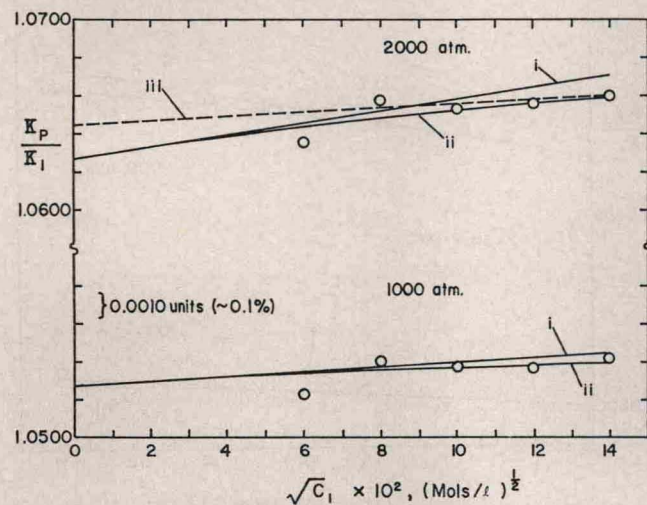

Figure 4. Concentration dependence of the pressure coefficient of conductance for RbCl solutions at 25°: i, limiting law: ii, eq 8 with $a_1 = 5.55$ Å and $a_p/a_1 = 1.00$; iii, preliminary slope.

concentration range explored, 3–20 mM. We have noted that the limiting-law prediction is that κ_p/κ_1 should increase with $\sqrt{c_1}$. We see that the deviations from limiting law are small (~0.1%) even at 20 mM. In addition, the preliminary hand-drawn slopes of the κ_p/κ_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[13] and Ellis.[9] The good agreement below 10 mM with the predictions of limiting law, which itself predicts the κ_p/κ_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.
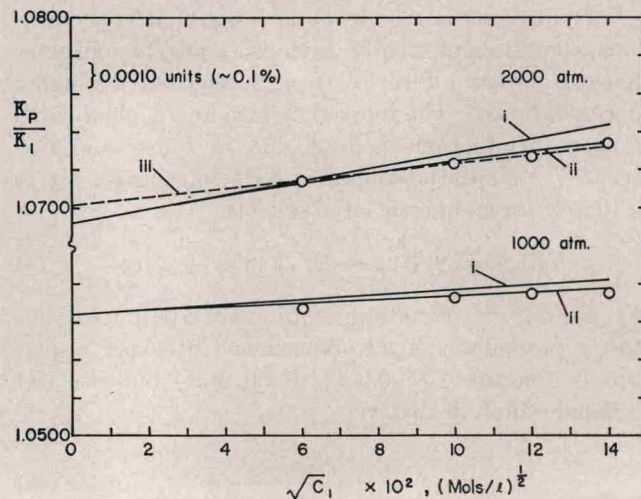

Figure 5. Concentration dependence of the pressure coefficient of conductance for NaCl solutions at 25°: i, limiting law; ii, eq 8 with $a_1 = 6.1$ Å and $a_p/a_1 = 1.00$; iii, preliminary slope.

Körber found that κ_p/κ_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[12] show that impurities, which affect the results most at low solution concentrations, invariably lead to high κ_p/κ_1 findings. Ellis' data showed much scatter, after large solvent corrections, and this concealed the concentration effect at high dilutions. At higher concentrations (~ 0.1 N), κ_p/κ_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° and 1 atm, 10 mM NaCl solutions have a conductance 0.8% greater than the limiting-law predicted value. The fact that the κ_p/κ_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) ~ 0.8%, and f(c_{2000}) ~ 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[22]

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

Aside from difficulties of analytic treatment with this