equation, the variation of A_p and B_p with P has to be determined empirically.[27] 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

$$\kappa_p/\kappa_1 = (\kappa_p/\kappa_1)^0$$

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

$$\frac{S_1}{\Lambda_1{}^0} \left\{ \left\{ \frac{S_1}{\Lambda_1{}^0} - \frac{S_p}{\Lambda_p{}^0} \left(\frac{\rho_p}{\rho_1} \right)^{1/2} \right\} \right\} c_1 +$$

$$\left. a_1 \chi_1 \left\{ \frac{a_p}{a_1} \left(\frac{\epsilon_1}{\epsilon_p} \right)^{1/2} \left(\frac{\rho_p}{\rho_1} \right) - \frac{S_1}{\Lambda_1{}^0} \right\} c_1 \right] \quad (8)$$

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 κ_p/κ_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 (κ_p/κ_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 κ_p/κ_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 κ_p/κ_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[28] 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.[26] 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 $(_pV/V_1)^{1/3}$. (1) Most of the distance represented by the a values comprises the ions themselves and not liquid H_2O; the ions themselves are much less compressible than liquid water. (2) It is generally believed that H_2O close to ions is much less compressible than is pure liquid H_2O.[29] 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.[30] In Figure 7, the a_p/a_1 values form a curve which is concave toward the
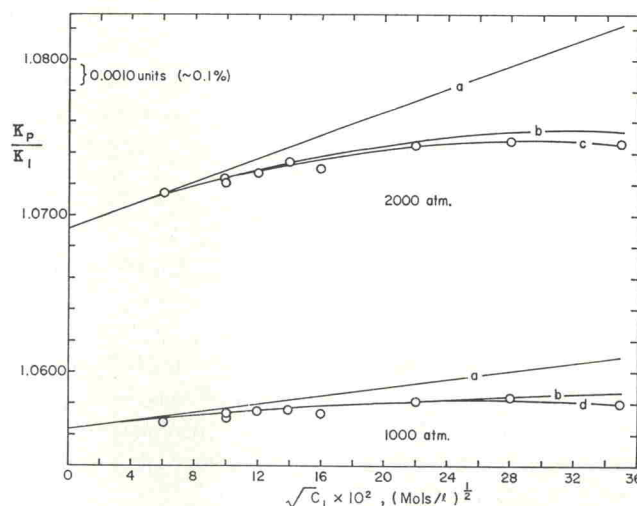

Figure 6. Higher concentration dependence of the pressure coefficient of conductance—NaCl solutions at 25°: a, Debye–Hückel–Onsager limiting law; b, eq 8 with $a_1 = 6.1$ Å and $a_p/a_1 = 1.00$; c, eq 8 with $a_1 = 4.4$ Å and $a_p/a_1 = 0.975$; d, eq 8 with $a_1 = 4.4$ Å and $a_p/a_1 = 0.994$.
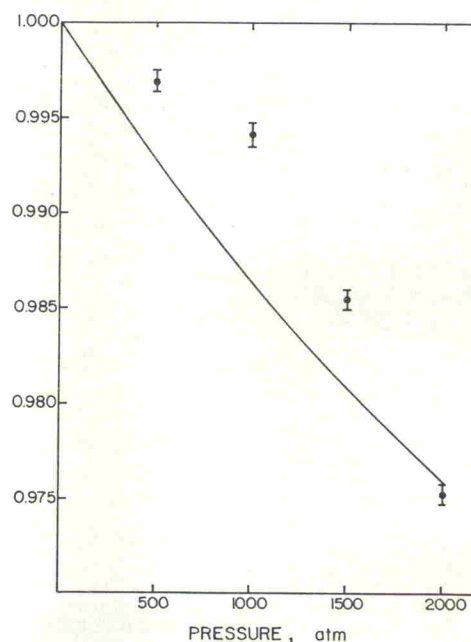

Figure 7. Variation of a_p/a_1 with pressure for NaCl solutions at 25°. Experimental data fitted to eq 8 with a_1 set equal to 4.4 Å. $\quad$ ⚡, a_p/a_1; ——, $(V_p/V_1)^{1/3}{}_{H_2O}$.

p axis, and the value at 2000 atm actually falls below the $(V_p/V_1)_{H_2O}{}^{1/3}$ 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 $c = 0.005$–0.1 M, 4.0 Å for $c = 0.1$–1 M, and 3.6 Å for $c = 0.1$–3 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 $a_1 = 6.0$–6.4 Å and $a_p/a_1 = 1.000$–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[22] 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 Å, as above, but of 6.1 Å. 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 H_2O is not compressible, as is generally accepted.[29]
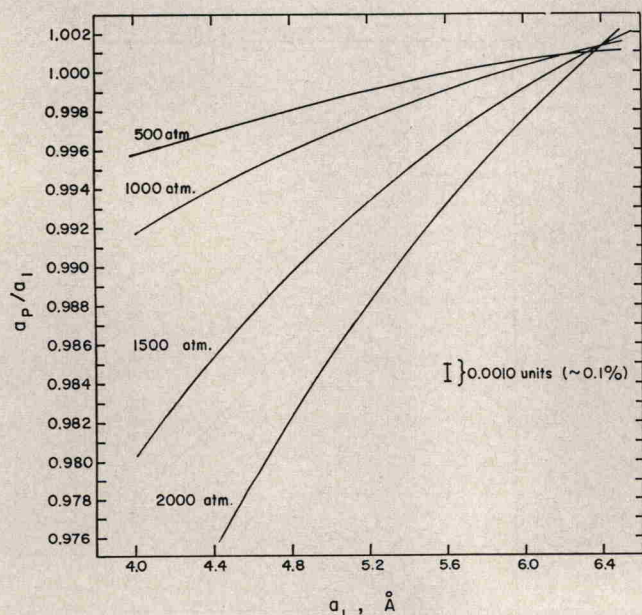

Figure 8. Relationship between a_p/a_1 and a_1 for NaCl solutions at 25° derived by fitting experimental data to eq 8.

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[22] value for a_1 of 6.1 Å assumes that the salt is associated. In practice an association constant at 1 atm, K_1, of 0.92 l./mol was determined. On this basis, NaCl is $\sim 1\%$ associated at 10 mM and $\sim 8\%$ associated at 100 mM. Yet we have taken no account of this effect in fitting eq 8 using $a_1 = 6.1$ Å. We note that the deviations of the data ($\sim 0.1\%$ at 100 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.

$$\frac{\kappa_p}{\kappa_1} = \left(\frac{\kappa_p}{\kappa_1}\right)^0 \frac{\alpha_p}{\alpha_1}\left[1 + \left(\frac{S_1}{\Lambda_1^0}\alpha_1^{1/2} - \frac{S_p}{\Lambda_p^0}\left(\frac{\alpha_p\rho_p}{\rho_1}\right)^{1/2}\right)\sqrt{c_1} + \right.$$

$$\frac{S_1}{\Lambda_1^0}\left(\frac{S_1\alpha_1}{\Lambda_1^0} - \frac{S_p\alpha_p}{\Lambda_p^0}\left(\frac{\rho_p}{\rho_1}\right)^{1/2}\right)c_1 +$$

$$\left. a_1\chi_1\left\{\frac{a_p}{a_1}\left(\frac{\epsilon_1}{\epsilon_p}\right)^{1/2}\left(\frac{\rho_p}{\rho_1}\right)\alpha_p - \frac{S_1\alpha_1}{\Lambda_1^0}\right\}c_1\right] \quad (9)$$

Here α_1 is the degree of dissociation at 1 atm and α_p is the degree of dissociation of the salt at p atm. a_1 was set equal to 6.1 Å, the precise value according to Fuoss, in preference to a value lying in the range 6.0–6.4 Å 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; α_1 from ref 22; α_{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° 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.[31] Typical K_{2000}/K_1 values are 0.43 for HAc[32] and 0.17 for NH_4OH.[33] K_{1000}/K_1 is 0.42 for H_2O.[34] The association constants for $MgSO_4$ and $MnSO_4$ in water decrease approximately one-half on going to 2000 atm.[35]

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 mM is only 0.1%, the experimental accuracy. It is evident that ion-association effects tend to cancel in the ratio κ_p/κ_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 α values differ widely (e.g., $\alpha_1 = 0.922$ and $\alpha_{2000} = 0.958$ at 100 mM for $w = 0.5$[36]).

The results of our study indicate then that the Robinson and Stokes equation is adequate to fit the 25° data out to 100 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 $1 - \alpha = \alpha^2\gamma_{\pm}^2cK_A$ 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.