

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  $c$

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

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  $\kappa_p/\kappa_1$  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

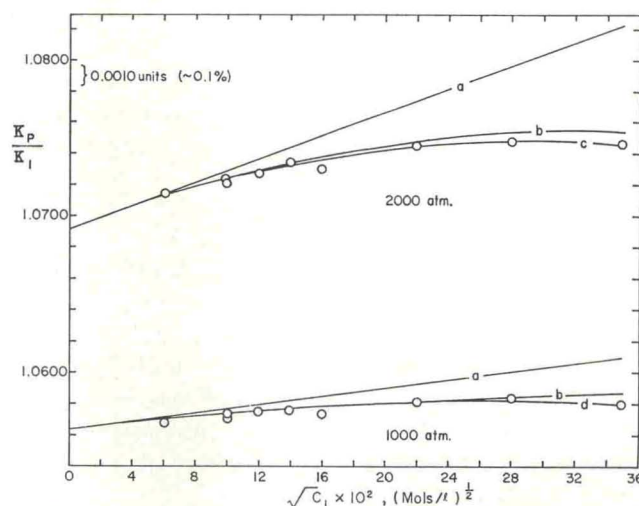


Figure 6. Higher concentration dependence of the pressure coefficient of conductance—NaCl solutions at 25°: a, Debye-Hückel-Onsager limiting law; b, eq 8 with  $a_1 = 6.1$  Å and  $a_p/a_1 = 1.00$ ; c, eq 8 with  $a_1 = 4.4$  Å and  $a_p/a_1 = 0.975$ ; d, eq 8 with  $a_1 = 4.4$  Å and  $a_p/a_1 = 0.994$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

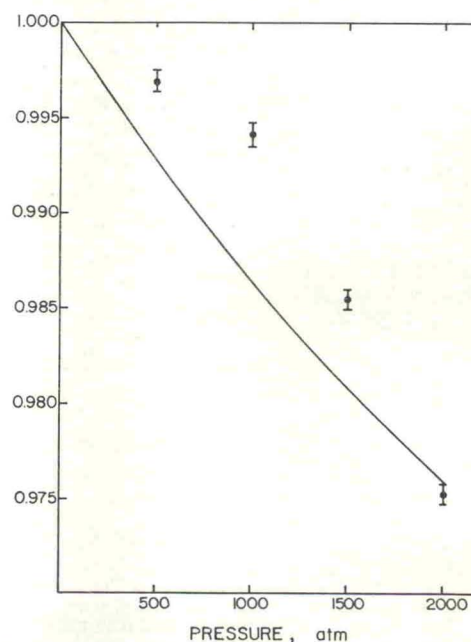


Figure 7. Variation of  $a_p/a_1$  with pressure for NaCl solutions at 25°. Experimental data fitted to eq 8 with  $a_1$  set equal to 4.4 Å.  $\times$ ,  $a_p/a_1$ ; —,  $(V_p/V_1)^{1/3}$  H<sub>2</sub>O.

$p$  axis, and the value at 2000 atm actually falls below the  $(V_p/V_1)^{1/3}$  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<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 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<sub>2</sub>O is not compressible, as is generally accepted.<sup>29</sup>

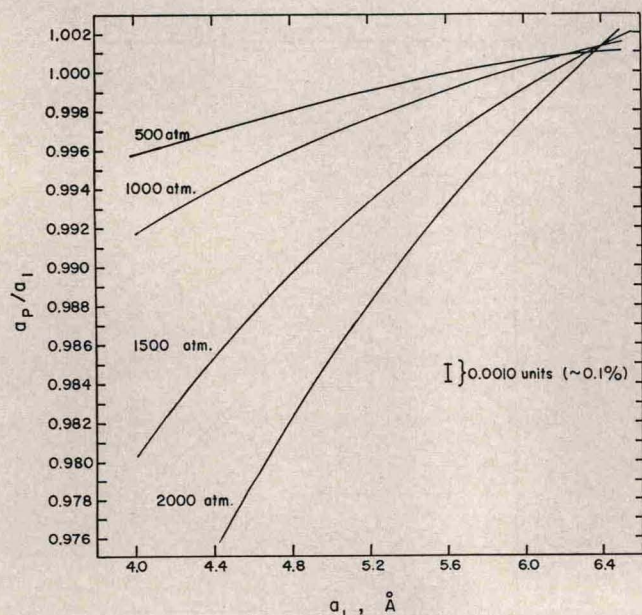


Figure 8. Relationship between  $a_p/a_1$  and  $a_1$  for NaCl solutions at 25° derived by fitting experimental data to eq 8.

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 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 ~1% associated at 10 mM and ~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 (~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.

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

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 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;  $\alpha_1$  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° 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 NH<sub>4</sub>OH.<sup>33</sup>  $K_{1000}/K_1$  is 0.42 for H<sub>2</sub>O.<sup>34</sup> The association constants for MgSO<sub>4</sub> and MnSO<sub>4</sub> 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 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 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° 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  $1 - \alpha = \alpha^2 \gamma_{\pm}^2 c K_A$  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.