



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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