

The graph was quite linear and encouraged a more thorough investigation.

I have proceeded to treat the data for NaCl,<sup>2b</sup> NaBr,<sup>2c</sup> NaI,<sup>2e</sup> and HBr,<sup>2d</sup> using eq 8 in the following manner; for each salt, initial values of  $\Delta H_s$  were obtained at each density for plots of  $\log K_d$  vs.  $1/T$  (eq 9). These values of  $\Delta H_s$  were used to form, at constant temperature, the sums  $(\log K_d + \Delta H_s/2.30RT)$ , which were then plotted vs.  $1/DT$  (eq 10). Recalling that the  $DT$  products showed some variation with temperature, Table I, the slopes from the plots vs.  $1/DT$ , being initial values of  $(e^2/2.30ak)$ , were used to correct for the variation of  $DT$  at constant density, eq 9. The sums  $(\log K_d + e^2/2.30akDT)$  were formed at each density and plotted vs.  $1/T$ . This gave new and improved values of  $\Delta H_s$  for each solvent density. These values of  $\Delta H_s$  were used again to form the sums, at constant temperature,  $(\log K_d + \Delta H_s/2.30RT)$ , which were again plotted vs.  $1/DT$ , eq 10. These revised plots are shown in Figure 2. The linearity of these plots of  $\log K_d$ , corrected for specific (ion, ion-pair)-solvent interaction, in terms of the variable  $1/DT$  furnish strong evidence that the data of Marshall, *et al.*, are in agreement with previous ideas concerning the influence of both solvent dielectric constant<sup>11</sup> and the influence of specific ion-solvent interaction,<sup>10b</sup> rather than requiring complete revision of our notions concerning the relative importance of these two factors.

Repetition of the calculational procedure beyond the point described in the paragraph above was not attempted for the following reasons; Marshall and Quist<sup>2b</sup> point out that the values of  $K_d$  ( $10^{-4}$  to  $10^{-5}$ ) at low densities are uncertain due to difficulties in extrapolating to infinite dilution, while I believe the values of  $K_d$  ( $10^{-1}$  to  $10^{-2}$ ) at high densities are uncertain since it is well known that the value calculated from a set of data when such a small fraction of the salt is ion paired depends on the particular form of the conductance equation used. The values of the dielectric constant of water at high temperatures and pressures<sup>13</sup> were obtained by extrapolation of experimental data at lower to higher temperatures. There is some uncertainty then in these resulting values of the dielectric constant of water. These are the same reasons I use here to argue that more sophisticated data-handling techniques such as least-squares procedures are of doubtful applicability in this case.

*Comparison of the Two Approaches.* The experimental limitations listed above should be kept in mind in the following discussion. Note that the plots of eq 10, Figure 2, for the several electrolytes, fall on the same straight lines at the two temperatures, 500 and 700°, with the exception of several sets of data at lowest densities. The approach to ion-pair dissociation outlined in this paper allows, at one temperature, for changes in differences in energies of solvation as the water density changes. The entropy differences had to be assumed

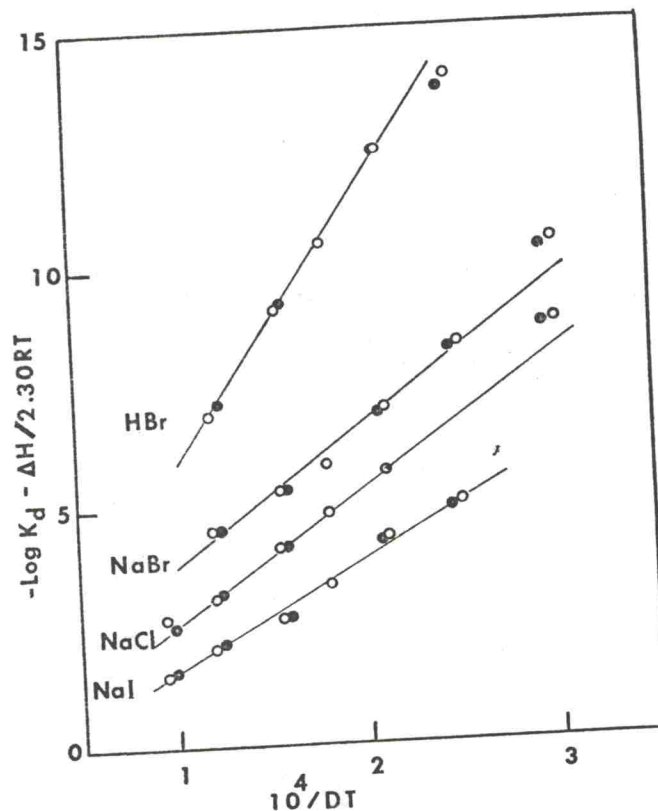


Figure 2. The logarithms of the ion-pair dissociation constants, corrected for specific ion-solvent and ion pair-solvent interaction, for HBr, NaBr, NaCl, and NaI at 500° (open circles) and at 700° (closed circles) vs. the reciprocal of the product of the dielectric constant and the temperature,  $1/DT$ .

to be constant. This approach also allows for the change in electrical free energy as the solvent dielectric changes. To be more specific, the free energy change, upon ion-pair dissociation, is assumed to contain three terms, an energy term ( $\Delta H_s$ ) which is independent of temperature and solvent dielectric constant, an energy term ( $W_{es}$ ) which is inversely proportional to the solvent dielectric constant, and an entropy term ( $T\Delta S$ ) which includes all other factors, is not dependent on the solvent dielectric constant, and of which the factor  $\Delta S$  itself is temperature independent. These are all simplifications of an admittedly complex process. It is difficult to imagine the process broken into discrete steps, the free energy changes for which would correspond to those outlined above.

Marshall and Quist, in their treatment of these data, allowed only for changes in the free energy of solvation through changes in the water concentration as the density changed. This approach has been shown above to be incorrect in principle. One of the most interesting aspects, to this author, of these data of Marshall and Quist is that they provide a vivid illustration of an experimental technique by means of which the contribution to  $K_d$  of changes in dielectric constant may be separated from the contribution to  $K_d$  of changes due to specific solvation effects.