

The thermodynamic quantities for ion association at 303.1°K are given in Table 3. They were derived from the mole fraction equilibrium constant ${}^xK_\gamma$, which is related to the molar equilibrium constant through the molar volume V of the solution by ${}^xK_\gamma = K_\gamma/V$, found at various temperatures and pressures.

The limiting molar conductance of an ion can be expressed in terms of the transition state theory⁴ by the equation:

$$\lambda_i^0 = (zeF/6h)L^2 \exp(-\Delta G^\ddagger/RT) \quad (3)$$

in which L is the jump distance through which an ion moves when it passes through the transition state, and the other symbols have their usual significance. The equation can be used to calculate ΔG^\ddagger if one assumes¹⁶ that $L = (V/N)^{1/3}$ (where V is the molar volume of the solvent and N is Avogadro's number), and uses experimental values of Λ^0 in place of the unknown ionic conductance λ_i^0 .^{4,5}

Differentiation of (3) with respect to temperature and pressure leads to equations (4) and (5)

$$\Delta H^\ddagger = RT^2(\delta \ln \lambda_i^0/\delta T)_P - \frac{2}{3}RT^2\alpha \quad (4)$$

$$\Delta V^\ddagger = -RT(\delta \ln \lambda_i^0/\delta P)_T - \frac{2}{3}RT\beta \quad (5)$$

in which α is the isobaric thermal expansivity and β the isothermal compressibility of the solvent. Values of the activation parameters evaluated from (3), (4), and (5) are given in Table 4.

TABLE 4
ACTIVATION PARAMETERS FOR CONDUCTANCE
 ΔG^\ddagger and ΔH^\ddagger in kJ mol⁻¹; ΔS^\ddagger in J mol⁻¹ K⁻¹; ΔV^\ddagger in cm³ mol⁻¹

| Parameter | Activation Parameters at 303.1°K for P (bar) | | | | |
|---------------------|--|----------------------------|-------|-------|-------|
| | 1 | 506 | 1013 | 2026 | 3040 |
| | | mmpI in Acetone | | | |
| ΔG^\ddagger | +9.37 | +9.75 | +10.3 | +10.9 | +11.6 |
| ΔH^\ddagger | +11.3 | +13.0 | +12.6 | +12.1 | +7.1 |
| ΔS^\ddagger | +6.7 | +10.9 | +7.9 | +4.6 | -14.6 |
| ΔV^\ddagger | | +9.1 | +8.4 | | +6.8 |
| | | mmpI in Bu ¹ OH | | | |
| ΔG^\ddagger | +16.4 | +17.4 | +18.1 | +19.3 | +20.3 |
| ΔV^\ddagger | | 17.7 | 14.3 | 12.4 | 9.8 |
| | | NaI in Bu ¹ OH | | | |
| ΔG^\ddagger | +16.8 | +17.8 | +18.5 | +19.7 | +20.7 |
| ΔH^\ddagger | +6.7 | +7.9 | +8.4 | +10.9 | +11.7 |
| ΔS^\ddagger | -33 | -33 | -33 | -30 | -29 |
| ΔV^\ddagger | | +15.0 | +13.5 | +12.8 | +10.3 |

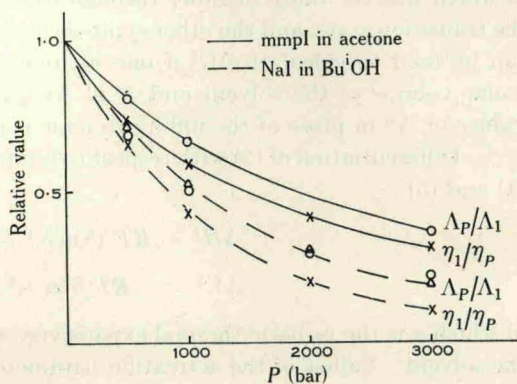
The volume change, ΔV , accompanying the formation of ion pairs can be calculated from the values of ΔG given in Table 3. The values of ΔV given in Table 3

¹⁶ Brummer, S. B., *J. chem. Phys.*, 1965, **42**, 1636.

are estimated to be accurate to $\pm 1 \text{ cm}^3 \text{ mol}^{-1}$. The increase in volume is due to the decrease in electrostriction of the solvent around the ions as these join to form ion pairs, and the effect rapidly decreases with rising pressure as the free solvent itself is compressed.

The decrease in K_γ with rising pressure means that the number of free ions in the solution increases, but Table 2 shows that the conductance of the solution decreases nonetheless. This is illustrated by Figure 2 in which the relative conductance, Λ_P/Λ_1 , and for comparison, the relative fluidity of the solvent, η_1/η_P , are

Fig. 2.—Relative conductance of solutions and relative fluidity of solvents as a function of pressure.



plotted as a function of pressure. The decrease in the relative conductance is smaller, and this shows that the increase in viscosity is partly compensated by the increase in the concentration of charge carrying ions. The degree of dissociation γ increases with pressure but at the lowest concentration (about $10^{-3} \text{ mol l}^{-1}$) and highest pressure (3000 bar) it still only reaches 0.9 for NaI in Bu¹OH and 0.82 for mmpI in acetone.

The decrease in relative conductance with pressure is more pronounced in Bu¹OH than in acetone and Figure 2 shows that this is due to a greater increase in the already large viscosity of Bu¹OH (see Table 1). The large viscosity also accounts for the low Λ^0 and large ΔG^\ddagger (Table 4) of mmpI in Bu¹OH.

Sodium iodide is less associated than mmpI in Bu¹OH but at the same time has a lower limiting conductance. This indicates that Na⁺ has a lower mobility than mmp⁺, presumably due to more extensive solvation of the smaller ion.

The conductances of some quaternary ammonium iodides in acetone were recently measured by Adams and Laidler⁵ over a range of pressures and temperatures and were used to find limiting conductances, association constants K_A (equation (1)), and activation parameters (equations (3)–(5)). Their values for Pr₄N⁺I⁻ are compared with our values for mmpI in Table 5 and show close agreement in Λ^0 , ΔV , and ΔV^\ddagger in spite of the difference in association constant. Values of ΔH^\ddagger , on the other hand, are different for the two electrolytes but show little pressure dependence.

Reynolds and Kraus¹⁷ derived a value for the limiting ionic conductance of I⁻ in acetone at 298°K from measurements on R₄N⁺FBPh₃⁻ and RN⁺I⁻ (R = n-butyl) and one can use this value to find the limiting conductance of the mmp⁺ cation

¹⁷ Reynolds, M. B., and Kraus, C. A., *J. Am. chem. Soc.*, 1958, **70**, 1709.