The Effect of Pressure on Electrical Conductance and Freezing Point of Molten Tetra-n-hexylammonium Tetrafluoroborate

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Summary The pressure dependence of the electrical conductance of a molten organic salt provides information on the significance of the intermolecular potential in liquid transport properties.

ACTIVATION volumes for equivalent conductance, $\Delta V_{\Lambda} = -RT\,(\partial \ln\Lambda/\partial P)_{T}$, have been measured previously for the fused alkali metal nitrates.[1,2] The conductance at 1 bar, and other physical properties, are known for several organic salts.[3] We present here what we believe to be the first reported electrical conductance activation volume for a molten organic salt.

The specific conductance κ, of $(\text{n-hexyl})_4N^+BF_4^-$ (m.p. 91°) was measured as a function of temperature up to 215° at the pressures 8, 254, 510, 754, and 1010 bar. The 80 data points may be represented by the empirical equation,

$$\log_{10}\kappa = 0{\cdot}322 - 3{\cdot}2 \times 10^{-5}P - (779{\cdot}4 + 0{\cdot}068P)/(T-160)$$

where P is the pressure in bar, and T is the temperature in °K. The standard deviation in $\log_{10}\kappa$ is 0·004 which may be compared with the estimated experimental error of ±0·8% in κ or ±0·0035 in $\log_{10}\kappa$. The greatest deviation of any point is 0·010; the only consistent deviation is at 510 bar where the experimental values of $\log_{10}\kappa$ average 0·003 less than is given by this equation. κ varies by a factor of 20 in the temperature range and by 50% in the pressure range at constant temperature.

The freezing point was determined as the temperature at which the conductivity decreased sharply, on cooling at the rate of 0·3°/min., and was reproducible to within ±0·1°. The freezing point was 91·1° at 8 bar, 99·4° at 254 bar, 105·5° at 510 bar and 110·2° at 755 bar.

The activation energy for equivalent conductance may be obtained using the equations

$$\begin{aligned} E_{\Lambda} &= -R\,[\partial \ln\Lambda/\partial(1/T)]_{P} \\ &= -2{\cdot}303\,R\,[\partial\log_{10}\kappa/\partial(1/T)]_{P} - \alpha RT^2 \end{aligned}$$

The expansivity α has an average value of $6{\cdot}5 \times 10^{-4}$ °K^{-1} at atmospheric pressure[4] and the value of αRT^2 is less than 1·2 kJ/mole. At 8 bar, $E_{\Lambda} = 45{\cdot}3$ kJ/mole at 107° and decreases monotonically to 34·7 kJ/mole at 207°, while E_{Λ} decreases linearly with pressure by 9% in 1000 bar at constant temperature.

The activation volume for equivalent conductance ΔV_{Λ} may be obtained if the compressibility β is known, using the equations

$$\begin{aligned} \Delta V_{\Lambda} &= -RT\,(\partial \ln\Lambda/\partial P)_{T} \\ &= -2{\cdot}303\,RT\,(\partial \log_{10}\kappa/\partial P)_{T} + \beta RT \end{aligned}$$

An estimate of β intermediate between that of the low melting, inorganic molten salts ($\beta = ca.\ 2 \times 10^{-5}$ bar)[5] and a mixture of polar organic liquids such as chloroform and acetone ($\beta = ca.\ 8 \times 10^{-5}$ bar)[6] seems reasonable. With $\beta = 5 \times 10^{-5}$ bar^{-1}, βRT has the values 1·6 ml at 120° and 2·0° ml at 207°; $\Delta V_{\Lambda} = 26{\cdot}3$ ml/mole at 120° and decreases monotonically to 24·5 ml/mole at 207°.

An internally-heated gas pressurized system similar to that described by Fray[2,7a] was used. Dissolution of the pressurising gas[1] was prevented by a loose fitting glass piston incorporating a 'Viton' 'O'-ring seal in a precision bore glass tube.[7b] The efficiency of this seal and the stability of the salt were demonstrated by the absence of hysteresis in the temperature cycle and the reproducibility of 8 bar data after a high pressure run. Values of equivalent conductance calculated by extrapolation and using the density data given by Lind *et al.*[4] are 2% to 4% lower than Lind's values.

It has been shown[8] that the activation volume for self diffusion (ΔV_D) for methane (12 ml/mole) is small compared with its molar volume (38 ml/mole) while ΔV_D values for liquid argon, krypton, and xenon are rather larger than the corresponding molar volumes. The small ΔV_D for the polyatomic, "globular" methane has been attributed to the steeper intermolecular potential shown by more complex molecules.[8–10] In a fused salt with cation and anion of different size, the electrical conductance is considered to be largely determined by the mobility of the smaller ion.[11] Also, transport properties are almost entirely determined by the short range part of the potential.[10,12] In fused sodium nitrate the ΔV_{Λ} value (3·8 ml/mole at 400°) is rather larger than the Na^+ volume (2·2 ml/mole). The present investigation shows that tetra-n-hexylammonium tetrafluoroborate, with an r_-/r_+ ion radius ratio value similar to the r_+/r_- ratio value of sodium nitrate, has $\Delta V_{\Lambda} =$ *ca.* 25 ml/mole while the polyatomic BF_4^- volume is twice as great, *ca.* 51 ml/mole. This supports the conclusion that the pressure dependence of transport properties is smaller when the intermolecular potential is steeper.

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