Partition of Viscosity B-Coefficients into Ionic Components

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Summary Resolution into ionic components of the viscosity B-coefficients for a number of salts in formamide has shown good agreement between values obtained by a correspondence technique based on ion entropies and by Krumgal'z method, but poor correlation with values derived using the assumptions of Cox and Wolfenden.

In aqueous electrolyte solution, the use of different methods of resolving viscosity B-coefficients into ionic components has generally produced concordant results. The most popular basis for partition is that of Cox and Wolfenden[1] who argued on the basis of the Stokes-Einstein equation that ionic B-coefficients could be determined by splitting the salt B-coefficient in the ratio of the 'volumes' of the solvated ions as determined from ionic mobilities. Gurney[2]

TABLE

Ionic B-coefficients/dm³ mol⁻¹ in formamide at 25 °C

Ion	I[a]	II[b]	III[c]
Li⁺	0·378	0·311	0·307
Na⁺	0·490	0·423	0·419
K⁺	0·264	0·197	0·192
Rb⁺	0·241	0·174	0·171
Cs⁺	0·215	0·148	0·144
Cl⁻	0·100	0·167	0·171
Br⁻	0·058	0·125	0·129
I⁻	0·028	0·095	0·099

[a] Data using Cox and Wolfenden method. [b] Data using Krumgal'z method. [c] Data obtained by a correspondence method based on ion entropies.

suggested special reasons for taking $B(\mathrm{K}^+) = B(\mathrm{Cl}^-)$ in aqueous solution. More recently Krumgal'z[3] has proposed a general method for any solvent, based on a postulated invariant 'radius' of large tetra-alkylammonium ions.

Partition of B-coefficients in formamide solution on the basis of the Cox and Wolfenden method and using limiting ionic conductances determined by Notley and Spiro[4] has been described previously.[5] In column I of the Table results are given for the application of this method to our most recent data.

B-Coefficients for tetrabutylammonium iodide and tetrapentylammonium iodide were measured at 25 °C. Hence

$$B(\mathrm{Bu_4N^+}) - B[(\mathrm{C_5H_{11}})_4\mathrm{N^+}]$$
$$= B(\mathrm{Bu_4N^+I^-}) - B[(\mathrm{C_5H_{11}})_4\mathrm{N^+I^-}]$$
$$= 0\cdot602 - 0\cdot801 = -0\cdot199$$

Also, after Krumgal'z,

$$B(\mathrm{Bu_4N^+})/B[(\mathrm{C_5H_{11}})_4\mathrm{N^+}] = (0\cdot385)^3/(0\cdot430)^3 = 0\cdot718$$

Solving gives $B(\mathrm{Bu_4N^+}) = 0\cdot507$ dm³ mol⁻¹ and hence $B(\mathrm{I^-}) = 0\cdot095$ dm³ mol⁻¹. The principle of additivity then gives the ionic B-values of column II in the Table.

The linear relationship between partial molar ionic entropy and B-coefficients was first demonstrated by Gurney,[2] who used aqueous ionic B-values as the basis for obtaining single ion entropies. Partial molar entropies of electrolytes in formamide, expressed in the molal standard state, have been determined by Criss *et al.*[6] These values were converted into the mole fraction standard state and the intrinsic entropy of the solute (as a hypothetical ideal gas, determined by the Sacker–Tetrode equation) was subtracted. The $S_{\mathrm{ion}}^{\ominus}$ values so determined were considered to represent the entropy change in the solvent due to the presence of the ion. A 'correspondence' plot was then drawn, as shown in the Figure. The best straight line was obtained with the ionic B-coefficients given in column III of the Table.
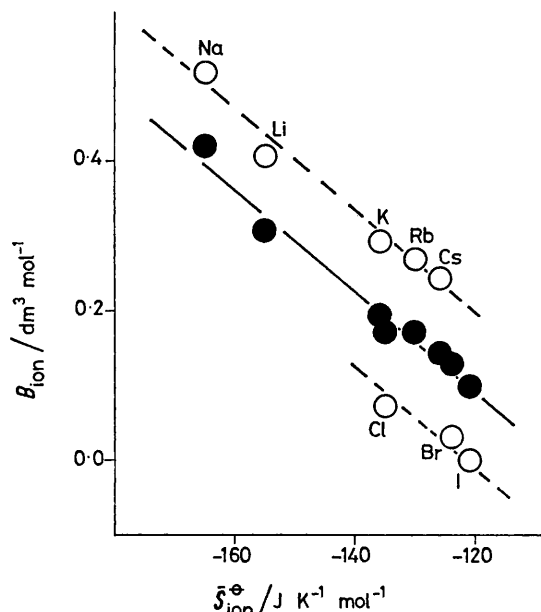

FIGURE. Plot of $S_{\mathrm{ion}}^{\ominus}$, the entropy change in the solvent due to the presence of an ion, *vs.* B_{ion}, the ionic B-coefficients for various ions in formamide at 25 °C. ○: data obtained by arbitrarily fixing $B(\mathrm{I^-})$ equal to zero; ●: data obtained by least squares fit for best straight line.

Excellent agreement is noted between the B-coefficients in columns II and III which were derived by methods having completely different basic assumptions. This finding both gives confidence in these B-values and suggests that the method of Krumgal'z may be the preferred technique for resolution of viscosity B-coefficients into their ionic components.

(*Received, 24th October* 1977; *Com.* 1118.)

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