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Viscosity *B*-Coefficients of Ions in Solution

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I. Introduction

The *B*-coefficients of the Jones–Dole[1] empirical expression of the relative viscosities of electrolyte solutions as a function of their concentration are important for a number of reasons.

(i) They offer an excellent source of *primary data*, in that measurement of the viscosity demands the highest precision on the part of the experimentalist. It is in the nature of the measurements that they readily reveal poor experimental technique.

(ii) The *B*-coefficients are known to provide information concerning the solvation of the ions and their effects on the structure of the solvent in the near environment of the solute particles.

(iii) Because of the nature of the *B*-coefficients and their ion-additive properties, potentially important correlations exist between these coefficients and other ion-additive properties (e.g., enthalpies, Gibbs free energies and entropies of hydration, solvation, and transfer between solvents). In this sense the *B*-coefficients may provide the key for the rationalization of a host of thermochemical data. This fact alone makes the critical review of the current *B*-coefficient data timely.

At present, a large collection of data on ionic *B*-coefficients is available for both aqueous and nonaqueous solvents at both ambient and other temperatures, although there exists so far no theory on the *B*-coefficients. It is the purpose of this review

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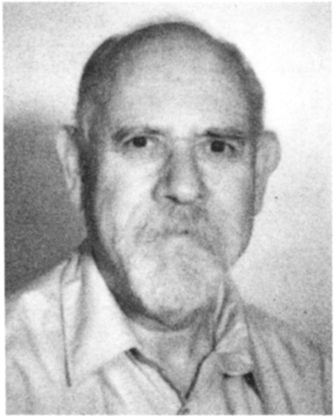
Harry Donald Brooke Jenkins received his first degree from UMIST in 1962 and his D.Phil from the University of Sussex in 1965 for work on the early development of molecular orbital theory. He holds the post of Reader in Chemistry at the University of Warwick. His research interests are concerned with the thermodynamics and theory of the computation of lattice potential energies of crystal lattices. Recently he has been concerned with the use of viscosity *B*-coefficients as a tool for the correlation of thermodynamic hydration and solvation properties of ions in aqueous and nonaqueous media. His main work, however, involves the study of complex layered phyllosilicates and the improvement of models to understand the properties and behavior of ions in the restricted geometry environments of the interlayer.



Yizhak Marcus, born in Germany and having immigrated to Israel, obtained his M.S. in 1952 and Ph.D. in 1956 from the Hebrew University of Jerusalem. He did radiochemical work at the Soreq Nuclear Research Center till 1965, when he was appointed professor of inorganic and analytical chemistry at the Hebrew University, where he continues to serve. His research interests concern solution chemistry, as evidenced by the titles of the books he (co)authored: *Ion Exchange and Solvent Extraction of Metal Complexes* (1969), *Introduction to Liquid State Chemistry* (1977), and *Ion Solvation* (1985). Presently he is interested in preferential solvation of ions and nonelectrolytes in solvent mixtures.

to provide a critical survey of the relevant data available to the end of 1993 and on the basis of this database to show the interesting correlations that can now be made. Since the discussion concerns the *B*-coefficients that are obtained for dilute solutions of electrolytes, the expressions and data pertaining to higher concentrations (that is, >0.1 mol dm^{-3}) are not included, nor are data pertaining to mixed solvents, since this would have broadened the review exceedingly much; thus only data for neat solvents are covered.

A. The Viscosity of Liquids

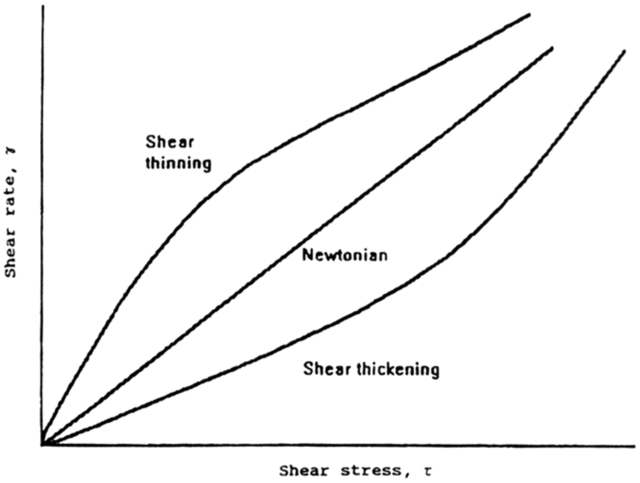


Figure 1. The shear rate, $\dot{\gamma}$, of different kinds of fluids plotted against the shear stress, τ.

A liquid can be defined as a material that deforms as long as it is subjected to a tensile or shear stress, τ. Under shear, the rate of deformation (or shear rate) $\dot{\gamma}$ is proportional to the shearing stress. Newton originally proposed that the ratio of the stress to the shear rate is a constant: the viscosity. According to Newton's law, the viscosity is independent of the shear rate. This is true for ideal or "Newtonian" liquids, but the viscosities of many liquids are not independent of the shear rate. Such "non-Newtonian" liquids can exhibit either shear-thinning or shear-thickening and are classified according to their viscosity behavior as a function of the shear rate (Figure 1).

The *dynamic viscosity* (η) of a liquid is equal to the gradient of the shear stress − the shear rate curve:

$$\eta = \mathrm{d}\tau/\mathrm{d}\dot{\gamma} \qquad (1)$$

The ratio $\tau/\dot{\gamma}$ is the absolute viscosity for a Newtonian liquid or the apparent viscosity of a non-Newtonian one. The *kinematic viscosity* (ν) of a liquid is the viscosity coefficient divided by the density of the liquid, ρ:

$$\nu = \eta/\rho \qquad (2)$$

The *fluidity* (φ) of a liquid is the reciprocal of its (dynamic) viscosity:

$$\varphi = 1/\eta \qquad (3)$$

The viscosities of the solutions measured to obtain the *B*-coefficients forming the subject of this review are obtained on the assumption that the fluids examined are Newtonian liquids throughout the concentration range considered (Figure 1). The viscosity is therefore assumed to be independent of the shear gradient, $\dot{\gamma}$.

The most common units for the viscosity η are dyn s cm^{-2} or g s cm^{-2}, which are called poise, P (named after Poiseuille;[2] see eq 6 below). Since the actual viscosity of both water and dilute aqueous solutions at ambient temperatures are nearly 100-fold lower, a commonly used unit is the centipoise, cP. Such units are being superseded by the SI units of pascal·second, Pa s, and the submultiple mPa s:

$$1 \text{ mPa s} = 1 \text{ cP} \qquad (4)$$

In the same way, the units of shear stress of dyne·cm^{-2} are being replaced by pascals, Pa, i.e., newtons per square meter:

$$1\ \mathrm{Pa} = 1\ \mathrm{N\ m^{-2}} = 10\ \mathrm{dyn\ cm^{-2}} \qquad (5)$$

The units of shear rate are s^{-1} in both systems. The common units for the kinematic viscosity, ν, are stokes, St (named after Stokes[3]), and centistokes, cSt, and the equivalent units are cm^2 s^{-1} and mm^2 s^{-1}, respectively.

B. Measurement of Viscosity

There are a range of viscosimeters available commercially for the measurement of viscosity. The selection of a viscosimeter depends on a number criteria: the magnitude of the viscosity to be measured, whether the liquid or solution are elastic, whether they are transparent or opaque, and the temperature dependence of the viscosity. Since the latter dependence can be appreciable, careful control of this parameter is vital if accurate, precise measurements are to be made. More errors are made and more disagreements arise because of incorrent temperature specification or temperature drift during the measurement than for any other reason. Commercially available thermostated baths or circulators can achieve the necessary control.

There are three basic types of viscosimeter: capillary, rotational, and moving-body.[4,5] Capillary flow measurement involves the liquid or solution draining (or being forced) through a fine-bore tube. The viscosity is determined from the measured flow rate, the applied pressure, and the dimensions of the tube, using the Hagen–Poiseuille equation:

$$\eta = \pi r^4 \Delta p t / 8 V l \qquad (6)$$

where r is the radius of the constant-bore capillary and l is its length, Δp is the pressure drop along the capillary, and V is the volume of liquid that flows during the time t. For a given viscosimeter, similar fluids, and a constant pressure drop, this equation reduces to:

$$\eta = Kt \qquad (7)$$

or, more commonly,

$$\nu = \eta/\rho = Ct \qquad (8)$$

where ν is the kinematic viscosity ($K = C\rho$). This means that the viscosimeter is calibrated with a reference liquid (R) of accurately known viscosity and that the viscosity of the liquid or solution that is examined is obtained (approximately) from the ratio of the flow times:

$$\nu = (t/t_\mathrm{R})\nu_\mathrm{R} \qquad (9)$$

For accurate work, however, corrections have to be applied.[4] The expression for Δp involves a buoyancy correction[6] for the corresponding volume of air. Corrections for the formation of streamlines at the entrance and exit of the capillary should also be made, as well as corrections for kinetic energy effects which accelerate the fluid at the mouth of the capillary.

Rotational viscosimeters involve two parts (usually concentric cylinders) separated by the liquid or solution to be tested. The relative movements of these parts produce a shearing action and the torque required to produce a given angular velocity is a measure of the viscosity. Moving-body viscosimeters involve a moving ball, bubble, plate, or rod, the rate of movement (fall) of which is monitored in order to determine the viscosity.

The capillary viscosimeter described above is almost exclusively used for the measurement of the viscosity *B*-coefficients. Typically used is the Ubbelohde[7] or the ASTM[6] type. Flow times of the order of 100 s are determined by monitoring the time the meniscus of the fluid takes to descend between two calibration marks (that are often above and below a bulb that contains a known volume (V) of the fluid) through the capillary. This monitoring may involve electro-optical detection devices,[8] but the positioning of the light source must not cause any heating of the viscosimeter, in view of the strong sensitivity of viscosity to temperature (up to 3% K^{-1} in water).

When all the necessary precautions are taken, including strict temperature control to ±0.01 K, the absolute viscosity (η) of a fluid can be measured to an accuracy of better than 0.25%. Relative viscosities (the ratio of the viscosity of a solution, η, and that of the solvent, η_o) can on the other hand be readily made to a precision of 0.01% or better.

C. Relevant Properties of Solvents

The solvents in which ionic *B*-coefficients have been determined are all polar, but their properties vary considerably. Table 1 lists such solvents and relevant properties for the present review. It includes the dynamic viscosity (η_o) in mPa·s (equivalent to cP), and its temperature coefficient $[-(\delta\eta_\mathrm{o}/\delta T)_p]$ in mPa s K^{-1}. One measure of the polarity is the permittivity (ϵ), which describes the attenuation of the force between charges in the medium due to the dipoles of the fluid. It is related to the permittivity of vacuum (ϵ^*) by

$$\epsilon = \epsilon_\mathrm{r}\epsilon^* \qquad (10)$$

where ϵ_r is the relative permittivity. The permittivity of a vacuum is 8.8542×10^{-12} C^2 N^{-1} m^{-2}. The relative permittivity (ϵ_r) is often loosely called the dielectric constant, abbreviated to ϵ_o for pure liquids in the following, and is dimensionless. Also included are the dielectric relaxation times, τ, in ps, that are involved in the relationship of the ionic conductivities and the solution viscosity. The values are cited for 25 °C and 1 atm (0.101325 MPa) and are taken mainly from Riddick et al.,[9] DIPPR,[10] and Buckley and Mariott.[11] Comments on the nature of the solvent—its structuredness[12] and whether protic or dipolar aprotic—are also included. The change of the viscosity of water with temperature and pressure has been discussed and reviewed,[13] but much less in this direction has been done concerning nonaqueous solvents.

Table 1. The Relevant Properties of the Solvents at 25 °C[a]

solvent	abbrev	η_o/cP	$-d\eta_o/dT$	ϵ	τ/ps[f]	comments
water		0.8903	0.0199	78.36	10	3-dimensional structd
methanol	MeOH	0.5513	*0.0078*	32.66	53	protic, lin. H-bonded
ethanol	EtOH	1.0826	*0.0205*	24.55	143	protic, lin. H-bonded
1-propanol	1PrOH	1.9430	*0.0469*	20.45	430	protic, lin. H-bonded
2-propanol	2PrOH	2.0436	*0.0568*	19.92	292	protic, lin. H-bonded
1-butanol	BuOH	2.5710	*0.0704*	17.51	668	protic, lin. H-bonded
1-pentanol	PeOH	3.5128	*0.0981*	13.9	927	protic, lin H-bonded
1-hexanol	HxOH	4.592	*0.1395*	13.3	1210	protic, lin. H-bonded
ethane-1,2-diol	EG	*17.712*	*0.721*	37.7	106	protic, highly structd
propane-1,2-diol	1,2PrG	*40.39*	*2.39*	32.0[d]		protic, structd
propane-1,3-diol	1,3PrG	*24.55*	*0.863*	35.0[d]		protic, structd
glycerol		945	*73.2*	42.5	3890	protic, highly structd
2-aminoethanol	MEA	19.346	*0.807*	37.72		protic, highly structd
triethanolamine	TEA	613.6	*45.0*	29.36		protic, structd
2-methoxyethanol	MeOEtOH	1.60	*0.0396*	16.93		protic
tetrahydrofuran	THF	0.460	*0.0047*	7.58	3	dipolar aprotic
acetone	Me_2CO	0.3029	*0.0029*	20.56	3	dipolar aprotic
2-butanone	MeCOEt	0.378	*0.0043*	18.51[d]	10	dipolar aprotic
sulfuric acid		*23.55*	*0.874*	100[e]		highly structd
acetic acid	HAcO	1.1302	*0.0163*	6.17[d]	23	self-associated
ethylene carbonate	EC	1.930[b]	*0.127*	89.78[b]		dipolar aprotic
propylene carbonate	PC	2.530		64.92		dipolar aprotic
pyridine	Py	0.884	*0.0133*	12.91	7	dipolar aprotic
formamide	FA	3.302	*0.0859*	111.0[d]	108[g]	protic, highly structd
N-methylformamide	NMF	1.65	*0.0263*	182.4	24[g]	protic, lin. H-bonded
N-methylacetamide	NMA	3.65[c]		191.3[c]	9[g]	protic, lin. H-bonded
N-methylpropanamide	NMP	5.215		175.5	12[g]	protic, lin. H-bonded
N,N-dimethylformamide	DMF	0.802	*0.0107*	36.71	15[g]	dipolar aprotic
tetramethylurea	TMU	139.50		23.60		dipolar aprotic
hexamethylphosphoric triamide	HMPT	3.10		30.0		dipolar aprotic
acetonitrile	MeCN	0.341	*0.0033*	35.94	5	dipolar aprotic
nitromethane	$MeNO_2$	0.614	*0.0074*	35.87[c]		dipolar aprotic
nitrobenzene	$PhNO_2$	*1.901*	*0.0335*	34.78	46	dipolar aprotic
dimethyl sulfoxide	DMSO	1.991	*0.0450*	46.45	21	dipolar aprotic
sulfolane	TMS	10.286[c]	*0.268*	43.26[c]		dipolar aprotic
dichloromethane		*0.4134*	*0.0383*	8.93	8	dipolar aprotic
1,2-Dichloroethane	1,2DClE	*0.770*	*0.0100*	10.37	7	dipolar aprotic

[a] Roman type numbers from ref 9; italic type numbers from ref 10. [b] At 40 °C, $\theta_m = 36.7$ °C. [c] At 30 °C, $\theta_m = 28.45$ °C. [d] At 20 °C. [e] from ref 201. [f] From ref 11 at 20 °C and other sources. [g] From ref 202, interpolated to 25 °C.

D. The Viscosity of Nonelectrolyte Solutions

The interpretation of the ionic B_i-coefficients defined in section II devolves qualitatively around concentration dependence of the relative viscosity of solutions of nonelectrolytes. This quantity was shown by Einstein[14] to be given by the equivalent quantity for suspensions of spherical macroscopic but very small (possibly colloidal but not molecular) particles. Einstein calculated the energy dissipated per unit time per unit volume by the resistance of the solvent, respectively the suspension, to the flow, and obtained therefrom the relationship of the viscosity of the suspension relative to the solvent. In a later paper[14] Einstein corrected a mistake in his original derivation and arrived finally at the expression

$$\eta = \eta_o(1 + 2.5v) \qquad (11)$$

Here v is the aggregate volume of the particles in a unit volume (1 cm^3) of the solution. He compared his calculated value with the datum for 1% by weight of sucrose in water, obtaining a reasonable result: a specific volume of the hydrated sucrose in the solution of 0.98 $cm^3\ g^{-1}$ compared with that of the solid of 0.61 $cm^3\ g^{-1}$ (also an estimate of Avogadro's number only 9% higher than the correct value resulted).

The coefficient of v in eq 11 is 2.5 for spherical particles, but can be called a in the general case of particles having other shapes, in which case it is larger than 2.5. Jefferey[15] and Simha[16] considered particles that are ellipsoids of rotation with the axial ratio R. An expression for log a that is approximately parabolic with log R is obtained, but is independent of the actual size of the particle. Stokes and Mills[7] gave a graphical presentation of this relationship. In fact,

$$a = 2.5 + 0.59(R - 1) + 2.40(R - 1)^2 \qquad (12)$$

is a good enough representation of the data, given the approximate nature of the correction.

If the term av (2.5v for spheres) is taken to be valid also for solutes of molecular size (large molecules of nonelectrolytes), then it is equivalent to the product of a coefficient times the molar volume of the (solvated) solute times the molar concentration, and this is assumed to be equivalent to the product Bc in the Jones–Dole expression (cf. section II.B).

II. The Jones–Dole Expression for Electrolyte Viscosities

In the historical review introducing their paper on the viscosity of aqueous solutions of strong electrolytes, Jones and Dole[1] mentioned that it was Poiseulle in 1847[2] who first noted that some salts increase the viscosity of water whereas others decrease it. In their attempt to interpret their own and others' viscosity data for dilute aqueous solutions of electrolytes, Jones and Dole rejected several expressions suggested earlier, e.g., that of Arrhenius,[17] $\eta/\eta_o = A^C$, where A was a solute and temperature dependent constant. They noted that the electrostatic forces which tend to maintain a quasilattice of the ions in the solution (an ionic atmosphere of oppositely charged ions) would stiffen the solution, i.e., increase its viscosity.[18] Since these forces are proportional to the square root of the concentration in very dilute solutions, it occurred to Jones and Dole to cast the expression for the relative fluidity, $\varphi/\varphi_o = 1/(\eta/\eta_o)$, in the form:

$$\varphi/\varphi_o = 1 + A'c^{1/2} + B'c \qquad (13)$$

where c is the molar concentration of the electrolyte in mol dm^{-3}. They expected the coefficient A' to be negative and the coefficient B' to be either positive or negative. They indeed found plots of $(\varphi/\varphi_o - 1)/c^{1/2}$ to be straight lines with a negative intercept (A'). The concentration range covered by their data extended from 0.005 to 1.0 mol dm^{-3}, but the square root term was dominant mainly for $c < 0.05$ mol dm^{-3}.

Later authors inverted the original Jones–Dole expression and recast it in terms of the relative viscosity (rather than fluidity):

$$\eta/\eta_o = 1 + Ac^{1/2} + Bc \qquad (14)$$

which is the form usually employed nowadays. Some electrolytes require an additional term in the square of the concentration at accessible concentrations:

$$\eta/\eta_o = 1 + Ac^{1/2} + Bc + Dc^2 \qquad (15)$$

with A, B, and D being coefficients depending on the solute, the solvent, and the temperature. For most salts the term in the square of the concentration is unimportant at $c < 0.5$ mol dm^{-3}, but its inclusion makes the empirical expression (15) valid at substantially higher concentrations.

As mentioned above, the A term depends on the interionic forces and can be evaluated theoretically (see section II.A). The B term, on the other hand, depends on ion–solvent interactions and is related to the volumes of the ions, but so far in a theoretically inaccessible manner (see section III). It is hoped that this review might stimulate further activity in this area.

A. The Jones–Dole *A*-Coefficient

If highly accurate data at sufficiently low concentrations (<0.05 mol dm^{-3}) are available, then A can be obtained from the intercept of the straight line dependence of the left hand side of eq 16 on $c^{1/2}$:

$$[(\eta/\eta_o) - 1]/c^{1/2} = A + Bc^{1/2} \qquad (16)$$

Otherwise it can be calculated theoretically, if the equivalent conductivities of the constituent ions are known. Soon after Jones and Dole[1] presented their empirical finding of the necessity of the inclusion of the ion–ion interaction term in the viscosity expression, Falkenhagen and Dole[19] gave a theoretical derivation of the A coefficient. It is based on the drag that the ion atmosphere causes that retards the movement of an ion and indirectly diminishes the fluidity of the solution. Its general form is

$$A = [A^*/\eta_o(\epsilon_o T)^{1/2}]f(\lambda_+^\infty,\lambda_-^\infty,z_+,z_-) \qquad (17)$$

where the constant A^* takes the form and has the value

$$A^* = Fe^2N_A{}^{1/2}(1 + \sqrt{2})/12\pi(\epsilon^*k)^{1/2}$$
$$= 1.113 \times 10^{-5}\ \mathrm{C}^2\ (\mathrm{m\ K\ mol}^{-3})^{1/2} \qquad (18)$$

Here F is a Faraday, 96 485 C mol^{-1}; e is the unit charge, 1.6021×10^{-19} C; N_A is Avogadro's constant, 6.022×10^{23} mol^{-1}; ϵ^* is the permittivity of a vacuum; and k is Boltzmann's constant, 1.3085×10^{-23} J K^{-1}. The value of A depends also on the viscosity of the solvent, η_o; its relative permittivity (dielectric constant), ϵ_o; and the temperature, T. The function f has the dimension of the reciprocal of the equivalent conductance (see below). The numerical constant A^* (eq 18) is valid when the quantities η_o and f are expressed in SI units, i.e., η_o in Pa s and f in S^{-1} m^{-2} mol, and then the A-coefficient is in m$^{3/2}$ mol$^{-1/2}$. If practical units are employed, i.e., if η_o is in cP, and f is in Ω cm^{-2} mol, A is then obtained in units of dm$^{3/2}$ mol$^{-1/2}$. In this case the constant A^* becomes:

$$A^* = 111.3\ \mathrm{cP\ (cm^2\ S\ mol^{-1})\ K^{1/2}\ dm^{3/2}\ mol^{-1/2}} \qquad (19)$$

The function f of the equivalent conductances at infinite dilution of the ions, $\lambda_\pm^\infty$, and their charges, $z_\pm$, takes the specific form:

$$f = [(\nu_+z_+)/(z_+ + |z_-|)]^{1/2}[(\lambda_+^\infty\lambda_-^\infty(1 + \sqrt{2})]^{-1} \times \left[\frac{(\lambda_+^\infty z_-{}^2 + \lambda_-^\infty z_+{}^2)}{4} - \frac{(\lambda_+^\infty|z_-| - \lambda_-^\infty z_+)^2}{[(\lambda_+^\infty + \lambda_-^\infty)^{1/2} + \{(\lambda_+^\infty|z_-| + \lambda_-^\infty z_+)(z_+ + z_-)/(z_+|z_-|)\}^{1/2}]^2}\right] \qquad (20)$$

where ν_+ is the number of cations in the formula of the electrolyte. This expression becomes much simpler in the case of symmetrical electrolytes, where $z_+ = |z_-| = z$:

$$f = [z^2(\lambda_+^\infty + \lambda_-^\infty)/4(2 + \sqrt{2})(\lambda_+^\infty\lambda_-^\infty)][1 - 4(\lambda_+^\infty - \lambda_-^\infty)^2/(1 + \sqrt{2})^2(\lambda_+^\infty + \lambda_-^\infty)^2] \qquad (21)$$

The second term in the second factor of eq 21 is relatively small when the difference in the equivalent conductances of the cation and anion is small, so that this entire factor can be removed as a first approximation in such cases.

A table of experimental as well as calculated A-coefficients was presented by Falkenhagen,[20] in-

Table 2. The *A*-Coefficients (in $dm^{3/2}$ $mol^{-1/2}$) of Aqueous Electrolytes at 25 °C[20]

electrolyte	exptl *A*	theoret *A*	electrolyte	exptl *A*	theoret *A*
HCl	0.0021	0.0022	$MgSO_4$	0.0225	0.0228
NaCl	0.0062	0.0060	$MnSO_4$	0.0231	0.0227
NaOH	0.0036	0.0035	$CuSO_4$	0.0230	0.0230
KCl	0.0052	0.0050	$ZnSO_4$	0.0229	0.0225
KBr	0.0047	0.0049	$CdSO_4$	0.0232	0.0225
KI	0.0047	0.0050	$LaCl_3$		0.0285
KNO_3	0.0050	0.0052	$CeCl_3$	0.031	0.030
$KClO_3$	0.0050	0.0054	$PrCl_3$		0.0285
$KBrO_3$	0.0058	0.0058	$NdCl_3$		0.0286
$KMnO_4$	0.0058	0.0056	$SmCl_3$		0.0288
CsI	0.0039	0.0048	$TbCl_3$		0.0293
$CsNO_3$	0.0043	0.0050	$DyCl_3$		0.0297
NH_4Cl	0.0052	0.0050	$HoCl_3$		0.0295
Et_4NI	0.0072	0.0073	$ErCl_3$		0.0296
$BaCl_2$	0.0201	0.0147	$Cr(SO_4)_3$	0.0495	0.0507
$FeCl_2$	0.0164	0.0168	$K_3Fe(CN)_6$	0.0370	0.0369
Li_2SO_4	0.0167	0.0166	$K_4Fe(CN)_6$	0.0405	0.0403
K_2SO_4	0.0135	0.0133			

cluding data for many electrolytes of several valence types and at several temperatures for aqueous solutions and a few values for nonaqueous solutions. For the latter, values of ϵ_o and η_o of the solvent and the $\lambda_\pm^\infty$ of the ions constituting the electrolyte are required in order to calculate *A*. The values of *A* (see Table 2) are rather small, and as mentioned above, the *A* term affects appreciably measured viscosities and the deduced values of *B* only for data at $c < 0.05$ mol dm^{-3}.

B. The Jones–Dole *B*-Coefficient

The *B*-coefficient is obtained from the slope of the dependence of the left hand side of eq 16 on $c^{1/2}$ or, with theoretically calculated *A* values, from

$$B = [(\eta/\eta_o) - 1 - Ac^{1/2}]/c \qquad (22)$$

which should be a constant and usually is for $c < 0.5$ mol dm^{-3}.

Values of the *B*-coefficients of 1:1 aqueous electrolytes consisting of small ions (i.e., not large, hydrophobic ones) are generally smaller than 0.2 dm^3 mol^{-1}. For many salts they are considerably smaller, e.g., $B(KCl,aq) = -0.014$ dm^3 mol^{-1} at 25 °C. For some aqueous salts they are negative, e.g., $B(CsNO_3,aq) = -0.090$ dm^3 mol^{-1}. For salts involving multivalent ions and salts involving large hydrophobic ions in aqueous solutions and for salts in nonaqueous solvents *B*-coefficients are commonly larger and almost always positive. For example, $B(LuCl_3,aq) = 0.66$ dm^3 mol^{-1}, $B[(C_4H_9)_4NCl,aq] = 1.27$ dm^3 mol^{-1}, and $B[KCl,in\ DMSO] = 0.80$ dm^3 mol^{-1}. Typical accuracies with which *B*-coefficients can be obtained with careful measurements (depending on careful maintenance of a constant temperature) are indicated by a relative error of 0.15% for 0.95 mol dm^{-3} aqueous KCl at 65 °C, as cited in the exemplary work of Out and Los.[21]

The additivity of the ionic *B*-coefficients was first tentatively assumed by Cox and Wolfenden.[22] This has been taken as proven in most subsequent studies, but has rarely been put to a rigorous test. This additivity, $B = \sum \nu_i B_i$, where the summation extends over all the ions present and the ionic *B*-coefficients, B_i, are constants for given ions in a specified solvent at a given temperature, is likely, when it is considered that the *B*-coefficients describe solely the ion–solvent interactions. Unfortunately, no comprehensive theory for the *B*-coefficients has been presented so far that is valid for all solvents at all temperatures. In practice, electrolyte viscosities leading to *B*-coefficients are often measured at concentrations where ion–ion interactions are also important, and the extrapolation to infinite dilution of the left hand side of eq 16 cannot always be made in a strictly linear manner.

In (nonaqueous) solvents, even at the low concentrations at which *B* is determined, partial association of the electrolyte takes place in cases of sufficiently low relative permittivities (Table 1; i.e., $\epsilon < 20$). Only the fraction α is then in the form of "free" (i.e., solvated) ions, the rest, $1 - \alpha$, being ion-paired. This must be taken into account, by modifying eq 22 to

$$[(\eta/\eta_o) - 1 - A(\alpha c)^{1/2}]/\alpha c = B_i + B_p(1 - \alpha)/\alpha \qquad (23)$$

where B_i pertains to the free ions and B_p to the ion pairs.[23] A plot of the left hand side of eq 23 against $(1 - \alpha)/\alpha$ yields B_i as the intercept, which is pertinent to the present review.

III. The Splitting of Electrolyte B-Coefficients into the Ionic Contributions

There is no experimental means of measuring individual ionic *B*-coefficients. However, it is possible to split the measured electrolyte *B*-coefficients into the ionic contributions on the basis of their additivity, first tentatively assumed by Cox and Wolfenden[22] and later taken by Asmus[24] and Kaminsky,[25] among others, as established. Such splitting can be done, provided that there are theoretical guides for doing this. As has already been noted, there exists no comprehensive theory for the *B*-coefficients that is valid for all solvents and at all temperatures. Recourse has therefore to be made to empirical relationships, tested according to their plausibility and their ability to produce ionic *B*-coefficients which correlate well with other ionic quantities. A general guideline to be heeded is the advisability to split a small electrolyte *B*-coefficient (say, -0.014 ± 0.002 dm^3 mol^{-1} for KCl in water at 25 °C) rather than a large one (say, 2.196 ± 0.007 for Ph_4PBPh_4 in water at 25 °C), provided compensation of cation and anion values is not to be expected.[25] In the former case, any absolute and relative errors that may be made should cause smaller errors for the other ions, calculated on the basis of additivity, than they would cause in the latter case.

A. Methods Based on a Reference Electrolyte

Intuitively, ions that have equal mobilities in a given solvent may have the same effect on the viscosity in dilute solutions and hence similar *B*-coefficients. Ionic mobilities have been established experimentally in many solvents on the basis of equivalent conductivities and transport numbers. Such data for nonaqueous solvents are, however, of relatively recent origin, whereas those for aqueous solutions were determined long ago. Cox and Wolfenden[22] were the first to employ such considerations for the splitting of electrolyte *B*-coefficients into the ionic contributions in aqueous solutions. Their considerations devolved qualitatively around the Einstein relationship,[14] given as eq 11 for suspensions of spherical particles and discussed in section I.D. The magnitude of the ionic *B*-coefficient is then presumed to be proportional to the molar "hydrated volume" of the ion. This should hold in particular for an ion for which the temperature coefficient of the mobility, u, obeys Stokes' law (i.e., depends on $d\eta_o/dT$ only, with a constant Stokes radius, r_s):

$$u = \lambda^\infty/|z|F = [F/6\pi N_A]/\eta_o r_s \qquad (24)$$

$$r_s = [(F^2/6\pi N_A)/\eta_o]|z|/\lambda^\infty \qquad (25)$$

The *B*-coefficient of such an ion, being proportional to its hydrated ionic volume, would, in turn, be proportional to the cube of its Stokes radius, r_s, and inversely proportional to the cube of the ion mobility u or the cube of the equivalent conductivity λ^∞. Cox and Wolfenden selected a pair of ions which obeyed this expectation, namely Li^+ and IO_3^-, and set

$$B(Li^+)/B(IO_3^-) = u^3(IO_3^-)/u^3(Li^+) = \lambda^\infty(IO_3^-)^3/\lambda^\infty(Li^+)^3 \qquad (26)$$

From this relationship and the demonstrated approximate ionic additivity they calculated *B*-coefficients for many ions involved in electrolytes for which accurate data had been available at the time at 18 °C and assumed it also to hold at 25 °C. This assumption was also adopted by Asmus.[24]

Gurney[26] preferred for aqueous solutions at 25 °C the convention that

$$B(K^+) = B(Cl^-) \qquad (27)$$

based on the fact that the ratios $(\lambda^\infty\eta_o)_{18°C}/(\lambda^\infty\eta_o)_{0°C}$ for the aqueous potassium and chloride ions are nearly equal. The arguments presented by Gurney in the final reckoning abandoned the direct relationship to the "hydrated volume" as proposed by Cox and Wolfenden[22] in favor of the equivalence of the mobilities of the selected ions. He followed in this, in fact, the assumption of Bingham,[27] of the approximate equality of the fluidity of the potassium and chloride ions as indicated by their conductances (at 25 °C). Kaminsky,[25] due to the lack of mobility data for the ions of $LiIO_3$ at temperatures other than 18 °C, preferred Gurney's[26] convention over Cox and Wolfenden's[22] and also adopted it at other temperatures. The mobilities u of potassium and chloride ions differ by <3% in the temperature range used by Kaminsky, 15–42.5 °C, which justified in his eyes this assumption, in spite of the resulting <9% difference in the volumes, hence the *B*-coefficients according to Cox and Wolfenden's consideration. However, the Gurney[26] and Cox and Wolfenden[22] scales for the ionic *B*-coefficients are in good agreement. The Gurney–Kaminsky assumption that $B(K^+) = B(Cl^-)$ at all temperatures in aqueous solutions has since been adopted and employed by a large number of investigators, but has also been challenged by a few.

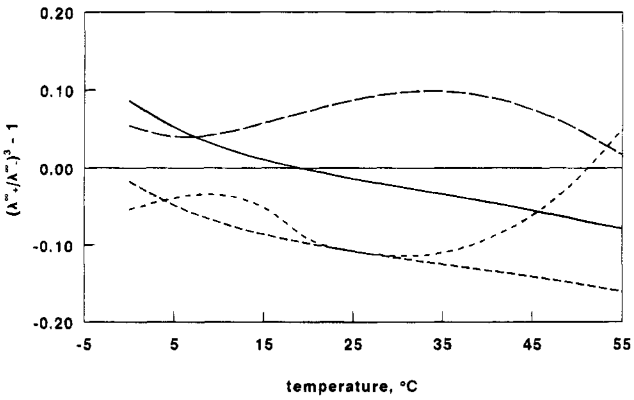


Figure 2. The cube of the ratio of the limiting equivalent conductivities of cation and anion, minus 1, of four salts, plotted against the celsius temperature: —, RbBr; – –, KNO_3; - -, KCl; ···, NH_4Cl.

Nightingale[28] proposed aqueous rubidium or cesium chlorides as having more nearly equal λ^∞ values of the cation and anion than potassium chloride. Jenkins and Pritchett[29] attempted to approach the problem in a novel way, employing Fajans' competition principle[30] and "volcano plots"[31] to determine their undetermined parameter θ_B. They concluded that cesium iodide is superior to potassium chloride for the envisaged role. Krumgalz[32] listed several salts (KNO_3, NH_4NO_3, RbBr, RbI, CsBr, and CsI) as being able to serve this purpose. The percentage deviations of the ratios of $(\lambda^\infty_+)^3/(\lambda^\infty_-)^3$ from unity over the temperature range 0–55 °C, within which most of the *B*-coefficients have been measured, are shown in Figure 2 for KCl and those salts for which these deviations do not exceed 10%. The overall least deviations are seen to pertain to rubidium bromide, and near room temperature they do not exceed 2%. Hence

$$B(Rb^+) = B(Br^-) \qquad (28)$$

is recommended in principle as the convention of having equal *B*-coefficients over the temperature range from 0 to 55 °C in aqueous solutions. The change from the KCl to the RbBr convention represents a very small modification, however, amounting to only −0.002 $dm^3\ mol^{-1}$ for cations and +0.002 $dm^3\ mol^{-1}$ for anions.

A major problem with these modes of splitting of the electrolyte *B*-coefficients into their ionic contributions (whether based on KCl or RbBr) is that they apply to aqueous solutions only. In other solvents the ratios of mobilities of these relatively small ions differ considerably from unity, and furthermore, their *B*-coefficients are much larger, hence large errors could accrue from this approach to the assignment of ionic values if used for nonaqueous solvents. Only in isolated instances have partitioning assumptions which have been employed for aqueous media been retained for nonaqueous systems. One example is the adoption of the Gurney–Kaminsky assumption (eq 27) by Criss and Mastroiani for methanol.[33]

For solutions in acetonitrile, Tuan and Fuoss[34] suggested splitting the *B*-coefficients according to the similar mobilities of the ions of tetrabutylammonium tetraphenylborate:

$$B(\mathrm{Bu_4N^+}) = B(\mathrm{BPh_4^-}) = {}^1/_2 B(\mathrm{Bu_4NBPh_4}) \tag{29}$$

Other pairs of cation and anion having similar mobilities (λ^∞ values) in a given solvent have been suggested for the splitting of B-coefficients in a manner similar to eq 29, e.g., tetraethylammonium and iodide in N-methylpropionamide.[35] The ratio of the cubes of the limiting equivalent conductivities has been used for the same purpose, with marginally different results:[34]

$$B(\mathrm{Et_4N^+})/B(\mathrm{I^-}) = \lambda^\infty(\mathrm{Et_4N^+})^3/\lambda^\infty(\mathrm{I^-})^3 \tag{30}$$

Other authors used conventions similar to eq 29 or 30 to effect the partitioning of the B-coefficients in nonaqueous solvents; see section V.

Yao and Bennion[36] preferred a different basis for the partitioning of the B-coefficients, using:

$$B(i\mathrm{Pe_3BuN^+}) = B(\mathrm{BPh_4^-}) \tag{31}$$

in dimethyl sulfoxide because of the equal spherical size and low surface charge density of the ions involved. This reference pair was subsequently employed by several authors for nonaqueous solvents, such as sulfolane, hexamethylphosphoric triamide, and ethylene carbonate[37] (see section V). The emphasis thus shifted from the mobilities to the volumes of the ions affecting the viscosity of the solution. However, whereas individual ionic mobilities can be determined experimentally, ionic partial molar volumes, $\bar{V}^\infty$, cannot, except approximately by means of ultrasonic vibration potentials.[38] The assignment of $\bar{V}^\infty$ values requires an assumption concerning the splitting of electrolyte volumes that is not any more rigorous than assumptions concerning the splitting of the B-coefficient themselves.

A way to circumvent this difficulty is to replace the partial molar volumes for large, minimally (if at all) solvated ions by their van der Waals volumes. A popular splitting mode recently adopted by authors for nonaqueous solvents at any temperature is

$$B(\text{cation})/B(\text{anion}) = V_{\mathrm{vdW}}(\text{cation})/V_{\mathrm{vdW}}(\text{anion}) = r_{\mathrm{vdW}}(\text{cation})^3/r_{\mathrm{vdW}}(\text{anion})^3 \tag{32}$$

implemented, for example, by Thompson et al.[39] as

$$B(\mathrm{Bu_4N^+})/B(\mathrm{BPh_4^-}) = r_{\mathrm{vdW}}(\mathrm{Bu_4N^+})^3/r_{\mathrm{vdW}}(\mathrm{BPh_4^-})^3 \tag{33}$$

The values chosen for the van der Waals radii may differ from worker to worker: Thompson et al.[39] used 5.35 and 5.00 Å as the van der Waals radii of the anion and cation, yielding $(5.00/5.35)^3 = 0.816$ for the ratio of their B-coefficients, a value adopted by many subsequent workers, and used as default in section V. Lawrence et al.[40] used instead 5.72 and 5.64 Å for the radii of these ions, respectively, yielding a ratio of 0.959 for the B-coefficients. A variation of this method is to set[41]

$$B(\mathrm{Bu_4N^+}) = B(\mathrm{Bu_4NBPh_4})[(r_{\mathrm{vdW}}(\mathrm{Bu_4N^+})^3/r_{\mathrm{vdW}}(\mathrm{BPh_4^-})^3) + 1] \tag{34}$$

If the solubility of a salt such as $\mathrm{Bu_4NBPh_4}$ in a given solvent (e.g., 2-methoxyethanol)[23] is insufficient for accurate measurements of the B-coefficient, then a combination of other salts, such as

$$B(\mathrm{Bu_4NBPh_4}) = B(\mathrm{Bu_4NX}) + B(\mathrm{NaBPh_4}) - B(\mathrm{NaX}) \tag{35}$$

can be used, with, for example, $\mathrm{X = ClO_4}$.[23] If the $\mathrm{BBu_4^-}$ anion is used instead of $\mathrm{BPh_4^-}$ (Lawrence et al.[40]), then the ratio of the van der Waals volumes is much nearer unity than is given by eq 33, so $B(\mathrm{Bu_4N^+}) \approx B(\mathrm{BBu_4^-})$ can be used. However, $\mathrm{BBu_4^-}$ is not the anion of particularly stable and readily accessible salts. A further variant is to employ in eq 32 the values for two tetraalkylammonium cations rather than a cation and an anion. An example is

$$B(\mathrm{Bu_4N^+})/B(\mathrm{Pe_4N^+}) = r_{\mathrm{vdW}}(\mathrm{Bu_4N^+})^3/r_{\mathrm{vdW}}(\mathrm{Pe_4N^+})^3 \tag{36}$$

used with

$$B(\mathrm{Bu_4N^+}) - B(\mathrm{Pe_4N^+}) = B(\mathrm{Bu_4NI}) - B(\mathrm{Pe_4NI}) \tag{37}$$

for solutions in formamide.[42]

Sacco et al.,[43] seeking to obtain a splitting method that would be independent of the solvent (and temperature), selected the TPTB (≈TATB) assumption that had been adopted for other ionic quantities, mainly thermodynamic ones (*cf.* Marcus[44,45]). Here TPTB stands for tetraphenylphosphonium tetraphenylborate and TATB stands for the analogous tetraphenylarsonium salt. Their equivalence was based on the sameness of the B-coefficients of the bromides of these tetraphenyl cations in water at both 25 and 35 °C, reported by Takaizumi and Wakabayashi.[46] The assumption was that

$$B(\mathrm{Ph_4P^+}) = B(\mathrm{BPh_4^-}) = {}^1/_2[B(\mathrm{Ph_4PBr}) + B(\mathrm{NaBPh_4}) - B(\mathrm{NaBr})] \tag{38}$$

at all temperatures in all solvents, particularly also in water. At 25 °C in water this causes a shift of $+(-)0.26\ \mathrm{dm^3\ mol^{-1}}$ of the B-coefficients of univalent cations (anions) relative to the $B(\mathrm{K^+}) = B(\mathrm{Cl^-})$ assumption, which is not negligible with respect to the values of such nonhydrophobic ions. If a negative ionic B-coefficient is taken to denote a water-structure-breaking ion, as is commonly done (see section VI.D), then this shift would cause potassium ions not to belong to this category, contrary to common experience. For nonaqueous solvents, however, this TPTB assumption does not conflict with other knowledge about the behavior of ions in them, but it does not take into account the known difference between the van der Waals radii and volumes of the constituent ions according to eq 32.

If the criterion of the effect of the ion on the structure of water is taken to be cardinal in the choice of a splitting assumption, then that made by Desnoyers and Perron[47] might be followed. They argued that tetraethylammonium ions are neither water-structure-breaking nor -making; hence its B-coefficient should be given by the Einstein relationship, eq 11:

$$B(\mathrm{Et_4N^+}) = 2.5[\bar{V}^{\infty}(\mathrm{Et_4N^+})/(\mathrm{dm^3\ mol^{-1}})] \quad (39)$$

This, however, shifts the problem from the splitting of the B-coefficients to the splitting of the standard partial molar volumes $\bar{V}^{\infty}$. They chose $\bar{V}^{\infty}(\mathrm{Et_4N^+}) = 0.1437$ dm^3 mol^{-1} in water at 25 °C to yield $B(\mathrm{Et_4N^+}) = 0.359$ dm^3 mol^{-1} and this causes a shift of $-(+)0.020$ dm^3 mol^{-1} in the B-coefficients of univalent cations (anions). This shift causes chloride ions to belong to the structure-making category, again contrary to general experience.

Assignments of B-coefficient values to some individual ions in non-aqueous solvents have occasionally been made in departure from the considerations presented above. Gillespie[48] assigned $B(\mathrm{HSO_4^-}) \approx 0$ in sulfuric acid and Criss and Mastroiani[33] assigned $B(\mathrm{Me_4N^+}) = 0.25$ dm^3 mol^{-1} in acetonitrile.

B. Methods Based on a Series of Ions

Besides methods for splitting electrolyte B-coefficients into the individual ionic contributions based on a single reference electrolyte (KCl or RbBr for aqueous solutions and $\mathrm{iPe_3BuNBPh_4}$, $\mathrm{Bu_4NBPh_4}$, $\mathrm{Ph_4PBPh_4}$, or $\mathrm{Bu_4NBBu_4}$ for nonaqueous ones), methods have also been proposed based on the properties of a series of ions. The B-coefficients have been shown to be linear with certain thermodynamic and other properties of ions at infinite dilution, such as the partial molar entropies (Gurney[26]), hydrated ionic volumes (Nightingale[28]), and structural components of the entropy of hydration (Krestov[49,50]). If individual ionic values are known for such quantities, then corresponding values of the B-coefficients can be inferred from such linear plots. However, this just shifts the problematics to the splitting of the thermodynamic quantities, without solving the problem.

Suppose that such thermodynamic values for individual ions are not available on an absolute basis, but that conventional values, based on the assignment of an arbitrary value to some one ion, are known. Then plots of similarly assigned conventional values of ionic B-coefficients against the conventional thermodynamic values are apt to produce two parallel straight lines, one for anions and one for cations (in the case of univalent ions). Such a plot was presented by Gordon et al.,[51] and the best straight line parallel to these two at equal distances from both was said to give acceptable individual ionic B-coefficients. Similar parallel line plots (not necessarily straight) might be obtained when plots are made against the ionic radii or volumes (crystal or van der Waals radii). Bhattacharya[52] reintroduced this concept, using the cube of the Pauling crystal ionic radii and the B-coefficients for aqueous solutions. Adjustment of the KCl-based values, given by Kaminsky,[25] by $+(-)0.052$ dm^3 mol^{-1} for the alkali metal cations (halide anions) produced Bhattacharya's scale (Figure 3). However, this method is not applicable for some ions in water (e.g., silver) nor for N-alkylamide solvents, as Bhattacharya admitted.[52]

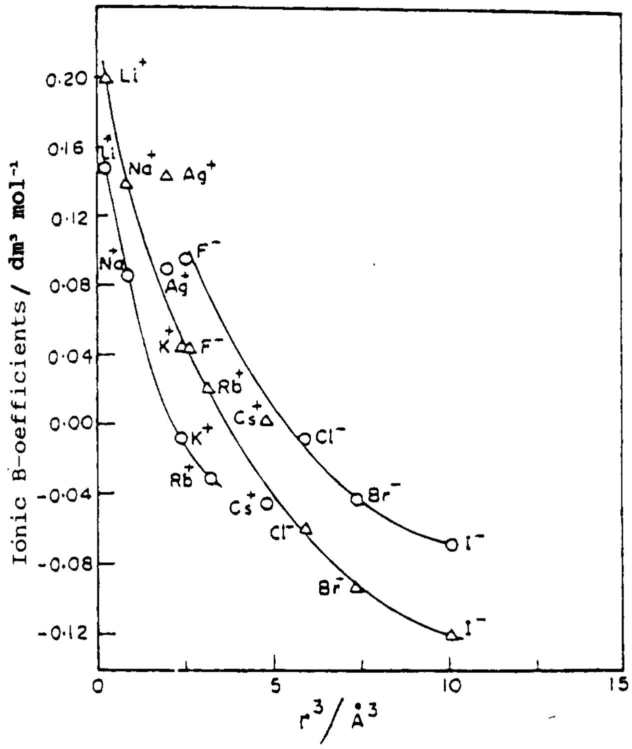


Figure 3. The ionic B-coefficients according to Kaminsky[25], ○, and according to Bhattacharya,[52] △, plotted against the cube of the crystal ionic radius of ions. Reproduced from ref 52 by permission of the publisher.

Krumgalz[37] proposed a method, to be applied for nonaqueous solvents, based on his contention that the larger tetraalkylammonium ions are essentially nonsolvated in such solvents (contrary to their hydrophobic solvation in water). Plots of the B-coefficients of iodides of these cations in several organic solvents against the cubes of the radii of the ions are indeed linear for $\mathrm{Bu_4N^+}$ and larger cations, values being known up to $\mathrm{Hp_4N^+}$ (Figure 4). (These salts are sufficiently soluble in polar nonaqueous solvents, though not in water.) The B-coefficients should have contributions only from the Einstein term (eq 11) and the destruction of structuredness of the solvent (due to dipole and similar interactions) near the ions, both effects being assumed to be proportional to the volumes of the ions. The intercepts of the straight lines should then give the B-coefficient of the counterion, iodide.

$$\lim_{r_{\mathrm{R_4N^+}}\to 0} B(\mathrm{R_4NI}) = \lim_{r_{\mathrm{R_4N^+}}\to 0} [B(\mathrm{I^-}) + br(\mathrm{R_4N^+})^3] = B(\mathrm{I^-}) \quad (40)$$

The slope depends on the solvent and the temperature. The B-coefficient of $\mathrm{Pr_4NI}$ may conform to the straight line determined by the larger cations in some solvents and not in others, whereas the values for $\mathrm{Et_4NI}$ and $\mathrm{Me_4NI}$ generally fall below the line. The electrical fields exerted by these smaller cations cause them to orient solvent molecules around them and to be solvated.

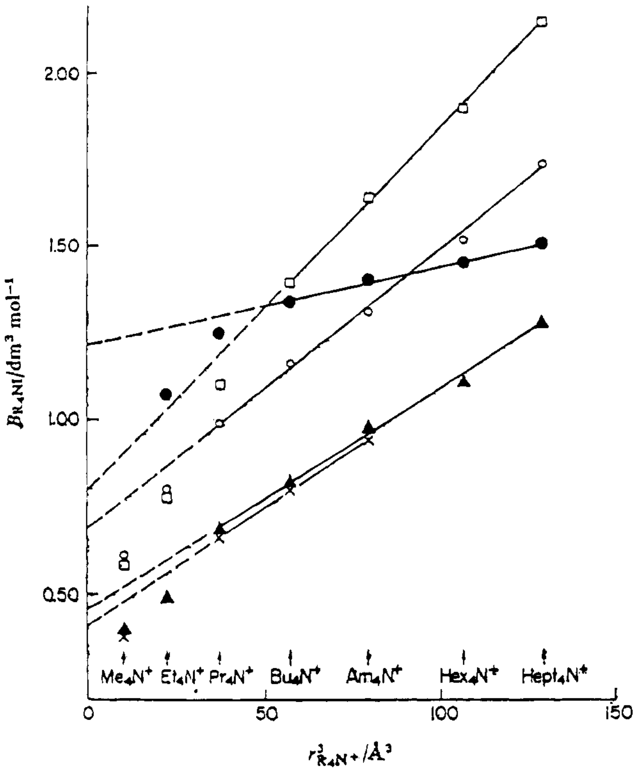


Figure 4. The B-coefficients of tetraalkylammonium iodides plotted against the cube of the van der Waals radius of the cations. The solvents are (×) methanol, (△) N-methylformamide, (●) N,N-dimethylformamide, (○) N-methylacetamide, (□) N-methylpropanamide. Reproduced from ref 37 by permission of the publisher.

Lawrence et al.[53] criticized this approach, in that plots of the B-coefficients of bromides of these cations against the van der Waals volumes, cubes of the Stokes radii, and the formula weights of the cations yield inconsistent intercepts for the bromide anion. This failure was obtained in two solvents (DMSO and HMPT) and appeared to be systematic.

IV. Ionic B-Coefficients in Aqueous Solutions

Many authors have made accurate determinations of the viscosities of dilute aqueous solutions of several electrolytes at room temperature (earlier at 18 °C, later at 25 °C). The early work of Jones et al.[1,54-62] and of Cox and Wolfenden,[22] followed by that of Bingham[27] and Asmus,[24] was summarized by Gurney,[26] whose work was influential in the recognition of the water-structure-making and -breaking effects of ions. Other influential early work was that of Kaminsky[25] and of Nightingale.[28,63] The book by Stokes and Mills[7] summarized the state of knowledge of the viscosity of aqueous electrolyte solutions up to that date, but gave numerical data mainly for the monovalent alkali metal, tetraalkylammonium, and halide ions. Divalent alkaline earth and transition metal ions have already been studied by some of the authors mentioned above, but most of the data on the rare earth cations was added only in the 1970s by Spedding's group.[64,65] More summaries of the work of other authors (e.g., Mandal[66] and Krestov[67]) and several further new ionic B-coefficients have been reported more recently. Widely accepted data for the alkali metal and halide ions over a wide temperature range were reported by Out and Los.[21]

A. Values at 25 °C

The available B-coefficient data are compiled in Table 3 for inorganic ions and in Table 4 for organic ions and summarized where possible as "selected" values. These are the unweighted averages of the reported values that are within $\pm 0.005|z|$ dm^3 mol^{-1}, where z is the charge on the ion. The electrolyte B-coefficient data in the columns "included in average" are the original data of the authors, split according to their adopted conventions as marked. For the "selected" values, however, the convention that $B(\mathrm{Rb^+}) = B(\mathrm{Br^-})$, discussed in section III.A, has been employed. Data that are outside the stated limits are also shown but not included in the calculation of the "selected" values. When, however, these are the only data available, then tentative "selected" values are presented where possible (in parentheses), based on the more consistent and reliable data in the judgement of the authors of this review.

Several of the reported values that are not included in the average which constitutes the "selected" value differ because of the splitting convention employed by the original authors. For instance, Desnoyers and Perron[47] assumed that since $\mathrm{Et_4N^+}$ can be taken to be neither structure-breaking nor structure-making (section III.A), its B-coefficient is given by the Einstein relationship $B/(\mathrm{dm^3\ mol^{-1}}) = 0.0025\bar{V}_i^{\infty}/(\mathrm{cm^3\ mol^{-1}}) = 0.359$ dm^3 mol^{-1}. If the "selected" value of 0.385 dm^3 mol^{-1} is used instead, i.e., cation values are adjusted by +0.026 and anion values by −0.026, then values are obtained that agree better with those reported by others. Similarly, if the splitting option of $B(\mathrm{K^+}) = B(\mathrm{Cl^-})$ given by Sacco et al.[43] as an alternative is employed instead of their own option $B(\mathrm{Ph_4P^+}) = B(\mathrm{BPh_4^-})$, then again better agreement is achieved. On the other hand, Bingham's tabulated fluidity increments,[27] from which the B-coefficients reported here are derived, pertain to 0.5 mol dm^{-3} and hence may not necessarily be valid for more dilute solutions.

Some further ionic B-coefficient values have been reported for aqueous solutions at 25 °C that are not presented in Tables 3 and 4. These include B-coefficients of picrate (Laurence,[68] Stokes and Mills,[7] Criss and Mastroiani[33]), alkyl sulfates (Tamaki[69]), substituted benzoates (Yasuda[70]), alkanecarboxylates, alkyl sulfonates, and alkylammonium ions with longer alkyl chains than in Table 4, naphthyltrimethylammonium (Yatome[71]), tetracyanoniccolate and -cadmate (Mathieson[72]), and hexaaminocobalt(III) (Mandal[66]).

B. Values at Other Temperatures

Once Jones and Dole[1] had established their expression for the relative viscosity of electrolyte solutions as a function of the concentration, Jones and coworkers[54-62] reported viscosity data (or B-coefficients) also at temperatures other than 25 °C and several others have followed since then. The list of ions for which data at such temperatures are available is much shorter than the lists in Tables 3 and 4.

Table 3. The *B*-Coefficients of Aqueous Inorganic Ions at 25 °C in dm^3 mol^{-1}

ion	selected	included in average	not included in average
H^+	0.068	0.069,[a] 0.070,[d] 0.072,[e] 0.071[g]	0.061[b]
Li^+	0.146	0.146,[a] 0.143,[b] 0.146,[c] 0.147,[d] 0.150,[e] 0.150,[f] 0.148,[g] 0.150,[h] 0.150,[i] 0.142[n]	0.124,[l] 0.134[m] 0.202[w]
Na^+	0.085	0.085,[c] 0.086,[d] 0.086,[e] 0.086,[f] 0.084,[n] 0.087,[g] 0.086,[h] 0.086,[i] 0.086[j]	0.094,[b] 0.066[l] 0.112,[p] 0.138[w]
K^+	−0.009	−0.008,[a] −0.008,[c] −0.007,[d] −0.007,[e] −0.007,[f] −0.007,[g] −0.007,[h] −0.007,[i] −0.007,[j] −0.007[n]	−0.002,[b] −0.026,[l] 0.045[w]
Rb^+	−0.033	−0.030,[a] −0.030,[c] −0.029,[d] −0.030,[e] −0.032,[g] −0.030,[h] −0.030[i]	−0.016,[b] −0.053,[l] 0.022[w]
Cs^+	−0.047	−0.046,[a] −0.046,[c] −0.045,[d] −0.045,[e] −0.045,[f] −0.046,[g] −0.045,[h] −0.041[i]	−0.023,[b] −0.064,[l] 0.007[w]
Ag^+	0.090	0.086,[b] 0.093,[c] 0.091,[d] 0.091,[j] 0.092[m]	0.143[w]
Tl^+	−0.036	−0.035[c]	
NH_4^+	−0.008	−0.008,[a] −0.004,[b] −0.008,[c] −0.007,[d] −0.007,[f] −0.007,[g] −0.007,[h] −0.007,[i,k]	−0.014[e]
Be^{2+}			0.504,[b] 0.392[e]
Mg^{2+}	0.385	0.390,[b] 0.379,[c] 0.385,[e] 0.385,[f] 0.385,[g] 0.385,[h] 0.383[p]	0.489[w]
Ca^{2+}	0.284	0.285,[c] 0.285,[e] 0.295,[g] 0.285[h]	0.326,[b] 0.389[w]
Sr^{2+}	0.261	0.265,[c] 0.265,[e] 0.266,[g] 0.265,[h] 0.263[p]	0.290,[b] 0.369[w]
Ba^{2+}	0.216	0.220,[c] 0.220,[e] 0.221,[g] 0.220,[h] 0.218[p]	0.254,[b] 0.324[w]
Mn^{2+}	(0.388)		0.388[b]
Fe^{2+}	0.412	0.416,[e] 0.416[h]	0.520[w]
Co^{2+}	0.372	0.384,[b] 0.384,[c] 0.360[h]	
Ni^{2+}	0.379	0.384,[c] 0.384,[j] 0.382[p]	0.424,[b] 0.306[h] 0.510[w]
Cu^{2+}	0.376	0.368,[b] 0.384,[c] 0.385,[j] 0.383[p]	0.332,[h] 0.434[w]
Zn^{2+}	0.369	0.378,[b] 0.370,[c] 0.370[j]	0.326,[h] 0.429[w]
Cd^{2+}	0.321	0.320,[c] 0.330[p]	0.398[b]
Hg^{2+}			0.116[b]
Pb^{2+}	0.228	0.233,[a] 0.231[p]	
UO_2^{2+}			0.167[k]
Al^{3+}	(0.744)		0.670,[c] 0.750[m]
Fe^{3+}	(0.690)		0.552,[b] 0.696[m] 0.768[p]
Cr^{3+}	(0.737)		0.519,[b] 0.743[m]
La^{3+}	0.576	0.585,[c] 0.588[f] 0.573[o]	0.731[w]
Ce^{3+}	0.570	0.576,[h] 0.576[o]	
Pr^{3+}	0.581	0.588,[h] 0.585,[o] 0.588[o]	0.739[w]
Nd^{3+}	(0.576)		0.582,[o] 0.734[w]
Sm^{3+}	(0.599)		0.605[o] 0.761[w]
Eu^{3+}	0.618	0.625,[o] 0.623[o]	
Gd^{3+}	0.640	0.645,[o] 0.647[o]	
Tb^{3+}	(0.647)		0.653,[o] 0.810[w]
Dy^{3+}	(0.656)		0.662,[o] 0.816[w]
Ho^{3+}	(0.667)		0.673,[o] 0.827[w]
Er^{3+}	(0.657)		0.663,[o] 0.823[w]
Tm^{3+}	0.672	0.679,[o] 0.676[o]	
Yb^{3+}	0.665	0.669,[o] 0.673[o]	
Lu^{3+}	0.675	0.682,[o] 0.680[o]	
Th^{4+}	(0.852)		0.860[m]
$Pt(NH_3)_6^{4+}$			0.406[dd]
F^-	0.107	0.097,[h] 0.120,[c] 0.097[cc]	0.138,[b] 0.155,[l] 0.045[w]
Cl^-	−0.005	−0.006,[a] −0.002,[b] −0.006,[c] −0.007,[d] −0.007,[e] −0.007,[f] −0.007,[g] −0.007,[h] −0.007,[i] −0.007,[j] −0.007[n]	0.014,[l] −0.033[r] −0.059[w]
Br^-	−0.033	−0.031,[a] −0.027,[b] −0.031,[c] −0.032,[d] −0.032,[f] −0.032[j]	−0.042,[e] −0.042[g] −0.042,[h] −0.040[n] −0.021,[l] −0.058,[r] −0.094[w]
I^-	−0.073	−0.079,[a] −0.079,[c] −0.080,[d] −0.069,[e] −0.069,[f] −0.069,[g] −0.069,[h] −0.076[n]	−0.063,[b] −0.060,[l] −0.094,[r] −0.121[w]
OH^-	0.122	0.122,[b] 0.120,[d] 0.119,[e] 0.120[k]	
SH^-			0.025[k]
SeH^-			0.006[k]
CN^-	(−0.024)		0.024,[b] −0.061,[k] −0.020[aa]
N_3^-	(−0.018)		0.018,[b] −0.014[aa]
OCN^-			−0.032[k]
SCN^-	(0.022)		−0.027,[b] 0.022[j]
HF_2^-			0.058[k]
NO_2^-			−0.024[k]
ClO_2^-			0.067[k]
ClO_3^-	−0.022	−0.023,[a] −0.023,[c] −0.024,[d] −0.024,[e] −0.024,[h] −0.024[k]	−0.008,[b] −0.076[w]
BrO_3^-	0.009	0.007,[a] 0.007,[b] 0.007,[c] 0.006[d] 0.006,[e] 0.006,[h] 0.006[k]	−0.046[w]
IO_3^-	0.140	0.135,[c] 0.140,[e] 0.140[h]	0.126,[b] 0.152,[d] 0.088[w]
NO_3^-	−0.043	−0.045,[a] −0.045,[c] −0.046,[d] −0.046,[e] −0.044,[g] −0.046,[h] −0.046,[j] −0.046[k]	−0.027,[b] −0.098[w]
ClO_4^-	−0.058	−0.062,[b] −0.056,[h] −0.061[k]	−0.026,[j] −0.091,[r] −0.108[w]
MnO_4^-	−0.057	−0.058,[c] −0.059,[d] −0.059,[h] −0.059[k]	−0.111[w]
ReO_4^-	(−0.055)		−0.055[k]
IO_4^-			−0.065,[h] −0.085[k]
BF_4^-			−0.093[k]
PF_6^-			−0.21[dd]
BH_4^-			−0.034[k]
$B(OH)_4^-$			0.233[s]
HCO_3^-			0.130,[b] 0.031[k]
HSO_4^-			0.127,[b] −0.025[k]
$H_2PO_4^-$			0.340[b]
$H_2AsO_4^-$			0.316[b]
$Ag(CN)_2^-$	(−0.038)		−0.038[k]
$Au(CN)_2^-$	(−0.040)		−0.040[k]
CO_3^{2-}	0.294	0.278,[b] 0.301[k]	
SiO_3^{2-}			0.170[b]
SO_3^{2-}	(0.282)		0.282[k]
SO_4^{2-}	0.206	0.200,[b] 0.210,[c] 0.200,[e] 0.209,[f] 0.209,[h] 0.209,[j] 0.210[k]	0.105[w]
SeO_4^{2-}			0.165[k]
CrO_4^{2-}	0.165	0.174,[b] 0.168,[c] 0.166,[h] 0.163[k]	0.062[w]
MoO_4^{2-}			0.220[k]
WO_4^{2-}			0.099[k]
HPO_4^{2-}			0.382[k]
$Cr_2O_7^{2-}$			0.084[b]
SiF_6^{2-}			0.374[k]
$PtCl_6^{2-}$			0.218[dd]
PO_4^{3-}			0.495,[b] 0.590[k] −0.065[w]
AsO_4^{3-}			0.520,[k] −0.092[w]
$Fe(CN)_6^{3-}$	0.129	0.138,[b] 0.108[q]	
$Co(CN)_6^{3-}$	(0.146)		0.146[q]
$Fe(CN)_6^{4-}$	(0.342)		0.400,[b] 0.342[q]
$Mo(CN)_8^{4-}$			0.230[q]

[a–dd] See Table 4 for assumptions and references.

Table 4. The *B*-Coefficients (in dm^3 mol^{-1}) of Organic Ions at 25 °C†

ion	selected	included in average	not included in average	ion	selected	included in average	not included in average	ion	selected	included in average	not included in average
$MeNH_3^+$			0.047^{x}	Et_3PrN^+			0.483^{v}	$BzMe_3N^+$			0.420^{z}
$Me_2NH_2^+$			0.112^{x}	$EtPr_3N^+$			0.717^{v}	$Bz_2Me_2N^+$			0.810^{z}
Me_3NH^+			0.117,^{x} 0.049^{bb}	$PrNH_3^+$			0.221,^{x} 0.223^{bb}	$BzEt_3N^+$			0.630^{z}
Me_4N^+	0.123	0.118,^{e} 0.118,^{e}	0.143,^{b} 0.099^{l}	Pr_4N^+	(0.916)		1.976,^{b} 1.092^{f}	Ph_4P^+	(1.072)		1.061,^{l} 1.098,^{r}
		0.118,^{g} 0.130,^{h}	0.106,^{n} 0.143,^{t}				0.800,^{i} 0.780^{l}				1.085^{y}
		0.123,^{i} 0.125,^{u}	0.183^{w}				1.092,^{t} 0.86^{u}	Ph_4As^+	(1.090)		1.090,^{l} 1.072,^{l}
		0.123^{v}					0.871,^{v} 0.934^{w}				1.085^{y}
Me_3EtN^+			0.188^{v}	$BuNH_3^+$			0.299^{bb}	HCO_2^-			0.052^{k}
$Me_2Et_2N^+$			0.247^{v}	Bu_4N^+	(1.275)		1.396,^{f} 1.218^{i}	$CH_3CO_2^-$	0.246	0.236,^{b} 0.245,^{x}	
$MeEt_3N^+$			0.323^{v}				1.168,^{l} 1.292^{t}			0.257^{x}	
$EtNH_3^+$			0.132,^{x} 0.142^{bb}				1.28,^{u} 1.039^{w}	$C_2H_5CO_2^-$	(0.339)		0.339^{x}
$Et_2NH_2^+$			0.293^{x}	$PeNH_3^+$			0.374^{bb}	$C_3H_7CO_2^-$	(0.419)		0.419^{x}
Et_3NH^+			0.385^{x}	$HxNH_3^+$			0.447^{bb}	$CH_3SO_3^-$	(0.127)		0.127^{x}
Et_4N^+	0.385	0.381,^{e} 0.381,^{e}	0.442,^{b} 0.395^{l}	$HpNH_3^+$			0.560^{bb}	$C_2H_5SO_3^-$	(0.215)		0.215^{x}
		0.383,^{g} 0.382^{h}	0.372,^{n} 0.379^{w}	$OcNH_3^+$			0.672^{bb}	$C_3H_7SO_3^-$	(0.305)		0.305^{x}
		0.380,^{i} 0.385,^{t}		$PhMe_3N^+$			0.310^{z}	BPh_4^-			1.144,^{l} 1.098^{r}
		0.38,^{u} 0.388^{v}									

† References and splitting assumptions (in **bold**; see explanation at end of footnote): [a]Cox,[22] **B**; [b]Bingham,[27] **A**; [c]Asmus,[24] **B**; [d]Gurney,[26] **A**; [e]Kaminsky,[25] **A**; [f]Stokes,[7] **A**; [g]Isono,[203] **A**; [h]Mandal,[66] **A**; [i]Feakins,[226] **A**; [j]Moulik,[76] **A**; [k]Krestov,[67] from entropies of hydration; [l]Desnoyers,[47] **C**; [m]Högnäs,[204] traceable (via $B(ClO_4^-)$) to **A**; [n]Out,[21] **A**; [o]Spedding,[64,65] **A**; [p]Doan,[205] traceable via $B(NO_3^-)$ to **A**; [q]Mathieson,[72] traceable via $B(K^+)$ to **A**; [r]Sacco,[43] **D**; [s]Corti,[206] **A**; [t]Nightingale,[63] **A**; [u]Kay,[82] traceable via $B(Br^-)$ to **A**; [v]Lowe,[207,208] **A**; [w]Bhattacharya,[52,79] **E**; [x]Tamaki,[209,210] **A**; [y]Takaizumi,[46] **D**; [z]Yatome,[71] **A**; [aa]Jenkins,[227] **A**; [bb]Desnoyers,[211] **A**; [cc]Nightingale,[169] traceable via $B(Na^+)$ to **A**; [dd]Nightingale,[80] **A**. Splitting assumption used: **A**, eq 27, $B(K^+) = B(Cl^-)$; **B**, eq 26, $B(Li^+)/B(IO_3^-) = \lambda^\infty(Li^+)^3/\lambda^\infty(IO_3^-)^3$; **C**, eq 39, $B(Et_4N^+) = 0.359$ dm^3 mol^{-1}; **D**, eq 38, $B(Ph_4P^+) = B(BPh_4^-)$; **E**, cf. Figure 3, B(cation) = B(anion) at same crystal ionic radius.

Averages of the *B*-coefficients (calculated by the present authors from the original relative viscosity data where required) are shown in Table 5 at intervals of 5 °C from 0 to 55 °C. Some further data were reported at 12.5,[73–75] 18,[22,73,74] 42.5,[74,75] 60,[76–78] 65,[21,79] 75 and 85,[21,77,78] and 95 °C.[21]

The problem of the splitting of the electrolyte *B*-coefficients into the ionic contributions at each temperature remains, as mentioned in section III. The assumption that $B(K^+) = B(Cl^-)$ in aqueous solutions, based on the near equal mobilities of these ions at ambient temperature, is more difficult to justify at all temperatures. The ratio of the cubes of the limiting equivalent conductivities of potassium and chloride ions deviates appreciably (>10%) from unity above 20 °C. For the pair of ions preferred in the present review, rubidium and bromide, this ratio is within 10% of unity in the range from 0 to 65 °C; see Figure 2. However, most of the data in Table 5 have been reported by the original authors according to the $B(K^+) = B(Cl^-)$ convention and their values are reproduced.

Several expressions have been proposed for the function $B = f(\theta)$, where θ is the centigrade temperature. A linear function,

$$B = a + b\theta \tag{41}$$

holds over a limited temperature span, say 30 °C, for all ions, and over a much wider range for some. For instance, $B(Na^+)$ and $B(Me_4N^+)$ are nearly constant ($b \approx 0$) above 10 °C up to 95 °C. It should be noted that $b = dB/dT$ can assume both positive and negative values, as originally pointed out by Kaminsky.[24] An exponential function with three coefficients

$$B = a' + b'e^{-c\theta} \tag{42}$$

was employed over the entire range from 5 to 95 °C by Out and Los.[21] (The coefficient reported for I^- in eq 42, $b' = -0.164$ dm^3 mol^{-1}, appears to be wrong; the reported data are fitted much better by $b' = -0.130$ dm^3 mol^{-1}.) Still another functional dependence derives from the energy of activation of viscous flow:

$$\ln(1 + B) = a'' + b''/RT \tag{43}$$

where b'' is the difference between these energies of activation for the solution and solvent. However, b'' was found not to remain constant over a large temperature range.[79]

The temperature coefficients dB/dT at 25 °C are shown in Table 6 as far as they could be determined from the data in Table 5. The sign of $(dB/dT)/B$ is also recorded, and it is noted that in most cases this sign is negative; i.e., the temperature coefficient has a sign opposite to that of B.[80] It is interesting to note that negative *B*-coefficients, signifying water-structure-breaking (see section VI.D) at ambient temperatures, becomes less negative or even positive as the temperature is increased. This is generally ascribed to there being less water structure to break at the more elevated temperatures. However, strongly structure-breaking ions, such as iodide and perchlorate, persist in this behavior up to (near) the normal boiling point of water.

Table 5. The Ionic *B*-Coefficients (in dm^3 mol^{-1}) in Aqueous Solutions at Temperatures of 0–25 °C and 30–55 °C

ion	0 °C	5 °C	10 °C	15 °C	20 °C	25 °C	ion	30 °C	35 °C	40 °C	45 °C	50 °C	55 °C
$\mathrm{Li^{+}}$ [a,b]	0.174	0.166	0.159	0.152	0.147	0.146	$\mathrm{Li^{+}}$ [a,b]	0.138	0.135	0.132	0.129	0.127	0.125
$\mathrm{Na^{+}}$ [a,b,c,d]	0.064	0.073	0.083	0.085	0.085	0.085	$\mathrm{Na^{+}}$ [a,b,c,d]	0.084	0.084	0.084	0.084	0.084	0.084
$\mathrm{K^{+}}$ [a,f,q]	−0.050	−0.039	−0.030	−0.022	−0.014	−0.009	$\mathrm{K^{+}}$ [a,f]	−0.001	0.004	0.009	0.014	0.018	0.021
$\mathrm{Cs^{+}}$ [n]	−0.096					−0.047	$\mathrm{NH_4^{+}}$ [a]		−0.003	0.002			
$\mathrm{NH_4^{+}}$ [a,q]		−0.031		−0.007		−0.008	$\mathrm{Ag^{+}}$ [f,g]	0.107	0.103				
$\mathrm{Ag^{+}}$ [f,g]	0.072				0.117	0.090	$\mathrm{Me_4N^{+}}$ [b,h]	0.123	0.123	0.123	0.123	0.123	0.123
$\mathrm{Me_4N^{+}}$ [b,h]		0.125	0.130	0.118	0.118	0.123	$\mathrm{Et_4N^{+}}$ [b,h]	0.358	0.346	0.334	0.324	0.315	0.307
$\mathrm{Et_4N^{+}}$ [b,h]	0.474	0.449	0.426	0.406	0.395	0.385	$\mathrm{Bu_4N^{+}}$ [d,h]	1.151		1.034		0.947	
$\mathrm{Ph_4P^{+}}$ [d,i]				1.22		1.072	$\mathrm{Ph_4P^{+}}$ [d,i]	1.040		0.950		0.879	
$\mathrm{Be^{2+}}$ [a,e]				0.438	0.417	0.392	$\mathrm{iPe_3BuN^{+}}$ [d]	1.318		1.200		1.104	
$\mathrm{Mg^{2+}}$ [a,e,j,q]		0.447		0.411	0.398	0.385	$\mathrm{Be^{2+}}$ [a,e]	0.371	0.346	0.308			
$\mathrm{Ca^{2+}}$ [q]		0.304				0.284	$\mathrm{Mg^{2+}}$ [a,e,j]	0.375	0.362				0.355
$\mathrm{Sr^{2+}}$ [q]		0.203				0.261	$\mathrm{Ca^{2+}}$ [o]		0.280	0.266	0.252		
$\mathrm{Ba^{2+}}$ [q]		0.203				0.216	$\mathrm{Ba^{2+}}$ [a,o]	0.234	0.276	0.266	0.265		
$\mathrm{Fe^{2+}}$ [a,e]				0.438		0.412	$\mathrm{Fe^{2+}}$ [a,e]				0.438		0.412
$\mathrm{Al^{3+}}$ [g]					0.907	0.910	$\mathrm{Ni^{2}}$ [r]	0.349		0.265		0.188	
$\mathrm{La^{3+}}$ [k]	0.594					0.576	$\mathrm{Zn^{2+}}$ [r]	0.266		0.180		0.158	
$\mathrm{Ce^{3+}}$ [e]				0.645		0.570	$\mathrm{Cu^{2+}}$ [p]	0.387	0.297	0.219	0.205		
							$\mathrm{Al^{3+}}$ [g]	0.885					
$\mathrm{F^{-}}$ [s]					0.138	0.107	$\mathrm{Ce^{3+}}$ [e]		0.598	0.570			
$\mathrm{Cl^{-}}$ [a,b,e]	−0.050	−0.039	−0.030	−0.022	−0.014	−0.005							
$\mathrm{Br^{-}}$ [b,d,h,i,k]		−0.079	−0.063	−0.058	−0.049	−0.033	$\mathrm{F^{-}}$ [s]	0.055					
$\mathrm{I^{-}}$ [a,b,d,h]	−0.162	−0.146	−0.131	−0.118	−0.106	−0.073	$\mathrm{Cl^{-}}$ [a,b,e]	−0.001	0.004	0.009	0.014	0.018	0.021
$\mathrm{OH^{-}}$ [t]				0.111	0.116	0.122	$\mathrm{Br^{-}}$ [b,d,h,i,k]	−0.033	−0.026	−0.020	−0.014	−0.008	−0.004
$\mathrm{NO_3^{-}}$ [l,m,q]	−0.107	−0.077				−0.043	$\mathrm{I^{-}}$ [a,b,d,h]	−0.066	−0.054	−0.049	−0.045	−0.043	−0.041
$\mathrm{ClO_4^{-}}$ [d,g]					−0.087	−0.058	$\mathrm{OH^{-}}$ [t]	0.125	0.128	0.131			
$\mathrm{MnO_4^{-}}$ [n]	−0.133					−0.057	$\mathrm{NO_3^{-}}$ [l,m,r]	−0.033		−0.011		0.004	0.011
$\mathrm{SO_4^{2-}}$ [f]	0.106			0.186	0.196	0.206	$\mathrm{ClO_3^{-}}$ [a]		−0.008				
$\mathrm{CrO_4^{2-}}$ [f]	0.054					0.165	$\mathrm{BrO_3^{-}}$ [o]	0.017	0.029		0.016		
$\mathrm{Fe(CN)_6^{4-}}$ [n]	0.273					0.342	$\mathrm{IO_3^{-}}$ [o]	0.157	0.148		0.148		
							$\mathrm{ClO_4^{-}}$ [d,g]	−0.063	−0.051	−0.044		−0.026	
							$\mathrm{SO_4^{2-}}$ [f,r]	0.216	0.227	0.239		0.254	
							$\mathrm{BPh_4^{-}}$ [d]	1.050		0.938		0.859	

[a] Kaminsky.[74,212] [b] Out.[21] [c] Jones.[59] [d] Sacco.[43] [e] Kaminsky.[73,74] [f] Jones.[61] [g] Högnäs.[204] [h] Kay.[82] [i] Takaizumi.[46] [j] Berecz.[213] [k] Jones.[60] [l] Appleby.[214] [m] Campbell.[215] [n] Jones.[57,58] [o] Das.[216] [p] Suryanarayana.[217] [q] Isono.[203] [r] Moulik.[76] [s] Nightingale.[28] [t] Hückel.[75]

Table 6. The Temperature Coefficient of *B* at 25 °C[a]

ion	$10^4\mathrm{d}B/\mathrm{d}T$	$(\mathrm{d}B/\mathrm{d}T)/B$	ion	$10^4\mathrm{d}B/\mathrm{d}T$	$(\mathrm{d}B/\mathrm{d}T)/B$
$\mathrm{Li^{+}}$	−11	<0	$\mathrm{Al^{3+}}$	−22	<0
$\mathrm{Na^{+}}$	0	0	$\mathrm{Ce^{3+}}$	−20	<0
$\mathrm{K^{+}}$	14	<0	$\mathrm{OH^{-}}$	9	>0
$\mathrm{Cs^{+}}$	18	<0	$\mathrm{F^{-}}$	−83	<0
$\mathrm{Ag^{+}}$	0	0	$\mathrm{Cl^{-}}$	14	<0
$\mathrm{NH_4^{+}}$	10	<0	$\mathrm{Br^{-}}$	16	<0
$\mathrm{Me_4N^{+}}$	0	0	$\mathrm{I^{-}}$	26	<0
$\mathrm{Et_4N^{+}}$	−27	<0	$\mathrm{NO_3^{-}}$	21	<0
$\mathrm{Be^{2+}}$	−25	<0	$\mathrm{BrO_3^{-}}$	37	>0
$\mathrm{Mg^{2+}}$	−20	<0	$\mathrm{IO_3^{-}}$	−83	<0
$\mathrm{Ca^{2+}}$	−18	<0	$\mathrm{ClO_4^{-}}$	22	<0
$\mathrm{Ba^{2+}}$	17	>0	$\mathrm{MnO_4^{-}}$	28	<0
$\mathrm{Fe^{2+}}$	−26	<0	$\mathrm{SO_4^{2-}}$	24	>0
$\mathrm{Ni^{2+}}$	−13	<0	$\mathrm{CrO_4^{2-}}$	44	>0
$\mathrm{Zn^{2+}}$	−82	<0	$\mathrm{Fe(CN)_6^{4-}}$	28	>0
$\mathrm{Cu^{2+}}$	−200	<0			

[a] The values of *B* are in dm^3 mol^{-1} and of d*B*/d*T* in dm^3 mol^{-1} K^{-1}.

The pressure dependence of the *B*-coefficient of sodium chloride at 10, 25, and 50 °C was studied by Sawamura,[81] who found values of *B* increasing with the pressure (up to 100 MPa) at 10 and 25 °C but remaining approximately constant at 50 °C. At higher pressures at all temperatures *B* decreases with increasing pressure. This mode of behavior is again ascribed to the decreasing extent of structure of the water (broken by chloride, enhanced by sodium ions) as either the temperature or the pressure or both are increased.

Table 7. Ionic *B*-Coefficients in dm^3 mol^{-1} in Heavy Water[a]

ion	25 °C	40 °C	ion	25 °C	40 °C
$\mathrm{Li^{+}}$	0.15	0.13	$\mathrm{Pr_4N^{+}}$	0.84	
$\mathrm{Na^{+}}$	0.08	0.08	$\mathrm{Bu_4N^{+}}$	1.31	
$\mathrm{K^{+}}$	−0.02	0.00	$\mathrm{Cl^{-}}$	−0.02	−0.00
$\mathrm{Cs^{+}}$	−0.07	−0.05	Br	−0.05	
$\mathrm{Me_4N^{+}}$	0.13		$\mathrm{I^{-}}$	−0.10	
$\mathrm{Et_4N^{+}}$	0.36[b]			−0.07[b]	

[a] Ibuki.[84] [b] Bare.[83]

C. The *B*-Coefficients in Heavy Water

The relative viscosities of dilute electrolyte solutions in heavy water, D_2O, were determined by Kay et al.[82] for tetraalkylammonium bromides and iodides at 10 and 25 °C, by Bare and Skinner[83] for tetraalkylammonium bromides at 25 °C, and by Ibuki and Nakahara[84] for lithium, sodium, potassium, and cesium chlorides at 25 and 40 °C, and potassium iodide at 25 °C. The derived ionic *B*-coefficients, on the basis that $B(\mathrm{K^+}) = B(\mathrm{Cl^-})$, are shown in Table 7.

It is noteworthy that negative *B*-coefficients are more negative in heavy water, D_2O, than in light water, H_2O, whereas there is little change in the positive *B*-coefficients on transfer from light to heavy water; see section VI.D.

V. Ionic B-Coefficients in Nonaqueous Solutions

Many accurate determinations of viscosity *B*-coefficients have been made for electrolytes in nonaque-

Table 8. Ionic B-Coefficients in $dm^3\ mol^{-1}$ in Methanol at 25 °C[†]

ion	B	ion	B
Li^+	0.30,[d]0.34,[e,f]0.51[g]	Pe_4N^+	0.48,[d]0.52[e]
Na^+	0.58,[a,g]0.27,[d]0.31,[e,f]0.23[e]	Ph_4P^+	0.91[a]
K^+	0.382,[b,c]0.23,[d]0.27,[e,f]0.56[g]	$(HOEt)_4N^+$	0.52[e]
Cs^+	0.03[d]	Cl^-	0.22,[a]0.382,[b,c]0.54,[d]0.48,[e]0.52[g]
Cu^+	0.35[g]	Br^-	0.358,[b,c]0.50,[d]0.46[e]
Ag^+	0.57[g]	I^-	0.293,[b,c]0.46,[e]0.42,[f]0.30[g]
NH_4^+	0.279,[b]0.13[d]	NO_3^-	0.29[g]
Me_4N^+	−0.03,[b,e]0.1,[d]0.02,[e]0.06[f]	ClO_4^-	0.11,[a]0.28[g]
Et_4N^+	0.30,[a]0.12,[b]0.02,[d]0.10[e]	picrate	0.83,[d]0.78[e]
Pr_4N^+	0.48,[a]0.30,[b]0.19,[d]0.24[e]	BPh_4^-	0.91,[a]0.79[g]
Bu_4N^+	0.66,[a]0.49,[b]0.34,[d]0.38,[e]0.65[g]		

[†] References and splitting assumptions (in **bold**; see explanation below): [a]Tominaga,[93] **A**; [b]Criss,[33] **B**; [c]Jones,[56,57] **B**; [d]Krumgalz,[32] citing Criss[33] as the source; [e]Krumgalz,[37] **C**; [f]Krumgalz,[32,37] **D**; [g]Gill,[218] **E**. Splitting assumptions: **A**, eq 38; **B**, eq 27; **C**, eq 32; **D**, eq 32, cation values adjusted by −0.04 $dm^3\ mol^{-1}$ to take into account the shift for anions of +0.04 $dm^3\ mol^{-1}$ found in refs 32−37, **E**, eq 33.

Table 9. Viscosity B-Coefficients of Salts in $dm^3\ mol^{-1}$ in Methanol at Various Temperatures[†]

salt	0 °C	10 °C	25 °C	30 °C	45 °C
LiCl			0.828[a]	0.822[a]	
NaCl			0.796[a]	0.794[a]	
NaI			0.652[e]		
KCl			0.764,[c] 0.793[d]		
KBr			0.740[c]		
KI			0.675[c]		
$KMnO_4$	0.180[c]		0.066[c]		
CsCl			0.563[a]	0.557[a]	
CsI	0.254[c]		0.123[c]		
NH_4Cl			0.661[c]		
Me_4NCl			0.45[f]		
Me_4NBr		0.35,[g] 0.42[f]	0.42,[b] 0.43,[f] 0.35[g]		
Me_4NI		0.38[a]	0.38[f]		
Me_4NPic[i]			0.78[f]		
Et_4NBr		0.58[f]	0.56,[f] 0.48[g]		0.50[g]
Pr_4NBr		0.73[f]	0.70,[f] 0.66[g]		0.67[g]
Pr_4NI		0.70[f]	0.66[f]		
Bu_4NCl			0.86[f]		
Bu_4NBr		0.89[f]	0.84,[h,f] 0.85[g]		0.86[g]
Bu_4NI		0.85,[f] 0.82[g]	0.80[f,g]		
Bu_4NPic[i]			1.13[f]		
Pe_4NBr			0.98[f]		
Pe_4NI			0.94[f]		
$(HOEt)_4NBr$		0.98[h]	0.98[h]		

[†] References: Einfeldt,[221] [b]Tuan,[34] [c]Jones,[56,57] [d]recalculated by Feakins[143,219] from data of Jones,[56,57] [e]Bare,[83] Kay,[220] [g]Kay,[82] [h]Cunningham.[222] [i]Pic = picrate.

Table 10. Values of $B(R_4NX)$ in $dm^3\ mol^{-1}$ in Methanol at 25 °C, Based on the Additivity Principle[†]

	Cl^-	Br^-	I^-
Me_4N^+	**0.45**[f]	**0.42**[b]	**0.38**[f]
Et_4N^+	(0.59)	(0.56[f])	(0.52)
Pr_4N^+	0.73	**0.70**[f]	**0.66**[f]
Bu_4N^+	0.87	**0.84**[b,f]	**0.80**[f,g]
Pe_4N^+	1.01	**0.98**[f]	**0.94**[f]

[†] Note: Values in **bold** correspond to experimental values from Table 9, as labeled.

ous solvents, although there is need for much additional work to provide a more extensive overview. In the sections that follow, the ionic B-coefficients which have been obtained in the solvents listed in Table 1 are summarized in the order presented in that table. No data are available for salts in ethanol, tetrahydrofuran, pyridine, and 1,2-dichloroethane.

A. Viscosity B-Coefficients in Methanol

The viscosity B-coefficients that have been measured in methanol are shown in Tables 8 and 9, in the former at 25 °C and split into the individual ionic contributions and in the latter for salts at several temperatures. The B-coefficients for the individual ions are based on eqs 27, 38, and 40, as indicated in Table 8.

Criss et al.[33,85] following a survey of the literature before 1971, obtained the values labeled *b* in Table 8. They assumed that eq 27 holds for splitting salt B-coefficients in methanol, on the basis of the fact that the ion mobilities of K^+ and Cl^- are equal in this solvent.[86] Krumgalz[32] has criticized this assumption and cites these authors as the source of values in his[32] Table 2, which are reproduced, labeled *d*, in Table 8. He states that these values should be treated with caution. In a later paper[37] he cites the values labeled *e* in Table 8, which result from using eq 40 and extrapolating data for bromide salts to zero cation size to obtain $B(Br^-)$.

It is seen in Table 8 that the viscosity B-coefficients for ions in methanol take on a wide variety of values, depending on the basis used to partition the salt data.

The indications in Table 9 are that dB/dT for the salts LiCl, NaCl, and CsCl are slightly negative, whereas dB/dT for the tetraalkylammonium bromides is almost zero or slightly positive. No viscosity measurements have been established for rubidium salts in methanol. The data for sodium and potassium salts could usefully be redetermined, since Table 9 shows that for the chloride series Li^+, Na^+, (K^+), and Cs^+ the B-coefficients generally *decrease* whereas the comparison of NaI and KI shows an *increase*. The lack of values for Et_4NCl and Et_4NI coupled with two disparate values for Et_4NBr makes the further study of the Et_4N^+ salts a requirement. In Table 10 is assembled an "additive" set of values of $B(R_4NX)$ in methanol. No such set could be assembled for the alkali metal halides because of insufficient data.

B. Viscosity B-Coefficients in 1- and 2-Propanol

The B-coefficients of sodium iodide at 25 °C in 1- and 2-propanol have been reported by Bare and Skinner[83] as $B(NaI) = 0.826 \pm 0.010$ and $0.842 \pm 0.009\ dm^3\ mol^{-1}$, respectively.

Table 11. Ionic *B*-Coefficients in dm^3 mol^{-1} in 1-Butanol at 25 °C[†]

ion	*B*	ion	*B*	ion	*B*
Na^+	1.13[a]	Et_4N^+	0.31[a]	I^-	0.30[a]
K^+	0.96[b]	Bu_4N^+	0.72[a]	SCN^-	0.29[b]
NH_4^+	0.92[b]	Cl^-	0.39[a]	BPh_4^-	0.70[a]
Me_4N^+	0.15[b]	Br^-	0.33[a]		

[†] References: [a]Banait,[87] [b]Banait.[88]

C. Viscosity *B*-Coefficients in 1-Butanol

The *B*-coefficient of sodium iodide at 25 °C in 1-butanol has been reported by Bare and Skinner:[83] B(NaI) = 0.883 ± 0.007 dm^3 mol^{-1}. This value is inconsistent with the data of Banait et al.,[87,88] who studied sodium iodide among several other salts in this solvent. The latter authors obtained ionic *B*-coefficients using the equations

$$B(\mathrm{Bu_4N^+})/B(\mathrm{Et_4N^+}) = \lambda^{\infty}(\mathrm{Bu_4N^+})^3/\lambda^{\infty}(\mathrm{Et_4N^+})^3 \quad (44)$$

and

$$B(\mathrm{Bu_4N^+}) - B(\mathrm{Et_4N^+}) = B(\mathrm{Bu_4NCl}) - B(\mathrm{Et_4NCl}) \quad (45)$$

Equation 44 is similar to eq 30 except that it involves two cations rather than a cation and an anion.

No viscosity data are available for halides other than those of sodium, potassium, and tetraalkylammonium up to Bu_4N^+. Assignments made to the ionic *B*-coefficients are shown in Table 11.

D. Viscosity *B*-Coefficients in 1-Pentanol and 1-Hexanol

The *B*-coefficients of sodium iodide at 25 °C in 1-pentanol and 1-hexanol have been reported by Bare and Skinner[83] as B(NaI) = 0.989 ± 0.007 and 1.135 ± 0.008 dm^3 mol^{-1}, respectively.

E. Viscosity *B*-Coefficients in 1,2-Ethanediol

The viscosity *B*-coefficients of potassium and cesium iodides in 1,2-ethanediol (ethylene glycol) at 25 °C have been reported by Crickard and Skinner.[89] The values are B(KI) = 0.033 and B(CsI) = −0.080 dm^3 mol^{-1}.

F. Viscosity *B*-Coefficients in 1,2- and 1,3-Propanediol

The viscosity *B*-coefficients of sodium, potassium, and cesium iodides in 1,2- and 1,3-propanediol at 25 °C have been reported by Bare and Skinner.[83] The values are B(NaI) = 0.475 ± 0.003, B(KI) = 0.069 ± 0.002, and B(CsI) = −0.106 ± 0.005 dm^3 mol^{-1} in the former and B(NaI) = 0.415 ± 0.007, B(KI) = 0.053 ± 0.002, and B(CsI) = −0.116 ± 0.005 dm^3 mol^{-1} in the latter solvent.

G. Viscosity *B*-Coefficients in Glycerol

The viscosity *B*-coefficient of sodium iodide in glycerol at 25 °C measured by Bare and Skinner[83] is B(NaI) = 0.357 ± 0.005 dm^3 mol^{-1}. Crickard and Skinner[89] reported the values B(KI) = −0.185 and B(CsI) = −0.408 dm^3 mol^{-1}, the former of which can be compared with the value determined by Briscoe and Rinehart,[90] −0.176 dm^3 mol^{-1}.

Table 12. Ionic *B*-Coefficients in dm^3 mol^{-1} in 2-Methoxyethanol at Various Temperatures[†]

ion	25 °C	35 °C	45 °C
Li^+	0.181[c,d]	0.349[c,d]	0.508[d]
Na^+	0.315,[a] 0.314[c]	0.188[a,c]	0.071[a]
K^+	0.168[c,d]	0.251[c]	
Rb^+	0.125[c]	0.171[c]	
Cs^+	0.081[c,d]	0.129[c]	
Me_4N^+	0.070[a]	0.142[a]	0.207[a]
Et_4N^+	0.112[a]	0.226[a]	0.338[a]
Pr_4N^+	0.207[a]	0.407[a]	0.600[a]
Bu_4N^+	0.304[a]	0.597[a]	0.885[a]
Pe_4N^+	0.488[a]	0.959[a]	1.419[a]
Hx_4N^+	0.585[a]	1.150[a]	1.707[a]
Hp_4N^+	1.138[b]		
Br^-	0.119,[b] 0.121[c]	0.200[c]	
ClO_4^-	0.079[a]	0.134[a]	0.185[a]
BF_4^-	0.092[d]	0.147[d]	0.204[d]
BPh_4^-	0.372[a]	0.732[a]	1.085[a]

[†] References: [a]Das,[23] [b]Dasgupta,[92] [c]Nandi,[223] [d]Das.[224] All used eq 33 as the splitting assumption.

Values for some tetraalkylammonium iodides at 25 °C have been published by Gopal, Hussain, and Singh:[91] B(Et_4NI) = −0.68, B(Pr_4NI) = −2.9, and B(Bu_4NI) = −1.9 dm^3 mol^{-1}. Me_4NI appears to have a positive *B*-coefficient.

H. Viscosity *B*-Coefficients in 2-Aminoethanol and Triethanolamine

The *B*-coefficients of sodium and cesium iodides at 25 °C in 2-aminoethanol (ethanolamine) and triethanolamine have been reported by Bare and Skinner:[83] B(NaI) = 0.843 ± 0.007 and B(CsI) = 0.385 ± 0.003 dm^3 mol^{-1} in the former and B(NaI) = 0.977 ± 0.007 and B(CsI) = 0.204 ± 0.010 dm^3 mol^{-1} in the latter solvent.

I. Viscosity *B*-Coefficients in 2-Methoxyethanol

Dasgupta et al.[92] and Das et al.[23] measured the viscosity *B*-coefficients of tetraalkylammonium salts in 2-methoxyethanol at several temperatures. Equations 33 and 35 with X = ClO_4 were used to effect their division and obtain the ionic *B*-coefficients listed in Table 12. Because Bu_4NBPh_4 is sparingly soluble in 2-methoxyethanol, the authors[23] used the relationship (35) with X = ClO_4 instead of the direct measurement of B(Bu_4NBPh_4). Note the unusual temperature trend ($\mathrm{d}B/\mathrm{d}T < 0$) and position in the alkali metal ion series of the data for sodium ions in Table 12, implying experimental difficulties.

J. Viscosity *B*-Coefficients in Acetone

The viscosity *B*-coefficients of various salts [including bis(2,9-dimethyl-1,10-phenanthroline)copper(I) perchlorate] in acetone at 25 °C have been measured by Tominaga.[93] Gill, Sharma, and Schneider[94] have compared the behavior of salts in *N,N*-dimethylformamide and acetone and measured the conductance and viscosity of several salts in acetone at 25 °C. The methods of splitting the salt values and the individual ionic *B*-coefficients so obtained are given in

Table 13. Ionic *B*-Coefficients in dm^3 mol^{-1} in Acetone at 25 °C†

ion	*B*	ion	*B*	ion	*B*
Na^+	0.44,^{a} 0.63^b	Pr_4N^+	0.46^a	I^-	0.10^b
K^+	0.74^b	Bu_4N^+	0.64,^{a} 0.70^b	NO_3^-	0.10^b
Ag^+	0.58^b	Ph_4P^+	1.05$_5$^{a}	ClO_4^-	0.40,^{a} 0.22^b
Et_4N^+	0.36^a	Cl^-	0.34^a	BPh_4^-	1.05,^{a} 0.86^b

[†] References: [a]Tominaga,[93] eq 38 for the chloride salt; [b]Gill,[94] eq 34.

Table 14. Ionic *B*-Coefficients in dm^3 mol^{-1} in Sulfuric Acid at 25 °C

ion	*B*	ion	*B*
Li^+	1.0	H_3O^+	−0.4
Na^+	0.8	NH_4^+	−0.1
K^+	0.2	Ba^{2+}	4.4

Table 13. It is noted that no data exist for any lithium, rubidium, cesium, and bromide salts in acetone and insufficient data are available to deduce further values using the additivity principle.

K. Viscosity *B*-Coefficients in 2-Butanone

Tuan and Fuoss[34] have measured the *B*-coefficient of Bu_4NBr in 2-butanone (methyl ethyl ketone), finding $B(Bu_4NBr) = 1.01$ dm^3 mol^{-1}. Gill et al.[95] have measured the viscosity of Bu_4NBPh_4 in this solvent and partitioned the *B*-coefficient so obtained using eqs 33 and 34 into the ionic contributions: $B(Bu_4N^+) = 0.91$ and $B(BPh_4^-) = 1.11$ dm^3 mol^{-1}. Hence, the value $B(Br^-) = 0.10$ dm^3 mol^{-1} can be deduced.

L. Viscosity *B*-Coefficients in Sulfuric Acid

The viscosity *B*-coefficients of a series of hydrogen sulfate salts have been measured at 25 °C in neat sulfuric acid by Gillespie.[96] He split them into ionic contributions on the premise[48,96] that $B(HSO_4^-) = 0$, leading to the results shown in Table 14.

M. Viscosity *B*-Coefficients in Acetic Acid

Despite the fact that acetic acid has been extensively studied as a nonaqueous solvent, few measurements of the viscosity of electrolytes dissolved in it have been made. Kapila et al.[97] measured the *B*-coefficients of several salts at 25 °C and Lakshminarayana and Krishnan[98] reported values for lithium, sodium, and potassium acetates at 35 °C. The former data were partitioned into ionic contributions based on the presumed lack of solvation of large tetraalkylammonium ions, as adopted by Gordon et al.[51] for solutions in formamide. The resulting values are shown in Table 15, and it should be noted that values could not be assigned to rubidium and chloride ions due to the lack of data for their respective salts.

Table 15. Ionic *B*-Coefficients in dm^3 mol^{-1} in Acetic Acid at 25 °C

ion	*B*^{a}	ion	*B*^{a}	ion	*B*^{a}
Li^+	0.39	Me_4N^+	0.28	Hx_4N^+	0.57
Na^+	0.59	Et_4N^+	0.31	Br^-	0.30
K^+	0.46	Pr_4N^+	0.35	I^-	0.61
Cs^+	0.19	Bu_4N^+	0.38	$CH_3CO_2^-$	0.41
NH_4^+	0.31	Pe_4N^+	0.53		

[a] The data of Kapila[97] were split by the use of eq 36 with $r(Bu_4N^+) = 0.385$ nm and $r(Pe_4N^+) = 0.430$ nm and eq 36 with bromide rather than iodide.

Table 16. Ionic *B*-Coefficients in dm^3 mol^{-1} in Ethylene Carbonate at 40 °C†

ion	*B*	ion	*B*
Li^+	0.63^a	*i*Pe_3BuN^+	0.59,^{a} 0.69^b
Na^+	0.71^a	Cl^-	0.10^a
K^+	0.58^a	Br^-	0.11^a
Rb^+	0.56^a	I^-	0.08^a
Cs^+	0.56^a	ClO_4^-	0.01^a
Bu_4N^+	0.46,^{a} 0.58^b	BPh_4^-	0.59^a

[†] References and splitting assumptions: [a]Petrella,[99] using eq 31; [b]Krumgalz,[37] using eqs 36 and 37.

Table 17. Ionic *B*-Coefficients in dm^3 mol^{-1} in Propylene Carbonate at Various Temperatures†

ion	25 °C	35 °C	45 °C
Li^+	0.792^a		
K^+	0.60^b		
Et_4N^+	0.258^a	0.246^a	0.242^a
Pr_4N^+	0.397^a	0.382^a	0.377^a
Bu_4N^+	0.585^a	0.577^a	0.564^a
Pe_4N^+	0.736,^{a} 0.66^b	0.717^a	0.695^a
Hx_4N^+	0.927^a	0.911^a	0.904^a
Hp_4N^+	0.996^a	0.988^a	0.980^a
Br^-	0.458^a	0.428^a	0.411^a
I^-	0.30^b		
BF_4^-	0.411^a		
ClO_4^-	0.27^b		
BPe_4^-	0.61^b		
BPh_4^-	0.717^a	0.706^a	0.692^a

[†] References and splitting assumptions: [a]Muhuri,[102] using eqs 33 and 34; [b]Krumgalz,[32] using eq 36.

N. Viscosity *B*-Coefficients in Ethylene Carbonate

Petrella and Sacco[99] have reported viscosity *B*-coefficients for several salts in ethylene carbonate at 40 °C. Krumgalz[37] summarized values for the BPh_4^-, Bu_4N^+, and *i*Pe_3BuN^+ ions in this solvent. Single ion values suggested by Petrella and Sacco, based on eq 31, are given in Table 16, and it should be noted that the values of the tetraalkylammonium cations based on eq 36 given by Krumgalz differ considerably.

O. Viscosity *B*-Coefficients in Propylene Carbonate

The viscosity *B*-coefficients of several electrolytes in propylene carbonate at 25, 35, and 45 °C have been reported by Mukherjee et al.[100,101] Ionic *B*-coefficients were calculated by Muhuri and Hazra[102] using eqs 33 and 34 and by Krumgalz[32] using eq 36, with the resulting values shown in Table 17.

P. Viscosity *B*-Coefficients in Formamide

Measurements of the *B*-coefficients of several alkali metal halide salts in formamide at 25, 35, 45, and 50 °C have been made by Vincent et al.[42,51,103] and are shown in Table 18. Viscosities of electrolytes measured by Davis et al.[104,105] at 25 °C but at only two concentrations and cited by Notley and Spiro[106] as the basis of their *B*-coefficient data (labeled *b* and *c* in Table 18) are unlikely to lead to accurate values.

The data in Table 18 have been partitioned into the ionic *B*-coefficients in Table 19 using a variety of

Table 18. Viscosity *B*-Coefficients of Salts in dm^3 mol^{-1} in Formamide at Various Temperatures†

salt	25 °C	30 °C	35 °C	40 °C	45 °C	50 °C
LiCl	0.487,[a] 0.54,[b] 0.55[d]					
LiBr	0.436,[a] 0.49,[b] 0.60[d]		0.407[a]		0.387[a]	
$LiNO_3$	0.47[b]					
LiOOCH	0.49[c]					
NaCl	0.590,[a] 0.56[b]					
NaBr	0.59,[a] 0.51,[b] 0.56[c]	0.55[f]	0.53[f]	0.50[f]		
NaI	0.38[b]					
$NaNO_3$	0.47[c]					
NaOOCH	0.53[c]					
NaOOCPh	0.85[c]					
NaO_3SPh	0.69[c]					
KCl	0.364,[a] 0.38,[b] 0.40[c]		0.345[a]		0.325[a]	
KBr	0.336,[a] 0.33,[b] 0.38[c]					
KI	0.25[b]					
KNO_3	0.40[c]					
KSCN	0.25[b]					
RbCl	0.41[b]					
RbBr	0.30[b]					
RbI	0.269,[a] 0.39[b]					
CsCl	0.315,[a] 0.41[b]		0.303[a]		0.289[a]	0.284[a]
CsBr	0.273[a]		0.262[a]		0.249[a]	0.243[a]
CsI	0.243[a]		0.228[a]		0.228[a]	0.223[a]
$CsNO_3$	0.30[c]					
NH_4Br	0.23[b]					
NH_4I	0.30[b]					
NH_4NO_3	0.15[c]					
NH_4OOCH	0.25[c]					
Me_4NCl	0.30[c]					
Et_4NCl	0.24[c]					
Bu_4NI	0.602[a]					
Pe_4NI	0.801[a]					

† References: [a]Martinus,[51,103] [b]Notley,[106] based on work of Davis;[104] [c]Notley,[106] based on the work of Davis;[105] [d] McDowell.[42]

approaches. Notley and Spiro[106] did not describe their method of partitioning, stating merely that additivity held within 0.04 dm^3 mol^{-1}. These workers have measured the limiting ionic conductances of the ions listed in Table 19. Vincent et al.[42,51,103] used three methods: (i) that of Cox and Wolfenden[22] with the above mentioned conductance data, (ii) eqs 36 and 37 with *B*-coefficients of Bu_4NI and Pe_4NI, and (iii) the linear relationship between the partial molar ionic entropy and the *B*-coefficients as demonstrated by Gurney.[26] The entropies of the electrolytes had been determined by Criss,[107] and a "correspondence plot" by Gordon, Martinus, and Vincent[51] yielded *B*-coefficients close to those obtained by method ii. Doménech and Rivera[108] have measured the viscosities of solutions of sodium bromide in aqueous formamide at 25, 30, 35, and 40 °C and extrapolated the data to give values for *B*(NaBr) in neat formamide, also shown in Table 18.

In Table 20 is assembled an "additive" set of values for the alkali metal halide salts in formamide based on the data in Table 18.

Q. Viscosity *B*-Coefficients in *N*-Methylformamide, -acetamide, and -propionamide

Rastogi[109] has reported *B*-coefficients in *N*-methylformamide at 25 °C and Krumgalz[32,37] has partitioned them into the ionic contributions shown in Table 21.

Table 19. Ionic *B*-Coefficients in dm^3 mol^{-1} in Formamide at Various Temperatures†

ion	25 °C	35 °C	45 °C	50 °C
Li^+	0.34,[b] 0.378,[c] 0.311,[d] 0.307,[e] 0.309,[f] 0.318[g]			
Na^+	0.48,[a] 0.36,[b] 0.490,[c] 0.423,[d] 0.419,[e] 0.421,[f] 0.436[q]	0.43[a]	0.39[a]	0.38[a]
K^+	0.29,[a] 0.18,[b] 0.264,[c] 0.197,[d] 0.192,[e] 0.195,[f] 0.211[g]	0.28[a]	0.26[a]	0.25[a]
Rb^+	0.18,[a] 0.214,[b] 0.174,[d] 0.171,[e] 0.173,[f] 0.181[g]			
Cs^+	0.21,[b] 0.215,[c] 0.148,[d] 0.144,[e] 0.146,[f] 0.153[g]	0.137[f]	0.125[f]	0.120[f]
NH_4^+	0.12[b]			
Me_4N^+	0.1[b]			
Et_4N^+	0.13[b]			
Bu_4N^+	0.507,[d] 0.514[g]			
Pe_4N^+	0.713[g]			
Cl^-	0.11,[a] 0.20,[b] 0.100,[c] 0.167,[d] 0.171,[e] 0.169,[f] 0.160[g]	0.11[a]	0.11[a]	0.11[a]
Br^-	0.08,[a] 0.15,[b] 0.058,[c] 0.125,[d] 0.129,[e] 0.127,[f] 0.118[g]	0.11[a]	0.10[a]	0.09[a]
I^-	0.11,[b] 0.028,[c] 0.095,[d] 0.099,[e] 0.097,[f] 0.088[g]			
NO_3^-	0.10[b]			
SCN^-	0.07[b]			
HCO_2^-	0.15[b]			
$PhCO_2^-$	0.49[b]			
$PhSO_3^-$	0.33[b]			

† References and splitting assumptions (in **bold**; see explanation below): [a]McDowell;[42] [b]Notely,[106] **A**; [c]Gordon,[51] **B**; [d]Gordon,[51] **C**; [e]Gordon,[51] **D**; [f]Martinus,[51,103] mean of **C** and **D**; [g]Krumgalz,[37] **C**. Splitting assumptions: **A**, unspecified; **B**, eq 26 with ions of appropriate mobilities in formamide; **C**, eqs 36 and 37; **D**, correspondence plot of entropy.

Table 20. Values of *B*(MX) in dm^3 mol^{-1} in Formamide at 25 °C, Based on the Additivity Principle†

	Cl^-	Br^-	I^-
Li^+	**0.54**[b]	**0.49**[b]	0.46
Na^+	**0.56**[b]	**0.51**[b]	0.48
K^+	**0.38**[b]	**0.33**[b]	0.30
Rb^+	**0.41**[b]	0.36	0.33
Cs^+	**0.32**[a]	0.27	**0.24**[a]

† Note: Values in **bold** correspond to experimental values from Table 18, as labeled.

Table 21. Ionic *B*-Coefficients in dm^3 mol^{-1} in *N*-Methylformamide at Various Temperatures†

ion	25 °C	35 °C	45 °C
Li^+	0.07[a]		
Na^+	0.09[a]		
K^+	0.11,[a] 0.10[b]	0.03[b]	−0.03[b]
Cs^+	0.15,[b] 0.14[b]	0.07[b]	0.03[b]
Me_4N^+	−0.07,[a] −0.08[b]	−0.09[b]	−0.06[b]
Et_4N^+	0.04,[a] 0.03[b]	0.01[b]	0.03[b]
Pr_4N^+	0.23,[a] 0.22[b]	0.20[b]	0.21[b]
Bu_4N^+	0.37,[a] 0.35[b]	0.34[b]	0.34[b]
Pe_4N^+	0.51[a,b]	0.49[b]	0.49[b]
Hx_4N^+	0.66,[a] 0.65[b]	0.64[b]	0.63[b]
Hp_4N^+	0.82[a,b]	0.79[b]	0.79[b]
Cl^-	0.52[a]		
Br^-	0.47[a]		
I^-	0.45,[a] 0.46[b]	0.51[b]	0.54[b]

† References and splitting methods: [a]Krumgalz,[32] using eqs 36 and 37; [b]Krumgalz,[37] using eq 40.

The viscosity *B*-coefficients of electrolytes measured by Thompson et al.[39] in *N*-methylacetamide are in poor agreement with those measured by Gopal and Rastogi.[35] For example, *B*(Bu_4NI) = 1.16[35] vs 0.619[39]

Table 22. Viscosity *B*-Coefficients of Salts in dm^3 mol^{-1} in *N*-Methylacetamide at Various Temperatures†

salt	35 °C	40 °C	45 °C	50 °C	55 °C
LiCl	0.97,^{a} 1.124^b	0.94^a	0.90^a	0.88^a	0.84^a
KI	1.01,^{a} 0.850^b	0.98^a	0.96^a	0.94^a	0.91^a
Me_4NI	0.61^a	0.65^a	0.68^a	0.72^a	0.77^a
Et_4NI	0.80^a	0.84^a	0.89^a	0.92^a	0.96^a
Pr_4NI	0.99^a	1.03^a	1.05^a	1.08^a	1.12^a
Bu_4NI	1.16,^{a} 0.619^b	1.19^a	1.23^a	1.25^a	1.28,^{a} 0.562^b
Pe_4NI	1.31^a	1.35^a	1.38^a	1.40^a	1.44^a
Hx_4NI	1.52^a	1.55^a	1.59^a	1.61^a	1.64^a
Hp_4NI	1.74^a	1.75^a	1.79^a	1.82^a	1.84^a

† References: ^{a}Gopal,[35] ^{b}Thompson.[39]

Table 23. Ionic *B*-Coefficients in dm^3 mol^{-1} in *N*-Methylacetamide at Various Temperatures†

ion	35 °C	40 °C	45 °C	50 °C	55 °C
Li^+	0.880^a				0.835^a
Na^+	0.714^a				0.694^a
K^+	0.735,^{a} 0.32^c	0.23^c	0.18^c	0.15^c	0.743,^{a} 0.07^c
Cs^+	0.632^a				0.614^a
Me_4N^+	0.240,^{a} −0.08^b	−0.10^b	−0.10^b	−0.07^b	0.237,^{a} −0.07^b
Et_4N^+	0.195,^{a} 0.11^b	0.09^b	0.11^b	0.13^b	0.12^b
Pr_4N^+	0.319,^{a} 0.30^b	0.28^b	0.27^b	0.29^b	0.28^b
Bu_4N^+	0.524,^{a} 0.47^b	0.44^b	0.45^b	0.46^b	0.429,^{a} 0.44^b
Pe_4N^+	0.62^b	0.60^b	0.60^b	0.61^b	0.60^b
Hx_4N^+	0.83^b	0.80^b	0.81^b	0.82^b	0.80^b
Hp_4N^+	0.944,^{a} 1.05^b	1.00^b	1.01^b	1.03^b	1.00^b
Ph_4As^+	0.735^a				0.652^a
Cl^-	0.243^a				0.219^a
Br^-	0.173^a				0.145^a
I^-	0.095,^{a} 0.69^b	0.75^b	0.78^b	0.79^b	0.133,^{a} 0.84^b
BBu_4^-	0.530^a				0.463^a
BPh_4^-	0.719^a				0.596^a

† References and splitting assumptions (in **bold**; see explanation below): ^{a}Thompson,[39] **A**; ^{b}Gopal,[35] **B**; ^{c}Gopal,[35] **C**. Splitting assumptions: **A**, eq 32; **B**, eq 40 with $B(I^-)$ from Krumgalz;[37] **C**, eq 40 but with $B(I^-)$ from Table 3 in ref 35.

at 35 °C and 1.28[35] vs 0.562[39] at 55 °C and $B(LiCl)$ = 0.97[35] vs 1.124[39] at 35 °C (all in dm^3 mol^{-1}). The latter authors considered their data accurate to better than ±0.005 dm^3 mol^{-1}, but it is difficult to make value judgements regarding the experimental accuracy of the two groups of workers. The values for the pure solvent reported by these groups agree fairly well at 35 and 55 °C, whereas at 40 and 50 °C the values reported by Gopal and Rastogi[35] agree closely with those of Dawson.[110] The electrolyte *B*-coefficients are shown in Table 22.

Different approaches have been used to split the data into the ionic *B*-coefficients, giving slightly, but significantly, different (±0.02 dm^3 mol^{-1}) results, the *average* of which is shown in Table 23. Equation 32 with the cation Bu_4N^+ or Ph_4As^+ and the anion BBu_4^- or BPh_4^- was employed in one approach and eq 40, with extrapolation against the molar mass or volume of the tetraalkylammonium ion, in the other.

Viscosity *B*-coefficients of salts in *N*-methylpropionamide were measured at several temperatures by Gopal and Rastogi[35] and by Hoover.[111] Equation 30 was used to split the data into the ionic *B*-coefficients, based on the results of Gopal and Rastogi[35] that the limiting equivalent conductances of Et_4N^+ and I^- are very nearly equal in the temperature range from 30 to 50 °C. Equation 40 was used by Krumgalz[37] to give another set of values, in poor agreement with the former one. The second approach yielded values lower for cations and higher for anions than the first approach by 0.38 dm^3 mol^{-1} at 20 °C, this difference increasing to 0.43 dm^3 mol^{-1} at 40 °C. It is difficult to make a value judgement between the two approaches. The values are shown in Table 24.

R. Viscosity *B*-Coefficients in *N*,*N*-Dimethylformamide

Several workers have measured the viscosity *B*-coefficients of electrolytes in *N*,*N*-dimethylformamide at a number of temperatures as shown in Table 25. To obtain the ionic *B*-coefficients Sacco et al.[112] used two equations of the form of (32) for the pairs of cations Bu_4N^+ or Ph_4As^+ and the anions BBu_4^- or

Table 24. Ionic *B*-Coefficients in dm^3 mol^{-1} in *N*-Methylpropionamide at Various Temperatures†

ion	20 °C	25 °C	30 °C	35 °C	40 °C
Li^+	0.85,^{a} 0.48^b	0.79,^{a} 0.38,^{b} 0.41^c	0.74,^{a} 0.32^b	0.69,^{a} 0.26^b	0.63,^{a} 0.19^b
K^+	0.96,^{a} 0.58^b	0.91,^{a} 0.50,^{b} 0.53^c	0.87,^{a} 0.45^b	0.83,^{a} 0.40^b	0.80,^{a} 0.35^b
Me_4N^+	0.16,^{a} −0.22^b	0.19,^{a} −0.22,^{b} 0.19^c	0.21,^{a} −0.21^b	0.23,^{a} −0.20^b	0.236,^{a} −0.19^b
Et_4N^+	0.37,^{a} −0.01^b	0.39,^{a} −0.02,^{b} 0.01^c	0.41,^{a} −0.02^b	0.43,^{a} 0.00^b	0.45,^{a} 0.02^b
Pr_4N^+	0.68,^{a} 0.30^b	0.71,^{a} 0.30,^{b} 0.33^c	0.72,^{a} 0.30^b	0.75,^{a} 0.32^b	0.77,^{a} 0.32^b
Bu_4N^+	0.99,^{a} 0.60^b	1.00,^{a} 0.59,^{b} 0.62^c	1.01,^{a} 0.59^b	1.02,^{a} 0.60^b	1.04,^{a} 0.59^b
Pe_4N^+	1.24,^{a} 0.86^b	1.25,^{a} 0.84,^{b} 0.88^c	1.27,^{a} 0.85^b	1.27,^{a} 0.84^b	1.28,^{a} 0.83^b
Hx_4N^+	1.49,^{a} 1.11^b	1.51,^{a} 1.10,^{b} 1.13^c	1.52,^{a} 1.10^b	1.53,^{a} 1.10^b	1.54,^{a} 1.10^b
Hp_4N^+	1.77,^{a} 1.39^b	1.77,^{a} 1.36,^{b} 1.39^c	1.79,^{a} 1.37^b	1.80,^{a} 1.37^b	1.80,^{a} 1.35^b
Cl^-	0.43,^{a} 0.81^b	0.46,^{a} 0.87,^{b} 0.84^c	0.48,^{a} 0.90^b	0.50,^{a} 0.93^b	0.51,^{a} 0.96^b
I^-	0.37,^{a} 0.75^b	0.39,^{a} 0.80,^{b} 0.77^c	0.41,^{a} 0.83^b	0.43,^{a} 0.86^b	0.45,^{a} 0.90^b

† References and splitting assumptions: ^{a}Gopal,[35] $B(Et_4N) = B(I^-)$; ^{b}Krumgalz,[37] eq 40; ^{c}Krumgalz,[32] eqs 36 and 37.

Table 25. Viscosity *B*-Coefficients of Salts in dm^3 mol^{-1} in *N*,*N*-Dimethylformamide at Various Temperatures†

salt	25 °C	30 °C	35 °C	40 °C	salt	25 °C	30 °C	35 °C	40 °C
LiCl	0.59^{a,c}	0.56^{a,c}	0.54^{a,c}	0.54^a	Et_4NI	1.07^a	1.06^a	1.06^a	1.07^a
$LiNO_3$	0.72^c	0.68^c	0.63^c		Pr_4NI	1.25^a	1.26^a	1.25^a	1.25^a
$LiClO_4$	1.06^c	1.00^c	0.93^c		Bu_4NI	1.34^a	1.35^a	1.35^a	1.36^a
$NaClO_4$	0.92^d	0.86^d	0.81^d		Pe_4NI	1.40^a	1.40^a	1.40^a	1.41^a
KI	1.10^a	1.08^a	1.08^a	1.07^a	Hx_4NI	1.45^a	1.44^a	1.44^a	1.46^a
$KClO_4$	0.86^d	0.79^d	0.73^d		Hp_4NI	1.51^a	1.50^a	1.50^a	1.50^a
Et_4NBr	0.63^b	0.63^b	0.60^b						

† References: ^{a}Gopal,[35] ^{b}Doménech,[225] ^{c}Doménech,[228] ^{d}Doménech[229].

Table 26. Ionic *B*-Coefficients in $dm^3\ mol^{-1}$ in *N,N*-Dimethylformamide at Various Temperatures[†]

ion	25 °C	30 °C	35 °C	40 °C
Na^+	0.72^{a}			
K^+	0.77,^{d} −0.15,^{e} −0.11^{f}	−0.16^{f}	−0.16^{f}	−0.18^{f}
Ag^+	0.70^{d}			
Et_4N^+	−0.17,^{e} −0.14^{f}	−0.18^{f}	−0.18^{f}	−0.18^{f}
Pr_4N^+	0.02,^{e} 0.04^{f}	0.02^{f}	0.01^{f}	0.00^{f}
Bu_4N^+	0.565,^{a} 0.119,^{e} 0.13,^{f} 0.84,^{d} 0.12^{e}	0.11^{f}	0.535,^{a} 0.11^{f}	0.11^{f}
Pe_4N^+	0.17,^{e} 0.19^{f}	0.16^{f}	0.16^{f}	0.16^{f}
Hx_4N^+	0.22,^{e} 0.24^{f}	0.20^{f}	0.20^{f}	0.21^{f}
Hp_4N^+	0.27,^{e} 0.30^{f}	0.26^{f}	0.26^{f}	0.25^{f}
Ph_4P^+	0.931^{b}		0.902^{b}	
Br^-	0.393,^{a} 0.400,^{b} 0.397^{c}		0.384,^{a} 0.368^{b}, 0.376^{c}	
I^-	1.21^{f}	1.24^{f}	1.24^{f}	1.25^{f}
BBu_4^-	0.568^{a}		0.538^{a}	
BPh_4^-	0.904,^{b} 1.02^{e}		0.876^{b}	

[†] References and splitting assumptions (in **bold**; see explanation below): ^{a}Sacco,[112] **A**; ^{b}Sacco,[112] **B**; ^{c}Sacco,[112] average of **A** and **B**; ^{d}Gill,[113] **C**; ^{e}Krumgalz,[32] **D**; ^{f}Krumgalz,[37] **E**. Splitting assumptions: **A**, eq 32, with Bu_4NBPh_4 and also Bu_4NBBu_4, $V_{vdW}(Bu_4N^+) = 179.1$, and $V_{vdW}(BBu_4^-) = 180.0\ cm^3\ mol^{-1}$; **B**, eq 32, with Ph_4PBPh_4, $V_{vdW}(Ph_4P^+) = 192.3$, and $V_{vdW}(BPh_4^-) = 186.8\ cm^3\ mol^{-1}$; **C**, eq 33; **D**, eq 36; **E**, eq 40.

Table 27. Ionic *B*-Coefficients in $dm^3\ mol^{-1}$ in Tetramethylurea at Various Temperatures[†]

ion	25 °C	35 °C	45 °C
Li^+	0.87,^{a} 0.84,^{b} 0.94^{c}		
Na^+	0.78,^{a} 0.84^{b,c}	0.84^{b}	0.8^{b}
K^+	0.59,^{a} 0.64^{c}		
Rb^+	0.56,^{a} 0.61^{c}		
Cs^+	0.39,^{a} 0.44^{c}		
NH_4^+	0.71^{c}		
Pr_4N^+	0.80^{a}		
Bu_4N^+	1.00,^{a} 0.90^{d}		
$i{\rm Pe_3BuN^+}$	1.12^{b}	1.05^{b}	0.99^{b}
Pe_4N^+	1.16^{a}		
Br^-	0.96,^{a} 0.89^{b,c}	0.75^{b}	0.64^{b}
SCN^-	0.79^{b}	0.68^{b}	0.68^{b}
ClO_4^-	0.70,^{a} 0.65^{e}		
BPh_4^-	1.12,^{a} 1.11^{d}	1.05^{b}	0.99^{b}

[†] References and splitting assumptions (in **bold**; see explanation below): ^{a}Jauhar,[119] **A**; ^{b}Jauhar,[118] **B**; ^{c}Jauhar,[118] **C**; ^{d}Gill,[95] **D**. Splitting assumptions: **A**, $B(ClO_4^-) = 0.70\ dm^3\ mol^{-}$; **B**, eq 31; **C**, eq 11 for nonsolvated ions; **D**, eq 33.

BPh_4^-. The resulting values are in close agreement. However, Gill and Sharma[113] reported $B(Bu_4NBPh_4) = 1.86\ dm^3\ mol^{-1}$, whereas Sacco et al.[114] obtained $B(Bu_4NBPh_4) = 1.462\ dm^3\ mol^{-1}$ by the application of eq 35 with X = Br and Ph_4P^+ instead of Na^+. The value $B(Bu_4NI) = 1.20\ dm^3\ mol^{-1}$ obtained by Gill and Sharma[113] is $0.26\ dm^3\ mol^{-1}$ larger than Sacco et al.'s value for $B(Bu_4NBr)$, a difference much larger than expected for the replacement of Br^- by I^-. Gill and Sharma[113] employed equations similar to those used by Sacco et al.[114,115] to partition the electrolyte data into the ionic contributions, as shown in Table 26.

S. Viscosity *B*-Coefficients in *N,N,N′,N′*-Tetramethylurea

Viscosity *B*-coefficients have been measured for some tetraalkylammonium salts in *N,N,N′,N′*-tetramethylurea by Barker and Caruso[116,117] and for alkali metal and ammonium salts by Jauhar et al.[118,119] at several temperatures. Fair agreement is observed for salts for which data are available from the two groups, e.g., $B(Bu_4NBr) = 1.91 \pm 0.05$ and $1.89\ dm^3\ mol^{-1}$, respectively. Gill, Chauhan, and Sekhri[95] measured $B(Bu_4NBPh_4)$ and derived the ionic *B*-coefficients shown in Table 27 using eq 33. Jauhar et al.[118,119] assumed that $B(ClO_4^-) = 0.70\ dm^3\ mol^{-1}$, on the basis of the assignment of this value in hexamethylphosphoric triamide by Sacco et al.,[120] which in turn was based on the assumption that eq 31 was valid in that solvent. Although the latter assumption appears to be sound, there is no *a priori* reason for it to hold when the solvent is changed. Hence the values in Table 27 labeled *a* are less reliable than those labeled *b*.

T. Viscosity *B*-Coefficients in Hexamethylphosphoric Triamide

Viscosity *B*-coefficients have been measured in hexamethylphosphoric triamide by Sacco, Lawrence, and their co-workers[40,43,53,114,121] for various salts at 25 and 35 °C. Several methods have been used by these authors to partition the data into the ionic *B*-coefficients. The results obtained by the TPTB assumption (eq 38) are labeled *b* or *d* in Table 28. Those obtained by the use of eq 32 are labeled *a* in this table. Krumgalz[37] obtained *B*-coefficients for $i{\rm Pe_3BuN^+}$, Bu_4N^+, and BPh_4^- and Gill, Chauhan, and Sekhri[95] obtained values for Bu_4N^+ and BPh_4^-, also shown in Table 28.

U. Viscosity *B*-Coefficients in Acetonitrile

Viscosity *B*-coefficients in acetonitrile (cyanomethane) have been measured at 25 °C for many salts by several authors[34,41,122–125] and at 15 and 35 °C by Ibuki and Nakahara.[125] Equations 33 and 34 were used to partition the data into the ionic *B*-coefficients, as shown in Table 29.[95,123,125] Criss and Mastroiani[33] assumed $B(Me_4N^+) = 0.25\ dm^3\ mol^{-1}$ as a basis for the splitting (labeled *c*) and Krumgalz,[32] using the data of Tuan and Fuoss,[34] obtained the data labeled *d*. In another approach, Krumgalz[37] used eq 33 but with the radii $r(Bu_4N^+) = 0.385$ nm and $r(BPh_4^-) = 0.408$ nm rather than 0.500 and 0.535 nm used by Syal, Chauhan, and Chauhan,[123] now more commonly used for this purpose.

Only the data by Ibuki and Nakahara[125] deal with the temperature dependence of the *B*-coefficients: $dB/dT < 0$ for Na^+, Bu_4N^+, and I^- but $dB/dT > 0$ for Li^+ and K^+ in the temperature interval from 15 to 35 °C.

V. Viscosity *B*-Coefficients in Nitromethane and Nitrobenzene

Tuan and Fuoss[34] have measured $B(Bu_4NBr) = 0.75\ dm^3\ mol^{-1}$ in nitromethane at 25 °C. Gill, Chauhan, and Sekhri[95] have measured $B(Bu_4NBPh_4) = 1.29\ dm^3\ mol^{-1}$, and using eqs 33 and 34, they obtained $B(Bu_4N^+) = 0.58$ and $B(BPh_4^-) = 0.71$; hence $B(Br^-) = 0.17\ dm^3\ mol^{-1}$. Blokhra and Parmar[126] have reported $B(Et_4NCl) = 0.54$, $B(Et_4NBr) = 0.046$, and $B(Et_4NI) = 0.005\ dm^3\ mol^{-1}$ at 30 °C.

The viscosity *B*-coefficients of some perchlorates have been measured in nitrobenzene by Tominaga[93] at 25 °C: $B(Pr_4NClO_4) = 0.84$, $B(Bu_4NClO_4) = 1.00$, and $B(Ph_4PClO_4) = 1.27\ dm^3\ mol^{-1}$. Gill, Chauhan,

Table 28. Ionic *B*-Coefficients in $dm^3\ mol^{-1}$ in Hexamethylphosphoric Triamide at 25 and 35 °C

ion	25 °C	35 °C	ion	25 °C	35 °C
Li^+	1.134,[a] 1.16[b]		Ph_4P^+	1.897[a]	1.784[a]
Na^+	1.171,[a] 1.21[b]		Cl^-	0.738,[a] 0.72[b]	
K^+	0.888,[a] 0.93[b]		Br^-	0.736,[a] 0.67,[b] 0.732[c]	0.674,[a] 0.678[c]
Rb^+	0.883,[a] 0.93[b]		I^-	0.602,[a] 0.54[b]	
Cs^+	0.870,[a] 0.91[b]		BBu_4^-	0.995,[a] 2.68[c]	0.937[a]
Bu_4N^+	0.991,[a] 1.03,[b] 1.34[d]	0.932[a]	BPh_4^-	1.843,[a] 1.55,[b] 1.65[d]	1.732[a]
$i$$Pe_3BuN^+$	1.262,[a] 1.55,[b] 3.19[c]				

† References and splitting assumptions (in **bold**; see explanation below): [a]Sacco,[114] **A**; [b]Sacco,[43] **B**; [c]Krumgalz,[37] **C**; [d]Gill,[95] **D**. Splitting assumptions: **A**, eq 32; **B**, eq 31 and TATB assumption; **C**, eq 32; **D**, eq 33.

Table 29. Ionic *B*-Coefficients in $dm^3\ mol^{-1}$ in Acetonitrile at Various Temperatures†

ion	15 °C	25 °C	35 °C
H^+		0.02,[d] 0.08[e]	
Li^+	0.48[b]	0.51,[a] 0.48,[b] 0.52[j]	0.50[b]
Na^+	0.52[b]	0.49,[a] 0.50,[b] 0.44,[c] 0.453,[h] 0.51[j]	0.50[b]
K^+	0.44[b]	0.51,[a] 0.44,[b] 0.50[j]	0.48[b]
Cu^+		0.54,[a] 0.55[j]	
Ag^+		0.52[a,j]	
Me_4N^+		0.25,[c] 0.32,[d] 0.38[e]	
Me_3PrN^+		0.36[d]	
Et_4N^+		0.32,[c] 0.39,[d] 0.45,[e] 0.46,[f] 0.33[h]	
Pr_3NH^+		0.42[d]	
Pr_3BuN^+		0.42,[d] 0.48[e]	
Pr_4N^+		0.37,[c] 0.48,[d] 0.50,[e] 0.54,[f] 0.39[h]	
Bu_3NH^+		0.53,[d] 0.59[e]	
Bu_4N^+	0.67[b]	0.61,[a] 0.64, *b* 0.56,[c] 0.62,[d] 0.675,[e] 0.65,[f] 0.50,[h] 0.616,[i] 0.59[j]	0.63[b]
$i$$Pe_3BuN^+$		0.74,[d] 0.735[g]	
Pe_4N^+		0.67[h]	
Hx_4N^+		0.78[h]	
Hp_4N^+		0.99[h]	
Ph_4P^+		0.810[h]	
Cl^-		0.35,[a] 0.37,[c] 0.42[j]	
Br^-		0.35,[a] 0.31,[d] 0.22,[e] 0.32[h,j]	
I^-	0.29[b]	0.28,[a] 0.27,[b] 0.34,[c] 0.25,[d] 0.20[e] 0.30,[h] 0.26[j]	0.25[b]
NO_3^-		0.25,[a] 0.24[j]	
ClO_4^-		0.23,[a] 0.22[j]	
$Picrate^-$		0.53,[c] 0.46,[d] 0.40[e]	
BBu_4^-		0.502[h]	
BPh_4^-	0.83[b]	0.74,[a,d] 0.79,[b] 0.87,[c] 0.675,[e] 0.73[j] 0.735,[g] 0.787,[h] 0.734[i]	0.78[b]

† References and splitting assumptions (in **bold**; see explanation below): [a]Syal,[124] **A**; [b]Ibuki,[125] **A**; [c]Criss,[33] **B**; [d]Krumgalz,[32] **C**; [e]Tuan,[34] **D**; [f]Syal,[124] **E**; [g]Krumgalz,[37] **F**; [h]Lawrence,[41] **G**; [i]Krumgalz,[37] **H**; [j]Gill,[218], **A**. Splitting assumptions: **A**, eqs 33 and 34; **B**, assuming $B(Me_4N^+) = 0.25\ dm^3\ mol^{-1}$; **C**, eq 36; **D**, assuming $B(Bu_4N^+) = B(BPh_4^-)$; **E**, taking $B(Br^-)$ from ref 124; **F**, eq 31; **G**, eq 34; **H**, eq 33 with $r(Bu_4N^+) = 0.3850$ nm and $r(BPh_4^-) = 0.4080$ nm.

and Sekhri[95] have measured $B(Bu_4NBPh_4) = 1.40$ $dm^3\ mol^{-1}$ as well as data for a few other salts, permitting the use of eqs 33 and 34 to derive the ionic *B*-coefficients shown in Table 30.

Table 30. Viscosity *B*-Coefficients of Salts[a] and Ions[b,c] in $dm^3\ mol^{-1}$ in Nitrobenzene at 25 °C†

salt/ion	*B*	salt/ion	*B*
Pr_4NClO_4	0.85[a]	Bu_4N^+	0.63[b]
Bu_4NClO_4	0.99[a]	Ph_4P^+	0.91[c]
Ph_4PClO_4	1.27[a]	$Cu(dmp)_2^+$	1.33[c]
$Cu(dmp)_2ClO_4$	1.69[a]	ClO_4^-	0.36[c]
Pr_4N^+	0.49[c]	BPh_4^-	0.77[b]

† References and splitting assumptions: [a]Tominaga;[93] [b]Gill,[95] eqs 33 and 34; [c]Derived from Tominaga,[93] using $B(Bu_4N^+) = 0.63\ dm^3\ mol^{-1}$ from Gill[95] to obtain $B(ClO_4^-) = 0.36\ dm^3\ mol^{-1}$.

W. Viscosity *B*-Coefficients in Dimethyl Sulfoxide

A large number of studies[41,53,123,127–139] concerned themselves with the viscosity *B*-coefficients of salts in dimethyl sulfoxide at 25, 35, 45, and 50 °C. The data have been split into the ionic *B*-coefficients using the alternative approaches given in Table 31, where the values are listed. The data by Blokhra and Parmar[126] are probably in error, as suggested by Bicknell et al.[130] Some studies have also been made of salts in mixtures of dimethyl sulfoxides with water or acetonitrile.[41,123,133,134]

X. Viscosity *B*-Coefficients in Tetramethylene Sulfone

The viscosity *B*-coefficients of several salts in tetramethylene sulfone (sulfolane) at 30, 40, and 50 °C have been determined by Sacco et al.[99,138,139] The data have been split into the ionic *B*-coefficients by means of eq 31 or 32 and are shown in Table 32.

The negative temperature coefficients, $dB/dT < 0$, for all the cations examined have been ascribed[138] to their structure-making behavior, increasing for the tetraalkylammonium ions from Me_4N^+ to Hx_4N^+, but decreasing with increasing size of the alkali metal cations (except for Li^+).

Y. Viscosity *B*-Coefficients in Dichloromethane

Viscosity *B*-coefficients of several salts in dichloromethane at 25 °C have been measured by Svorstøl et al.[140] They have been split into the ionic contributions using the analog of eq 29 with BBu_4^- replacing BPh_4^-. The resulting values are shown in Table 33.

Z. Further Work

There are many instances where data are missing in Tables 8–33 concerning viscosity *B*-coefficients of ions in nonaqueous solvents, and further experimental work would be of considerable value. There are cases, as mentioned in section VI, where data at temperatures other than 25 °C would be useful, e.g., in solvents such as acetone and acetonitrile. For some solvents the basis for the splitting of the electrolyte data into the ionic contributions is not as firmly established as for others and little data are

Table 31. Ionic *B*-Coefficients in $dm^3\ mol^{-1}$ in Dimethyl Sulfoxide at Various Temperatures†

ion	25 °C	35 °C	45 °C	50 °C
Li^+	0.608,[b] 0.426[c] 0.534,[h] 0.59[j]	0.586,[b] 0.409[c]	0.565[b]	
Na^+	0.35,[a] 0.534[b] 0.352,[c] 0.54[j]	0.33,[a] 0.509,[b] 0.332[c]	0.29[a] 0.484[b]	0.28[a]
K^+	0.544,[b] 0.362[c] 0.55[j]	0.522,[a] 0.345[b]	0.502[b]	
Rb^+	0.523,[b] 0.341[c]	0.505,[b] 0.328[c]	0.489[b]	
Cs^+	0.492,[b] 0.310[c]	0.474,[b] 0.297[c]	0.459[b]	
Cu^+	0.43[j]			
Ag^+	0.55[j]			
Me_4N^+	0.405,[g] 0.367[h]	0.359[g]	0.375[g]	
Et_4N^+	0.478,[g] 0.443[h]	0.47[g]	0.445[g]	
Pr_4N^+	0.268,[f] 0.555[g] 0.515[h]	0.244,[f] 0.504[g]	0.494[g]	
Bu_4N^+	0.422,[c,d,f] 0.47[e] 0.614,[g] 0.583[h] 0.65[j]	0.394,[c,d] 0.391,[f] 0.609[g] 0.65,[f] 0.50,[h] 0.616[i]	0.583[g]	
iPe_3BuN^+	0.79,[a] 0.714[b] 0.580[c]	0.74,[a] 0.669,[b] 0.545[c]	0.72[a] 0.630[b]	
Pe_4N^+	0.521[f]	0.486[f]		
Hx_4N^+	0.626[f]	0.588[f]		
Hp_4N^+	0.783[f]	0.748[f]		
Cl^-	0.258,[b] 0.440[c] 0.30[j]	0.230,[b] 0.407[c]	0.216[b]	
Br^-	0.299,[b] 0.482[c,e] 0.31[j]	0.274,[b] 0.451[c,e]	0.255[b]	
I^-	0.272,[b] 0.454[c] 0.285,[h] 0.30[j]	0.251,[b] 0.428[c]	0.238[b]	
NO_3^-	0.27[j]			
SCN^-	0.26[a]	0.27[a]		
ClO_4^-	0.26[a]	0.26[a]		
$CH_3SO_3^-$	0.47[i]			
$CF_3SO_3^-$	0.28[a]	0.28[a]	0.29[a]	
BBu_4^-	0.425,[c,d] 0.38[e]	0.395[c,d]		
BPh_4^-	0.79,[a] 0.714[b] 0.848,[c] 0.861,[d] 0.715[h]	0.74,[a] 0.669,[b] 0.793[c] 0.805[d]	0.72,[a] 0.630[b]	

† References and splitting assumptions (in **bold**; see explanation below): [a]Yao,[36] **A**; [b]Bicknell,[135] **A**; [c]Lawrence,[40] **B**; [d]Lawrence,[40] **C**; [e]Lawrence,[40] **D**; [f]Lawrence,[53] **E**; [g]Das,[132] **F**; [h]Das,[132] **G**; [i]Krumgalz,[32] **H**; [j]Syal,[124], **B**. Splitting assumptions: **A**, eq 31; **B**, eq 32 for the ions of Bu_4NBBu_4; **C**, assuming that $B(Bu_4N^+) = B(BBu_4^-)$ and $B(Ph_4P^+) = B(BPh_4^-)$; **D**, eq 30 for the ions of Bu_4NBBu_4, using Gopal's[136] value $\lambda^\infty(Bu_4N^+) = 11.8$ and Gill's[137] value $\lambda^\infty(BBu_4^-) = 12.70\ \Omega^{-1}\ cm^2\ mol^{-1}$, **E**, derived from the results of Bicknell[135] and Lawrence,[40] assuming $B(Br^-)/dm^3\ mol^{-1} = 0.481$ at 25 °C and 0.451 at 35 °C; **F**, assuming $B(Br^-)/dm^3\ mol^{-1} = 0.299$ (25 °C), 0.274 (35 °C), and 0.255 (45 °C) and $B(I^-)/dm^3\ mol^{-1} = 0.272$ (25 °C), 0.251 (35 °C), and 0.238 (45 °C); **G**, eq 33 and 35 with X = Br; **H**, data as listed.

available, e.g., 2-butanone and nitrobenzene. For some common electrolyte solvents no data are available at all, e.g., ethanol, tetrahydrofuran, and pyridine. Some notable instances of solvent/ion combinations where data are lacking (cf. Tables 8–33) are D_2O/Rb^+; acetone/Li^+, Rb^+, Cs^+, Me_4N^+, Br^-; acetic acid/Rb^+, Cl^-; ethylene carbonate/Me_4N^+, Et_4N^+; propylene carbonate/Na^+, Rb^+, Cs^+, Me_4N^+; formamide/Rb^+; *N,N*-dimethylformamide/Li^+, Rb^+, Cs^+, Me_4N^+; *N*-methylacetamide/Rb^+; *N*-methylpropionamide/Na^+, Rb^+, Cs^+, Br^-; tetramethylurea/Me_4N^+, Et_4N^+, Cl^-, I^-; hexamethylphosphoric triamide/Me_4N^+, Et_4N^+, Pr_4N^+; and acetonitrile/Rb^+, Cs^+. Although some of these combinations might not represent feasible experimental combinations (due to limited solubilities), efforts to acquire additional data in these systems would be useful.

Table 32. Ionic *B*-Coefficients in $dm^3\ mol^{-1}$ in Sulfolane at Various Temperatures†

ion	30 °C	40 °C	50 °C
Li^+	1.07[b]	1.00[b]	0.97[b]
Na^+	1.30[b]	1.17[b]	1.09[b]
K^+	1.11[b]	1.03[b]	0.97[b]
Rb^+	1.04[b]	0.95[b]	0.90[b]
Cs^+	0.91[b]	0.85[b]	0.79[b]
Me_4N^+	0.45[c]	0.40[c]	0.38[c]
Et_4N^+	0.55[c]	0.46[c]	0.40[c]
Pr_4N^+	0.64[c]	0.54[c]	0.46[c]
Bu_4N^+	0.84,[a] 0.79[b,c]	0.79,[a] 0.69[b,c]	0.79,[a] 0.61[b,c]
Pe_3BuN^+	1.00,[a] 0.95[b,c]	0.94,[a] 0.84[b,c]	0.94,[a] 0.75[b,c]
Pe_4N^+	0.90[c]	0.79[c]	0.73[c]
Hx_4N^+	1.00[c]	0.86[c]	0.79[c]
Cl^-	−0.01[b]	0.00[b]	0.02[b]
Br^-	0.06[b]	0.06[b]	0.08[b]
I^-	0.04[b]	0.05[b]	0.04[b]
ClO_4^-	−0.07[b]	−0.05[b]	−0.04[b]
BPh_4^-	0.95[b]	0.84[b]	0.75[b]

† References and splitting assumptions (in **bold**, see explanation below): [a]Krumgalz,[37] **A**; [b]Sacco,[115] **B**; [c]Sacco,[139] **C**. Splitting assumptions: **A**, eq 32; **B**, eq 31; **C**, using $B(I^-)$ and $B(ClO_4^-)$ from ref 99.

Table 33. Ionic *B*-Coefficients in $dm^3\ mol^{-1}$ in Dichloromethane at 25 °C

ion	*B*	ion	*B*	ion	*B*
Et_4N^+	0.40[a]	Dc_4N^+	1.70[a]	I^-	0.23[a]
Pr_4N^+	0.50[a]	Ph_4As^+	0.75[b]	SCN^-	0.23[a]
Bu_4N^+	0.69[a]	$(Ph_3P)_2N^+$	1.40[a]	ClO_4^-	0.13[a]
Hx_4N^+	0.98[a]	Cl^-	0.33[a]	BBu_4^-	0.69[a]
Oc_4N^+	1.35[a]	Br^-	0.29[a]	BPh_4^-	0.75[b]

† References and assumptions: [a] Svorstøl,[140] assuming $B(Bu_4N^+) = B(BBu_4^-)$; [b] Svorstøl,[140] assuming $B(Ph_4As^+) = B(BPh_4^-)$.

VI. Relationships of the B-Coefficients to Other Properties

A cursory look at the values of the ionic *B*-coefficients in water (section IV) and nonaqueous solvents (section V) shows them to be rather higher in most nonaqueous solvents than in water. Also, negative values of *B* are found almost exclusively in water, a fact ascribed to the effects of the ions on the structure of the solvent. For series of ions of a common structure, *B* in some cases (e.g., tetraalkylammonium ions) changes monotonically with the size of the ions, but in other cases (e.g., spherical ions with inert gas electron shells) there is an extremum for one ion in the series. These observed features are explained in this section.

A. Relation to the Properties of the Solvent

If the *B*-coefficients of a given ion or a given electrolyte in various solvents are compared, it is evident that they have some relation to the molar volumes, V_s, of the solvents.[141] Taking for instance the solvents water ($V_s/cm^3\ mol^{-1} = 18$), formamide (40), ethylene carbonate (67), sulfolane (95), tetramethylurea (120), and hexamethylphosphoric triamide (176) and an electrolyte such as lithium bromide, the corresponding $B/dm^3\ mol^{-1}$ values are 0.113, 0.436, 0.74, 1.13, 1.83, and 1.866 (at 25 °C, except for sulfolane at 40 °C). Thus, water, having the smallest molar volume, also generally exhibits the smallest *B*-coefficients. To put this on a more quantitative basis, the transition state theory has been invoked by Nightingale and Benck[142] and applied in a somewhat different manner by Feakins, Freemantle, and Lawrence.[143] The following description follows the latter approach.

The viscosity of a liquid is given according to this theory by:

$$\eta_s = (hN_A/V_s)\exp(\Delta G_s^{\ddagger}/RT) \qquad (46)$$

where *h* is Planck's constant, N_A is Avogadro's number, and $\Delta G_s^{\ddagger}$ is the Gibbs free energy of activation for the viscous flow. The logarithm of the relative viscosity of a solution is then

$$\ln(\eta/\eta_s) = \ln(V_s/V) + (\Delta G^{\ddagger} - \Delta G_s^{\ddagger})/RT \qquad (47)$$

where quantities without a subscript pertain to the solution. At the limit of infinite dilution, where only the solute–solvent interactions need to be considered, the quantity on the left hand side of eq 47 equals *Bc*. Furthermore, at this limit $\ln(V_s/V)$ equals $(V_s - V_E)c/1000$ and $(\Delta G^{\ddagger} - \Delta G_s^{\ddagger})/RT$ equals $V_s c(\Delta G^{\ddagger}_E - \Delta G_s^{\ddagger})/1000RT$, where the subscript E denotes the electrolyte or ions, and the division by 1000 is for volumes in cm^3 mol^{-1} and concentrations in mol dm^{-3}. The resulting expression given by Feakins et al.[143] is

$$B = (V_s - V_E)/1000 + V_s(\Delta G^{\ddagger}_E - \Delta G_s^{\ddagger})/1000RT \qquad (48)$$

Rearrangement of (48) yields

$$1000B + V_s\Delta G_s^{\ddagger}/RT = V_s(1 + \Delta G^{\ddagger}_E/RT) - V_E \qquad (49)$$

where the left hand side can be calculated for a given electrolyte (or ion) in a series of solvents with known values of *B* and values of $\Delta G_s^{\ddagger}/RT$ obtained from eq (46) as

$$\Delta G_s^{\ddagger}/RT = \ln[0.399(\eta_s/10^{-3}\ \text{Pa s})(V_s/\text{cm}^3\ \text{mol}^{-1})] \qquad (50)$$

The left hand side of eq 49 is linear in V_s, provided $\Delta G^{\ddagger}_E$ and V_E are independent of the solvent.

Figures 5, 6, and 7 test this proposition for tetraalkylammonium bromides, alkali metal iodides, and potassium halides and perchlorate, respectively. Electrolytes, rather than single ions, have been selected for these presentations, since different splitting methods have been employed to obtain single ion *B* values for different solvents (see section V). In spite of the considerable scatter noted, the correlation coefficients for the linear regressions are ≥0.84, ≥0.96, and ≥0.96 for these three series of salts (exclusion of Et_4NBr and Pr_4NBr raises the former value to ≥0.90). The partial molar volumes of the electrolytes, V_E, do vary with the solvents (Marcus, Hefter, and Pang[144]), but their variation is considerably smaller than the values of the left hand side of eq 49. The values of $\Delta G^{\ddagger}_E/RT$ have been previously reported (Feakins et al.[143]) for only a few solvents, e.g., for KCl: 22.6 in MeOH, 14.9 in NMF, 21.3 in NMP, 14.1 in DMSO,[145] but only 3.4 in water. The slopes of the regression of eq 49, 18 ± 1, correspond to a constant value of 17 ± 1 for $\Delta G^{\ddagger}_E/RT$ for the three series of electrolytes shown in Figures 5–7 for some 15 solvents.

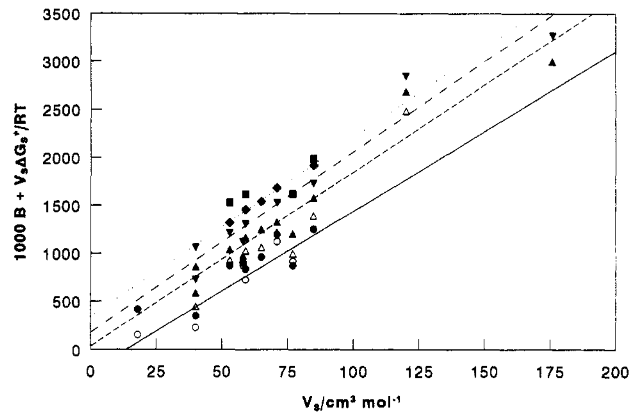


Figure 5. The left hand side of eq 49 (*B* in dm^3 mol^{-1} and V_s in cm^3 mol^{-1}) for tetraalkylammonium bromides vs the molar volumes of the solvents: (○) Me_4NBr, (●) Et_4NBr, (△) Pr_4NBr, (▲) Bu_4NBr, (▽) Pe_4NBr, (◆) Hx_4NBr, (■) Hp_4NBr.

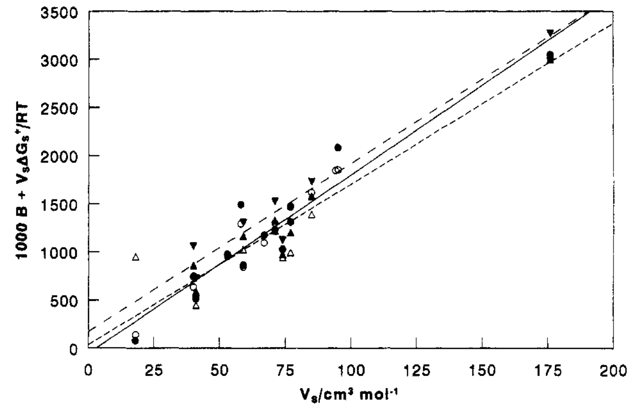


Figure 6. The left hand side of eq 49 (*B* in dm^3 mol^{-1} and V_s in cm^3 mol^{-1}) for alkali metal iodides vs the molar volumes of the solvents: (○) LiI, (●) NaI, (△) KI, (▲) RbI, (▽) CsI.

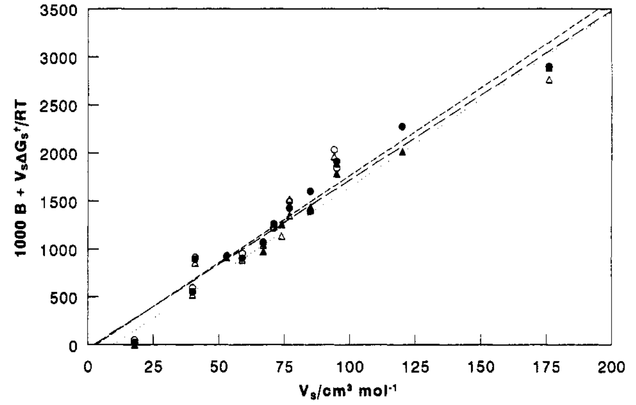


Figure 7. The left hand side of eq 49 (*B* in dm^3 mol^{-1} and V_s in cm^3 mol^{-1}) for potassium salts vs the molar volumes of the solvents: (○) KCl, (●) KBr, (△) KI, (▲) $KClO_4$.

The observed linearity is a substantial confirmation of the theoretical derivation proposed by Feakins et al.[143] The common value for $\Delta G^{\ddagger}_E/RT$ of the electrolytes may arise from the solvation of the smaller ions, letting them have volumes similar to those of the (unsolvated) larger ions. However, there is no way of deriving $\Delta G^{\ddagger}_E/RT$ in a manner independent of the *B*-coefficients obtained from measured viscosities of dilute solutions, although Feakins et al.[145] provided a qualitative model for this quantity. Therefore, values of $\Delta G^{\ddagger}_E/RT$ reported in the literature do not convey information additional to that inherent in the *B* values themselves (values of $dB/d(1/T)$ yield $\Delta H^{\ddagger}_E/RT$ but not $\Delta G^{\ddagger}_E/RT$).[7] The intercepts of the lines according to eq 49 ought to equal $-V_E$, the negative of the partial molar volume of the electrolytes, but although the intercepts are specific for each electrolyte, they are much larger than $-V_E$ and do not have the expected sign. It cannot, therefore, be claimed that the activation process for viscous flow of solutions is well understood.

B. Ionic Conductivity and Viscosity

When an infinitely dilute solution of an electrolyte flows under shear forces, as is the case with viscosity measurements, the solvated ion moves in concert with the bulk of the solvent. The drag is exerted on the fluid having properties modified by the presence of the ions, but with no net macroscopic movement of the ions relative to the solvent. When, however, an external electric field causes the ions to move in a stationary fluid, as is the case with conductivity experiments, the resistance to the movement arises from both viscosity drag and the rearrangement of the solvent ahead and behind the moving ion (assuming ion atmosphere effects to be absent at infinite dilution). This is true also when the forces acting are not due to an external electric field but to a concentration gradient, as in diffusion experiments. In the latter case retardation due to the ionic atmosphere must also be taken into account,[7] since infinite dilution precludes a concentration gradient. In view of the above, there cannot exist a direct relationship between the viscosity *B*-coefficient and the limiting equivalent conductivity of an ion. An indirect relationship may yet exist, however.

The molar conductivity of electrolytes at infinite dilution, Λ^{∞}, can be determined accurately, provided adequate expressions are used for extrapolation to infinite dilution that take all the relevant interactions, including possible ion pairing, into account. So also can the limiting ionic equivalent conductivity, λ_i^{∞}, provided the transference number extrapolated to infinite dilution, t_i^{∞}, has been determined by means of suitable experimental methods, such as the Hittorf, the moving-boundary, or the emf of cells with transference methods. Then $\lambda_i^{\infty} = t_i^{\infty}\Lambda^{\infty}$ and the additivity

$$\Lambda^{\infty} = \sum_i \nu_i \lambda_i^{\infty} \tag{51}$$

(Kolrausch's law) is maintained, where ν_i is the number of ions (i) into which the electrolyte dissociates.

If the limiting equivalent conductivities of a given ion in diverse solvents and at different temperatures are compared, it is found that Walden's rule (Walden's product)[146]

$$\lambda_i^{\infty}/\eta_s = \text{const} \tag{52}$$

is approximately followed, where the value of the constant depends only on the ion. This is due to the approximate proportionality of Walden's product to the reciprocal of the radius of the ion, which is presumed to be independent of the solvent and the temperature. However, for many ions and solvents this rule is not followed. If the ions are large relative to the molecules of the solvent, then Stokes' law,[3] dealing with the movement of macroscopic spherical bodies through unstructured fluid media, is obeyed. If it is assumed that Stokes' law applies also to ions moving in an electric field, then (cf. eq 24)

$$\lambda_i^{\infty} = |z_i|F^2/6\pi N_A \eta_s r_{si} = 8.20|z_i|/\eta_s r_{si} \tag{53}$$

Here the numerical coefficient 6 in the denominator holds for the assumed perfect slipping of solvent at the surface of the body (the coefficient becomes 4 in the case of perfect sticking) and the coefficient 8.20 applies for λ_i^{∞} in units of S cm^2 mol^{-1}, η_s in Pa s, and r_{si} in pm. In the Stokes law expression, r_{si} is the so-called Stokes radius, which is equal to the radius in the case of a macroscopic moving sphere, but may differ from the radius in the case of an ion. Krumgalz[147] showed that Walden's rule holds for ions larger than Pr_4N^+ in many solvents. In fact, setting $r_{si} = r_{ci}$, the crystallographic radius, or $r_{si} = r_{vdWi}$, the van der Waals radius of the ion, in eq 53 yields with the solvent viscosities η_s approximately correct values of λ_i^{∞} for such ions.

For small ions, however, the Stokes radius is generally larger (but in some cases smaller) than the crystallographic radius which has been shown to be applicable also to solutions.[148,149] This is due to the fact that for such ions there exists dielectric retardation, due to the drag caused by the relaxation of the oriented solvent dipoles as the ion moves. Zwanzig,[150,151] following Boyd,[152] proposed the following expression to account also for this effect:

$$\lambda_i^{\infty} = |z_i|F^2/N_A 6\pi\eta_s[r_{ci} + (e^2\tau/18\pi\eta_s)(\epsilon_o - \epsilon_{\infty})/\epsilon_o^{\,2} r_{ci}^{\,3}] \tag{54}$$

Here e is the unit charge, τ the dielectric relaxation time, ϵ_o the static permittivity (i.e., that at low frequency), and ϵ_{∞} the high-frequency permittivity. Whereas values of ϵ_o and of τ are shown in Table 1, no values of ϵ_{∞} are needed to be shown there for the present purposes. This quantity ranges from 1.9 to 5.2 for many polar liquids,[11] and therefore is relatively small compared with ϵ_o for such liquids (cf. Table 1). Hence, as the term involving it is only a correction term, the approximations $\epsilon_{\infty} \approx n_D^2 \approx 2.5$, where n_D is the refractive index of the liquid at the sodium D-line, can be made for polar solvents. Exceptions might be tetrahydrofuran, acetic acid, and dichloromethane, among the solvents dealt with in this review, that have $\epsilon_o < 10$. The dielectric relaxation dependent term has r_{ci}^3 in the denominator and hence is applicable only to small ions, and is quite negligible for ions larger than Pr_4N^+ (i.e., ions for which $r_{ci} > 0.38$ nm).

The Boyd–Zwanzig expression (54) does not after all lead to accurate λ_i^∞ values, as shown by Kay et al.[153] and Sadek.[154] Hubbard and Onsager[155] and Hubbard[156] suggested modified expressions to overcome this, involving a characteristic radius (r_{HO}) given by

$$r_{HO} = [(e^2\tau/16\pi\eta_s)(\epsilon_o - \epsilon_\infty)/\epsilon_o^{\,2}]^{1/4} \qquad (55)$$

and leading essentially to changed numerical coefficients of the dielectric relaxation term (1/3 in the Zwanzig expression (54)). The result is that for small ions the viscous drag is nearly independent of the ionic size, and the main effect differentiating between ions is the reorientational friction, governed by an expression involving ϵ_o, ϵ_∞, and τ. Note that both the Boyd–Zwanzig expression (54) and the modified expression of Hubbard add a positive quantity (the dielectric drag) to the viscosity drag in the denominator of the Stokes' law expression (53).

For the larger ions, say Me_4N^+ to Pr_4N^+, neither does the constancy of the Walden product in different solvents necessarily hold[157] nor does the Boyd–Zwanzig expression apply. For such ions Gill[158–160] has proposed an empirical expression involving a negative quantity added to the viscosity drag:

$$\lambda_i^\infty = |z_i|F^2/6\pi N_A\eta_s[r_{Gi} - (0.0103\epsilon_o + r_y)] \qquad (56)$$

where r_y = 85 pm for non-hydrogen-bonding liquids and r_y = 113 pm for hydrogen-bonded liquids. In this expression r_{Gi} is Gill's selection for the crystallographic radius of the ions involved: 320 pm for Me_4N^+, 460 pm for Et_4N^+, and 500 pm for Pr_4N^+. These radii are larger than what are the commonly accepted values: 280, 337, and 379 pm, respectively.[161,162] The method was criticized by Krumgalz and Fleisher[163] as being incapable of yielding correct experimental Walden products, even with the specified radii of Et_4N^+, Pr_4N^+, and Bu_4N^+. Gill[159] admitted that the method does not work for solvents with very high relative permittivities, such as formamide and *N*-methylformamide.

Although it is accepted that the larger tetraalkylammonium ions are practically unsolvated, the flexibility of the alkyl chains may cause them to have different shapes in different solvents, leading to departures from the Walden rule. Ionic limiting equivalent conductivity data, λ_i^∞, obtained from measured accurate Λ^∞ data and transference numbers since Krumgalz's work,[147] do not confirm his premise that Walden's rule is strictly obeyed for, say, tetrabutyl-, tetrapentyl-, tetrahexyl-, and triisopentylbutylammonium and tetraphenylborate ions. Irrespective of the mode of splitting of Λ^∞ between cation and anion, the difference of $\lambda_i^\infty\eta_s$ of any two of these large cations should remain solvent and temperature independent, but this is not the case. For instance, with increasing temperatures the Walden product of such ions in acetonitrile increases[164] but it decreases in sulfolane.[165]

The view has been expressed by Barthel et al.[164] that in "simple" solvents, such as acetonitrile, charge transport in electrolyte solutions at infinite dilution and fluidity of the solvent are controlled by energy barriers of almost equal heights, which depend almost exclusively on the solvent properties. This view is based on the equality of $-d(\ln \lambda_i^\infty)/d(1/T)$ and $d(\ln \eta)/d(1/T)$. The relationship between the Walden product for ions and their *B*-coefficients is of interest[154] and is shown for water at 25 °C in Figure 8. *Structure-breaking* ions (those with negative *B*-coefficients, see section E below) are seen to have higher Walden products than *structure-making* ones, and the *hydrophobic structure-making* ions have still lower Walden products. The direct calculation of *B* and d*B*/d*T* in several solvents from the Hubbard–Onsager theory[155,156] was attempted but was only partly successful (see below). Any direct theoretical relationship between the *B*-coefficients and the limiting equivalent conductivities of ions has, therefore, not yet been established.

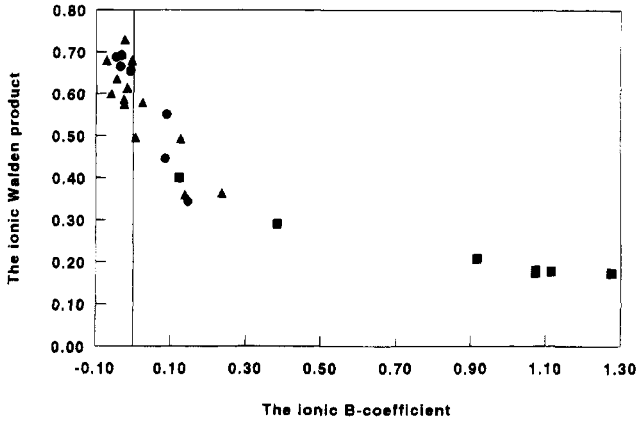


Figure 8. The Walden products $\lambda^\infty\eta_s$ (in cm^2 Ω^{-1} mol^{-1} cP) for aqueous ions vs their *B*-coefficients (in dm^3 mol^{-1}) at 25 °C.

C. Relationship to the Properties of the Ions

The earliest attempts to relate the ionic *B*-coefficients to properties of the ions are connected with the method for splitting the electrolyte *B* values into the ionic contributions (Cox and Wolfenden[22]). Ulich[166] plotted the function $F_{18/100} = (\eta_s\lambda_i^\infty)_{18}/(\eta_s\lambda_i^\infty)_{100}$ of some univalent ions, a measure of the deviations from Walden's rule (52), against their B_{18} values, where the subscripts denote the centigrade temperature, and obtained a linear plot. Asmus[24] extended this treatment to additional ions, including divalent ones, obtaining two linear segments each for both $F_{18/100}$ vs B_{18} and $F_{25/100}$ vs B_{25}. Asmus ascribed the break in the plots to the building up of a second hydration shell for lithium and ions of higher charge. Another linear relationship was shown by Asmus[24] between the *B*-coefficients and the lyotropic numbers of the anions.

A further relationship pointed out by Asmus[24] was that between the ionic *B*-coefficients and the ionic hydration entropies (at 25 °C). Again, the plot exhibited two linear segments and was explained in a manner analogous to that stated above. The notion of the relationship between the ionic *B*-coefficients and the ionic entropy of hydration was subsequently taken up by other authors. Gurney[26] proposed the following linear expression with regard to the standard partial molar entropies, $\bar{S}^\infty$, of monoatomic ions in water:

$$B/\mathrm{dm^3\,mol^{-1}} = 0.131 - 0.0292(\bar{S}^\infty/\mathrm{J\,K^{-1}\,mol^{-1}}) \quad (57)$$

(at 25 °C, converted to SI units, and based on $\bar{S}^\infty(\mathrm{H}^+) = -23.0\ \mathrm{J\,K^{-1}\,mol^{-1}}$, near the recommended value[167] of $-22.2\ \mathrm{J\,K^{-1}\,mol^{-1}}$). Burns[168] proposed for salts (rather than ions) an alternative expression:

$$B/\mathrm{dm^3\,mol^{-1}} = 0.2675 - 0.00677(\bar{S}^\infty/\mathrm{J\,K^{-1}\,mol^{-1}}) \quad (58)$$

Nightingale[169] used the hydration entropies instead and obtained a linear plot for both mono- and polyatomic ions:

$$B/\mathrm{dm^3\,mol^{-1}} = 0.131 - 0.00178(S^\circ_{\mathrm{hyd}}/\mathrm{J\,K^{-1}\,mol^{-1}}) \quad (59)$$

A further relationship was suggested by Krestov,[49,50,67] where the relevant entropy is ΔS_{II}, the total change of the entropy of water per mole of ions in the process of hydration, or $\Delta S'_{\mathrm{II}}$, corrected for loss of rotational entropy of polyatomic ions in this process. Values of ΔS_{II} for monoatomic ions and $\Delta S'_{\mathrm{II}}$ for polyatomic ones have been tabulated,[50] and the resulting expression is

$$B/\mathrm{dm^3\,mol^{-1}} = 0.011 - 0.007(\Delta S_{\mathrm{II}}(\text{or } \Delta S'_{\mathrm{II}})/\mathrm{J\,K^{-1}\,mol^{-1}}) \quad (60)$$

Marcus[170] related the *B*-coefficients of aqueous ions to their "structural entropy", S_{str}, obtained by subtraction of the electrostatic and neutral components from the standard molar entropy of hydration. These deal with the entropic effects of the temperature derivatives of the relative permittivities in the first hydration shell and the surrounding region and those of the formation of the cavity for the accommodation of the ion and its dispersion interactions with the surroundings. The relationship obtained is

$$B/\mathrm{dm^3\,mol^{-1}} = 0.033(z^2 + |z|) - 0.00165(S_{\mathrm{str}}/\mathrm{J\,K^{-1}\,mol^{-1}}) \quad (61)$$

This expression is valid for both cations and anions of charges $1 \le |z| \le 4$, but for the large hydrophobic ions the alternative expression

$$B/\mathrm{dm^3\,mol^{-1}} = 0.37 - 0.0063(S_{\mathrm{str}}/\mathrm{J\,K^{-1}\,mol^{-1}}) \quad (62)$$

should be employed.

The relationship of the ionic *B*-coefficients to the radii of the ions has been demonstrated by several authors. Podolsky[171] (see also Sadek[154]) plotted them against the crystal ionic radii and obtained a U-shaped curve. Nightingale[28] interpreted the width of the curve as showing that the difference between the effective radius of the hydrated ions, r_{h}, and their crystal radius, r_{c}, for large and small ions is of the order of the diameter of a water molecule. Marcus[170] showed that, for cations, the available *B*-coefficients of which pertain to monoatomic ions, the empirical expression

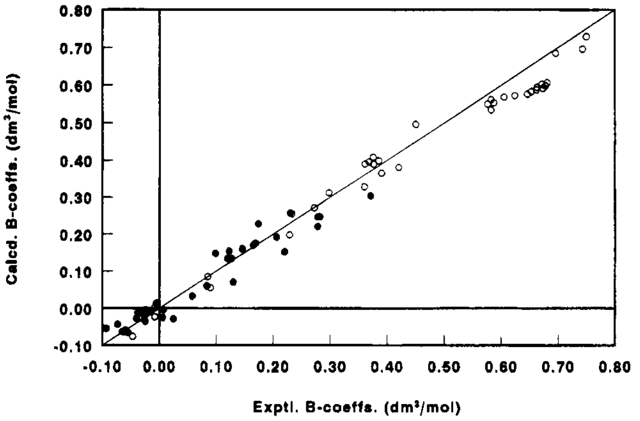


Figure 9. The calculated *B*-coefficients, according to eq 63 for cations (○) and eq 64 for anions (●) vs the experimental values for the aqueous ions at 25 °C.

$$B/\mathrm{dm^3\,mol^{-1}} = 0.307z - 0.00205r_{\mathrm{c}}z^{1/2} - 1.0 \times 10^{-6}r_{\mathrm{c}}^{2} \quad (63)$$

holds, whereas for anions, most of which are polyatomic, the corresponding expression is

$$B/\mathrm{dm^3\,mol^{-1}} = 0.747 - 0.00617(r_{\mathrm{c}}/|z|) + 11.72 \times 10^{-6}(r_{\mathrm{c}}/|z|)^2 \quad (64)$$

Figure 9 shows the *B*-coefficients calculated from eqs 63 and 64 vs the experimental ones. Nightingale[28] preferred to relate the ionic *B*-coefficients to the radii of the hydrated ions, r_{h}, but obtained several straight lines for ions of different kinds. For some solvents (e.g., ethylene carbonate, sulfolane, formamide, hexamethylphosphoric triamide, and acetic acid) whereas not for others (e.g., water, methanol, dimethyl sulfoxide, *N*-methylformamide and -acetamide, and tetramethylurea) the *B*-coefficients of the alkali metal cations have a maximum at sodium. This cannot be explained in terms of the variation of the solvated radii, taken as the Stokes radii (r_{St}) according eq 53, since these do not have an extremum for this cation.[147] The relative order of the *B*-coefficients of the alkali metal cations does not depend on the splitting assumption applied to the experimental data, so that the observed maximum at sodium appears to be a real, unexplained phenomenon.

More general agreement has been obtained when the ionic *B*-coefficients (for aqueous ions) are related to the ionic standard partial molar volumes, $\bar{V}^\infty$. This is due to the presumption that a major contribution to *B* arises from the volume of the ion in the solution, as if it were a nonelectrolyte, obeying the Einstein relationship (11).[14] This should be most appropriate for the large hydrophobic ions, which are sparingly solvated, but in aqueous solutions there is a water-structural contribution to *B*. According to Krumgalz,[162]

$$B/\mathrm{dm^3\,mol^{-1}} = 2.5(\bar{V}^\infty/\mathrm{dm^3\,mol^{-1}}) + B_{\mathrm{str}} \quad (65)$$

for such ions. However, $B/\bar{V}^\infty$ for such ions in several nonaqueous solvents, where B_{str} should be negligible, is not constant and deviates from 2.5. Desnoyers and Perron[47] considered that B_{str} vanishes for the aqueous tetraethylammonium ion, which does not affect the structure of water. Accordingly, for this ion $B/\mathrm{dm^3\ mol^{-1}} = 2.5(\bar{V}^\infty/\mathrm{dm^3\ mol^{-1}})$, used for the splitting of the B-coefficients of salts into the individual ionic contributions (cf. section IIIA). More general empirical expressions,

$$B/\mathrm{dm^3\ mol^{-1}} = a\bar{V}^\infty + b \qquad (66)$$

have been proposed by other authors for ions, both aqueous[52,79] and nonaqueous,[140] with a and b specific to certain groups of ions. Other authors prefer to use the volumes of hydrated ions (V_h) instead of $\bar{V}^\infty$, with the coefficient a nearer to 5 or 6,[66] or of hydrated salts with $a = 2.83$,[41] i.e., 5.7 per ion. This approach has hardly been applied to B-coefficients in nonaqueous solvents, but the nonmonotonic values for the alkali metal cations noted above for some solvents cannot be explained in terms of either the partial molar volumes[144] or the solvated volumes (cubes of the Stokes radii) that vary monotonically.

The Hubbard–Onsager theory of dielectric friction[155,156] was applied by Ibuki and Nakahara[172–177] to the B-coefficients. The resulting expression is

$$B = (4\pi N_A/3000)r_{HO}^3 f(r/r_{HO}) \qquad (67)$$

where r_{HO} is given by eq 55 and $f(r/r_{HO})$ had to be calculated numerically from a solution of the differential equation of shear velocity, but the values have not been disclosed. This expression was applied successfully for univalent ions, not only in water (where $r_{HO} = 0.150$ nm) but also in methanol ($r_{HO} = 0.324$ nm), formamide ($r_{HO} = 0.150$ nm), and N-methylacetamide ($r_{HO} = 0.222$ nm). Its application to dB/dT, assuming r_{HO} to be approximately independent of the temperature, was less successful. The sign of the temperature coefficient dB/dT of aqueous ions was found by Gorski[178] to agree with that of the activation energy for solvent exchange between the hydration shell and bulk water ($E^\ddagger$) according to Samoilov.[179] A linear correlation of B itself with $E^\ddagger$ (via linear correlations of both with the structural entropy, S_{str}) is suggested by the work of Marcus.[180] The correlation

$$E^\ddagger/\mathrm{kJ\ mol^{-1}} = -1.10 + 17.2(B/\mathrm{dm^3\ mol^{-1}}) \qquad (68)$$

with a correlation coefficient of 0.963 is found for 25 °C. A similar correlation is obtained for the effect of ions on the proton relaxation rate in water. Using the data of Engel and Hertz,[181] where τ_1 is the longitudinal NMR relaxation time of the dilute solution and τ_1° is that of water, the correlation

$$B' = (\tau_1^\circ - \tau_1)/c\tau_1 = -0.14 + 0.845(B/\mathrm{dm^3\ mol^{-1}}) \qquad (69)$$

is found for 25 °C, but with a poorer correlation coefficient, 0.919.[180]

D. Cross-Correlations of Ion-Additive Data

Consider the curve produced when an ion-additive property (like the viscosity B-coefficient, obeying $B = \sum \nu_i B_i$) is plotted against any other ion-additive property for a series of n salts M_iX_j, with variable cations M_i ($i = 1, 2, ..., n$) and a common anion X_j. Then corresponding plots of the same properties for further similar series of salts but with different anions X_j ($j = 1, 2, ..., m$) produce a family of nested curves. The existence of such relationships (which may be linear, yielding parallel lines) means that knowledge of one ion-additive property can be readily used to estimate incomplete data for another. This is of considerable interest when the quality of the known property is high, as is the case for the B-coefficients. Jenkins and co-workers[182–188] have demonstrated the use of the B-coefficients in just such a situation linked specifically with an appropriate thermochemical cycle.

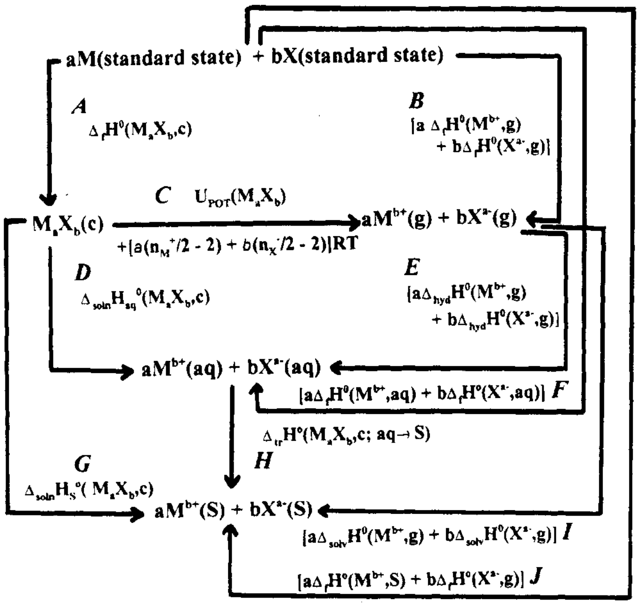


Figure 10. Thermochemical cycle for a salt, M_aX_b, involving its dissolution in water and in a nonaqueous solvent, S.

Accordingly, consider the Born–Fajans–Haber thermochemical cycle for a crystalline salt M_aX_b, dissolved in an aqueous (aq) and nonaqueous (S) solvent medium. It takes the form of Figure 10, where limb A represents the standard enthalpy of formation of the crystalline salt, limb B represents the combined standard enthalpies of formation of the a gaseous cations M^{b+} and the b gaseous anions X^{a-}, and limb C is the total lattice enthalpy, i.e., the sum of the lattice energy $U_{pot}(M_aX_b)$ and $[a(n(M^{b+})/2 - 2) + b(n(X^{a-})/2 - 2)]RT$, where $n(M^{b+})$ and $n(X^{a-})$ are equal to 3 for monoatomic ions, 5 for linear polyatomic ions, and 6 for nonlinear polyatomic ions. Limb D represents the standard enthalpy of solution of M_aX_b in water, and limb G that in the nonaqueous solvent S. Limb E represents the combined standard hydration enthalpies of the gaseous cations M^{b+} and the gaseous anions X^{a-} in water, and limb I the corresponding solvation enthalpy of these ions in S. Limbs F and J are, respectively, the standard enthalpies of formation of the aqueous and the nonaqueous cations M^{b+} and anions X^{a-}, and limb H represents the combined standard enthalpies of transfer of the a cations M^{b+} and the b anions X^{a-} from water to the solvent S.

If a given problem is confined to obtaining enthalpy changes for the various processes in Figure 10, the limbs of the thermochemical cycle can be divided into two categories: (i) those limbs for which experimental measurements can be made *directly* (A, D, G, H) or for which a *combination* of accessible experimental data enables the establishment of further data (F obtainable once A and D are known; J obtainable once A and G or A, D, and H are known), and (ii) those limbs (B, E, and I) which all involve ion-additive quantities and for which an additional connecting limb in the form of a lattice enthalpy, C, is needed before individual values can be assigned to them.

The lattice energies, $U_{\mathrm{pot}}(\mathrm{M}_a\mathrm{X}_b)$, for many simple salts (made up of monoatomic ions) and a number of complex salts are well established.[189-192] Although the results are, on the whole, regarded as reasonably reliable,[193] there have been demands in the literature[194-197] for further initiatives to extend and improve the associated computational methods. Jenkins, Morris, and co-workers[182-188] have utilized for this purpose the excellent rectilinear correlation that exists between the combined hydration enthalpies of the ions of 1:1 electrolytes (limb E) and the experimental viscosity *B*-coefficients (usually adjusted for additivity) of the electrolytes concerned. For alkali metal salts they found

$$[\Delta H_{\mathrm{hyd}}{}^\circ(\mathrm{M}^+,\mathrm{g}) + \Delta H_{\mathrm{hyd}}{}^\circ(\mathrm{X}^-,\mathrm{g})]/\mathrm{kJ\ mol^{-1}} = KB(\mathrm{MX,aq})/\mathrm{dm^3\ mol^{-1}} + I(\mathrm{M}^+) \quad (70)$$

where $K/\mathrm{dm^3\ kJ^{-1}} = -1108.7$ and $I/\mathrm{kJ\ mol^{-1}} = -737.7$ for Li^+, -692.5 for Na^+, -712.0 for K^+, -709.9 for Rb^+, and -710.0 for Cs^+. This fact enables the *B*-coefficients to be used as an alternative limb to E in the thermochemical cycle of Figure 10. The standard enthalpies of formation of polyatomic gaseous ions have been obtained in this manner: $\Delta H_f{}^\circ(\mathrm{NO_3}^-,\mathrm{g})$,[182] $\Delta H_f{}^\circ(\mathrm{CN}^-,\mathrm{g})$,[186] and $\Delta H_f{}^\circ(\mathrm{OH}^-,\mathrm{g})$.[184] The lattice energies, $U_{\mathrm{pot}}(\mathrm{NH_4X})$, of ammonium halide salts have also been obtained from viscosity and limb D data,[183] in agreement with established values. Key thermodynamic data relating to the proton affinity of ammonia were estimated[185] and more recently a controversy between experimental, thermochemical, and quantum-mechanical estimates of the stability of the azide anion was examined,[187,188] by utilizing viscosity *B*-coefficients in this way. There appears to be considerable further potential in extending this approach to obtaining enthalpies of solvation and of transfer between solvents of ions, for which no data are currently available. Such work is currently in progress, rectilinear correlations similar to eq 70 having been shown to exist in certain nonaqueous solvents.[198]

E. Ionic *B*-Coefficients and the Structure of Water

Most of the early determinations of the *B*-coefficients were done on aqueous solutions and the previously noted fact that some electrolytes decrease the viscosity relative to that of pure water was put on a quantitative basis. For example, cesium nitrate has $B = -0.092$ dm^3 mol^{-1} at 25 °C[54,55] and for cesium iodide $B = -0.258$ dm^3 mol^{-1} at 0 °C![58] Cox and Wolfenden[22] were the first to mention the notion of water structure in this connection. They reported the generally accepted explanation of the "negative viscosity", i.e., the negative values of *B*, as due to "depolymerization" of the solvent water, adding in a footnote that, according to the hypothesis of Bernal and Fowler,[199] this behavior is equivalent to a "rise (in its) structural temperature". As the temperature rises, there is less structure in the water,[200] and a similar effect is caused by ions having negative *B*-coefficients. However, the foremost proponent of the relation of the *B*-coefficients of aqueous ions to their effect on the structure of water was Gurney,[26] and his book is most often quoted in this connection. Gurney spoke of a "local loosening of the water structure" for ions with $B < 0$ at room temperature. He also used the concept of the solvent cosphere of the ion, and "local order-disorder" is equated with "order-disorder in the ionic cosphere". In the following only a few of the many papers that deal with the relation of the *B*-coefficients of aqueous ions with their effects on the structure of the water can be discussed.

Nightingale[80] placed great weight on the temperature coefficient of the viscosity of solutions, defining the activation energy for viscous flow[142] as

$$\Delta E^\ddagger = R\ \mathrm{d}(\ln \eta_s)/\mathrm{d}(1/T) + R\ \mathrm{d}[\ln(1 + Bc)]/\mathrm{d}(1/T) \quad (71)$$

and splitting $\Delta E^\ddagger$ (in an undisclosed manner) between cation and anion. Similar information can, however, be obtained also from the d*B*/d*T* recorded in Table 6. Nightingale classified the ions into four classes: (I) structure-making ions with $B > 0$ and $\mathrm{d}B/\mathrm{d}T < 0$; (II) anomalous structure-making ions, with $B > 0$ but $\mathrm{d}B/\mathrm{d}T$ also >0; (III) structure-breaking ions with $B < 0$ and $\mathrm{d}B/\mathrm{d}T > 0$; and (IV) large structure-making ions with "aperipheral hydration" with $B > 0$ and $\mathrm{d}B/\mathrm{d}T < 0$. "Aperipheral hydration" means that the ion is unhydrated, the energy change for the movement of a water molecule away from the ion being much less than the energy for its moving away from another water molecule. It is not clear, however, why the particular ions Ba^{2+}, OH^-, $\mathrm{IO_3}^-$, $\mathrm{SO_4}^{2-}$, $\mathrm{CrO_4}^{2-}$, and $\mathrm{Fe(CN)_6}^{4-}$ belong to class II, i.e., are anomalous in their behavior. On the other hand, the behavior of class III ions is clear: there being less water structure to begin with at the higher temperatures, the structure-breaking ions have less structure to break. In this sense, the few "anomalous" ions belonging to class II show reasonable behavior: when there is less structure to begin with, these structure-making ions produce more structure and have positive d*B*/d*T* values. It is the class I ions that behave in a not readily understood manner, producing less structure at higher temperatures, although they are structure makers.

This behavior is analogous, but in the opposite direction, to the water hydrogen isotope effect (section IV.C): there being more structure in heavy water than in light water,[200] the structure-breaking ions have more negative *B* values in $\mathrm{D_2O}$ (Table 7). On the other hand, structure-making ions of class I cannot form more structure, and their *B* in $\mathrm{D_2O}$ is about the same as in H_2O. Class IV ions show small and random water hydrogen isotope effects for so far unknown reasons. It is generally agreed, however, that the structure making by class IV ions differs in its nature from that of class I ions, the former enhancing the inherent structure of the water, whereas the latter producing a certain amount of new, centrally oriented structure that exhibits increased friction with the rest of the water.

An interesting view was expressed by Feakins et al.,[145] who argued that the negative *B*-coefficients exhibited by large univalent inorganic ions is not due to the breaking of water–water bonds in the ground state but to ion–solvent bond-making in the transition state for the viscous flow. On the basis of eq 48, these authors pointed out that the sign of *B* depends on the sign of $\Delta G^{\ddagger}_{E} - \Delta G_{S}^{\ddagger}$ and proposed a model for $\Delta G^{\ddagger}_{E}$. As the ion moves in the flowing medium, it moves from one cavity to an adjacent one, so that in the transition state between the two (superscript ‡) it occupies a larger cavity than in the ground state. This yields a positive contribution to $\Delta G^{\ddagger}_{E}$, due to ion–solvent bond breaking. A similar argument pertains to the movement of a water molecule and $\Delta G_{S}^{\ddagger}$. Since the water–water bonds are weaker in the transition state than in the ground state, the relative weakly hydrated large ions have an opportunity to bind more water molecules in the transition state, thus helping these extra water molecules along and increasing the fluidity of the solution. This view of Feakins et al.[145] has, however, not been taken up by others nor given independent evidence.

The structure-making and -breaking properties of ions have been related by Marcus[170,200] to the standard molar Gibbs free energy of transfer of the ions from light to heavy water, ΔG_{tr}^{*}. The change in the average number of hydrogen bonds that a water molecule participates in a solution relative to that in pure water, ΔG_{HB}, is given by

$$\Delta G_{HB} = (-\Delta G_{tr}^{*}/\text{kJ mol}^{-1})/0.929 \qquad (72)$$

where 0.929 kJ mol^{-1} is the difference in hydrogen-bond energies between light and heavy water, obtained from the sublimation enthalpies of the two kinds of ice. Fairly accurate values of ΔG_{HB} are available for the alkali metal and halide ions, all except those of Li^+ and F^- being negative, and a ΔG_{HB} scale has been set up as a measure of the effects of the ions on the structure of water. This scale is compatible with that of the *B*-coefficients,[170]

$$\Delta G_{HB} = (-0.54 \pm 0.11) + (4.75 \pm 1.39)(B/\text{dm}^3\ \text{mol}^{-1}) \qquad (73)$$

though less well than with the structural entropies,

$$\Delta G_{HB} = (-0.14 \pm 0.06) - (8.16 \pm 1.01) \times 10^{-3}(S_{str}/\text{J K}^{-1}\ \text{mol}^{-1}) \qquad (74)$$

as the correlation coefficients (0.790 and 0.925, respectively) indicate. Still, the values calculated from eq 73 permitted the establishment of structure-making and -breaking values on the ΔG_{HB} scale for a large number of ions, the structural effects of which could not be placed on a quantitative basis otherwise.

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