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On the Partitioning of the NMR *B′*-Coefficient. The Evaluation of Single Ion *B′*-Coefficients by a New Method and the Correlation with the Viscosity *B*-Coefficient, Partial Molal Volume and Electrostatic Entropy of Solvation of Ions in Aqueous and Nonaqueous Systems

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A new method of division used for the viscosity *B*-coefficient has now been extended to the partitioning of the NMR *B′*-coefficient both in aqueous and various nonaqueous systems. The derived set of B_i'-values, unlike those obtained by other methods in water are found to be quantitatively related to the ionic molal volumes obtained by the UVP method. The usual assumption of equal contributions of K^+ and Cl^- ions has been discarded. Abraham et al.'s electrostatic entropy of solvation of ions has also been found to give excellent linear correlation with the derived NMR B_i'-values in different solvents. The striking feature is that the NMR B_i'-values as derived by Abraham and coworkers by a different method are almost identical to the present values in all the nonaqueous solvents studied. The slight disagreement observed for the aqueous system has been discussed as being due to encroaching of the disordered second layer to the first layer of solvation, thereby making the absolute entropy estimates less certain. Both the cationic and anionic B_i'-values are represented by a single smooth parabolic curve against the crystal ionic radii as predicted by the theory. The hydration number for Cl^- ion as derived from this work agrees excellently with the widely accepted value.

Recently, there are many attempts[1–5] to derive the single ion values of various thermodynamic and transport properties of electrolytes both in aqueous and nonaqueous systems. However, similar activities for the NMR *B′*-coefficient, first introduced by Hertz and co-workers,[6] are rather limited. From the NMR measurements concerning the molecular motion in solutions, these authors proposed the following equation (1), in analogy with the viscosity *B*-coefficient,[7] of the relative proton relaxation rate for pure solvent ($1/T_1^\circ$) and solution ($1/T_1$) as a function of concentration:

$$\frac{1/T_1}{1/T_1^\circ}=1+B'c+C'c^2+\cdots \qquad (1)$$

The NMR *B′*-coefficient in equation (1) gives information about the reorientational behavior of solvent molecules in the first coordination sphere of the ions.

A survey of the literature shows that there has been no generally accepted method of division for the *B′*-coefficient in any solvent. In aqueous solution, Hertz et al.[6] partitioned the *B′*-coefficient assuming $B'_{K^+}=B'_{Cl^-}$ at all temperatures in analogy with the partitioning of the *B*-coefficient by Kaminsky.[8] Very recently, Sacco and co-workers[9] have utilized the same method as adopted for the *B*-coefficient in dimethyl sulfoxide (DMSO) by Bicknell et al.[10] for the separation of the *B′*-coefficient in the same solvent. Abraham and co-workers[11] have also partitioned both the NMR *B′* and viscosity *B*-coefficient by means of correspondence plots with the theoretically estimated electrostatic entropy of solvation of ions in various protic and aprotic solvents.

Very recently, a general method of separation of the viscosity *B*-coefficient applicable to both aqueous and various nonaqueous systems has been developed by the author.[12] Since the NMR *B′*-coefficient has almost all the attributes of the viscosity *B*-coefficient and also the fact that the NMR relaxation rate has better theoretical models than the viscosity, it is interesting to see how far the new method is applicable to the division of the *B′*-coefficient. Moreover, it is also imperative to study the relative merits of the various methods of division of the NMR *B′*-coefficient as far as the basis of suitable criteria is concerned. With these ends in view, we have compiled the various NMR *B′*-coefficient of different electrolytes reported by Hertz and co-workers,[6,13] Sacco and co-workers[9] in water, methanol, formamide, *N*-methylformamide (NMF), DMSO, and ethylene glycol at 25 °C.

Derivation of the Model

Now, that the NMR *B′*-coefficient is not only additive and a measure of ion-solvent interaction like the *B*-coefficient, but the hydration number from the two coefficients can also be evaluated from the two analogous expressions as follows:

$$B'^{\pm}=(\tau_c^{\pm}/\tau_c^{\circ}-1)\,n_h^{\pm}/55.5 \qquad (2)$$

$$B^{\pm}=(\eta_c^{\pm}/\eta_0-1)\,n_h^{\pm}/55.5 \qquad (3)$$

where $\tau_c^{\pm}$ is the rotational correlation times,[6,13] $\eta_c^{\pm}$ is the coefficient of viscosity for the hydrated ions,[14] $n_h^{\pm}$ is the hydration number of ions, 55.5 and the subscript zero are respectively the number of moles of water per kg of water and the corresponding property for pure solvent.

Table 1. Single Ion Values of NMR B_i' Coefficient/kg mol^{-1}, $\overline{V}_i^\circ$/cm^3 mol^{-1}, $\Delta S_{I,II}$/cal K^{-1} mol^{-1} and B_i-Coefficient/dm^3 mol^{-1} for Monovalent Ions Together with the Estimated Values[a)] in Various Solvents by Different Methods at 25 °C

Ion	Water					Methanol					Formamide				
	Present B_i' (0.075)[a)]	Abraham et al. B_i'	$\overline{V}_i^\circ$ (UVP)	$\Delta S_{I,II}$	Present B_i	Present B_i' (0.034)[a)]	Abraham et al. B_i'	$\overline{V}_i^\circ$ (UVP)	$\Delta S_{I,II}$	Present B_i	Present B_i' (0.014)[a)]	Abraham et al. B_i'	$\overline{V}_i^\circ$ (Mukerjee)	$\Delta S_{I,II}$	Present B_i
Li^+	0.215	0.17	−11.2	−30.4	0.2015	0.259	0.25	—	−34.2	0.486	—	—	−4.0	−27.4	0.345
Na^+	0.135	0.09	−7.4	−17.4	0.1383	0.149	0.14	−18.6	−28.7	0.454	0.164	0.16	−2.5	−27.4	0.448
K^+	0.065	0.02	3.4	−1.5	0.045	0.119	0.11	−4.9	−21.7	0.422	0.089	0.08	8.4	−20.5	0.222
Rb^+	0.035	−0.01	9.0	3.1	0.022	0.089	0.08	−2.8	−17.2	—	0.074	0.06	12.4	−16.0	0.199
Cs^+	0.025	−0.02	15.5	7.1	0.007	0.079	0.07	3.3	−13.8	0.221	0.064	0.07	18.7	−12.5	0.173
$(CD_3)_4N^+$	0.255	—	—	—	—	—	—	—	—	—	—	—	—	—	—
F^-	0.065	0.11	3.3	−9.9	0.0445	—	—	−1.2	−20.7	—	—	—	—	—	—
Cl^-	−0.085	−0.04	23.7	10.6	−0.059	0.041	0.05	13.0	−9.9	0.342	0.041	0.04	23.6	−8.4	0.142
Br^-	−0.115	−0.07	30.2	15.9	−0.094	0.021	0.03	17.1	−7.0	0.318	0.021	0.03	30.0	−5.4	0.115
I^-	−0.155	−0.11	41.4	23.5	−0.1205	−0.009	0.00	30.0	−1.5	0.253	−0.004	0.005	42.4	0.2	0.07

Ion	NMF			DMSO					Ethylene glycol	
	Present B_i (0.022)[a)]	Abraham et al. B_i'	$\Delta S_{I,II}$	Present B_i' (0.064)[a)]	Lawrence et al. B_i'	$\overline{V}_i^\circ$ (Criss et al.[11)])	$\Delta S_{I,II}$	Present B_i	Present B_i' (0.025)[a)]	$\overline{V}_i^\circ$ (UVP)
Li^+	0.124	0.13	−38	—	—	−9	−42	0.508	—	−10.3
Na^+	0.094	0.11	−33	0.109	0.118	−2	−40	0.434	0.125	−4.9
K^+	0.084	0.095	−26	0.110	0.119 (0.11)[b)]	2	−33	0.444	0.045	4.4
Rb^+	0.074	0.08	−22	0.096	0.105	7	−29	0.423	0.025	9.1
Cs^+	0.064	0.07	−18	0.088	0.097	8	−25	0.392	0.010	15.4
F^-	—	—	−25							12.5
Cl^-	0.056	0.04	−14	—	—	15	−21	0.358	−0.005	26.2
Br^-	0.046	0.04	−11	0.067	0.060	22	−18	0.399	−0.020	31.9
I^-	0.036	0.03	−5	0.044	0.035 (0.04)[b)]	36	−12	0.372	−0.035	42.5

a) Different estimated values. b) Ref. 11.

Thus, considering the similarity of the two definitions in Eq. 2 and 3, it is now assumed that the ionic NMR B'-values like the viscosity B_i-values should be a monotonic function of crystal radii cubed, independent of the sign of the charge.[12] The above assumption is implicit in the treatment of Couture and Laidler[15] that for large monoatomic monovalent ions, B_i' like $\overline{V}_i^\circ$ is not dependent on the sign of the charge, as the two parameters are also similar in nature. Figure 1 shows two different smooth curves of B_i' versus r_i^3 plots, one for the alkali metal ions and the other for the halide ions on the basis of $B'_{K^+}=B'_{Cl^-}$[6] in aqueous system. According to the assumption, a smooth curve representing all the cations and anions is only obtained, if an estimated correction term of 0.075 is added to the cationic B_i'-values and the same is subtracted from the anionic values. The smooth fusion of the two curves into a single one as also the same derived values obtained for K^+ and F^- ions add support to the above assumption. This is also illustrated in the figure. It is striking to note that the only alkali metal ion off the curve is Cs^+, as was similarly observed for the viscosity B-coefficient in aqueous system.[12]

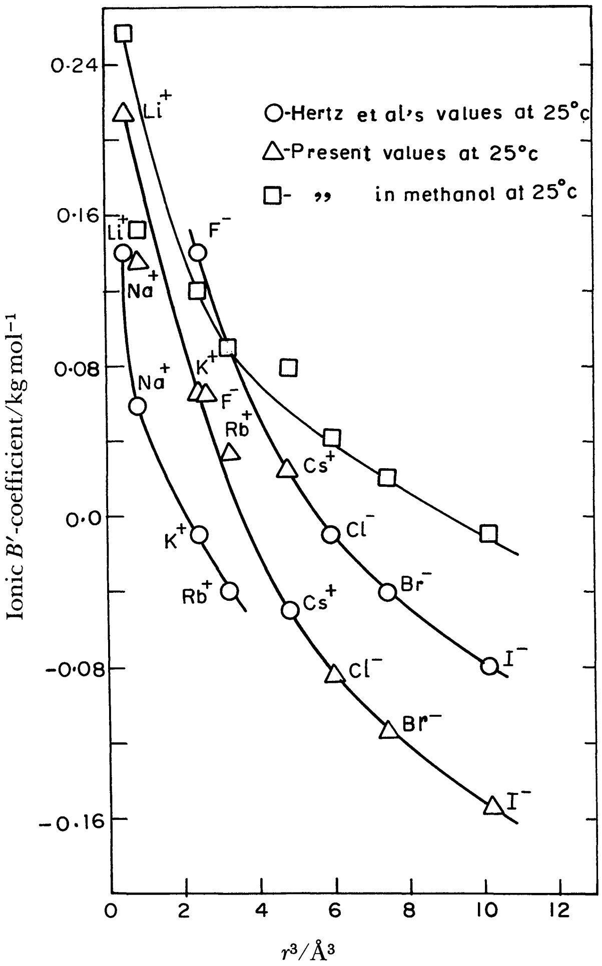

Fig. 1. The NMR B'-coefficient of alkali metal ions and halide ions plotted against r_i^3 in methanol as well as the same for two different values of B_i' based on (i) $B'_{K^+}=B'_{Cl^-}$ scale and (ii) the present scale for aqueous system.

The method of partitioning the B'-values for aqueous system at 25 °C has been extended to other temperatures also, viz. 50 °C, 80 °C with the respective correction terms being 0.080 and 0.070. Thus, in order to get B_i'-values of any ion at any temperature, one requires to add [Z] times the corresponding correction term to the cationic B'-values and subtract the same from the anionic B'-values, as obtained on the assumption that $B'_{K^+}=B'_{Cl^-}$, where Z is the charge on the ion. The correction term which is the direct consequence of the assumption signifies that cations are more and anions are less solvated relative to what are obtained from the assumed equality of B_i'-values for K^+ and Cl^- ions or any other ions. Since the additivity law holds good for the B'-coefficient, the magnitude of the correction term for the oppositely charged ions becomes the same though with opposite sign.

Following the same model, the partitioning of B'-coefficient[6] in methanol, formamide, NMF, DMSO, and ethylene glycol has been carried out at 25 °C. The initial tentative B_i'-values are obtained on the basis of $B'_{Cs^+}=B'_{I^-}$ in formamide, NMF, and DMSO, whereas in methanol and ethylene glycol, $B'_{K^+}=B'_{I^-}$ and $B'_{K^+}=B'_{Cl^-}$ respectively are followed. The different correction terms estimated in various solvents are 0.034, 0.014, 0.022, 0.064, and 0.025 respectively. Also, Fig. 1 illustrates a smooth curve representing the relation between the derived B_i'-values of all the simple ions and r_i^3 in methanol only, thereby confirming the justification of the present method of division in nonaqueous systems. The thus derived B_i'-values together with the corresponding viscosity B_i-values for monovalent ions are recorded in Table 1. Also included in the table are the various ionic entropy of solvation of different ions reported by Abraham et al,[11] as also the corresponding ionic partial molal volumes mostly derived by the ultrasonic vibration potential method.[16,17]

Results and Discussion

The ionic partial molal volume also measures the ion-solvent interaction and is more akin to the B or B'-coefficient than either the more sensitive entropy of solvation[18] or the ion conductance.[19] As there are now reliable estimates of the $\overline{V}_i^\circ$-values from the definitive experimental measurements,[16,17] any quantitative correlation of this parameter with any of the derived B_i'-values by different methods would be the reasonable criterion to evaluate the relative merits of such methods. Moreover, the good linear correlations between the entropy parameter ($\Delta S_{I,II}$) and the derived B' or B-coefficient obtained by Abraham and co-workers,[11] are in fact, the direct consequence of the

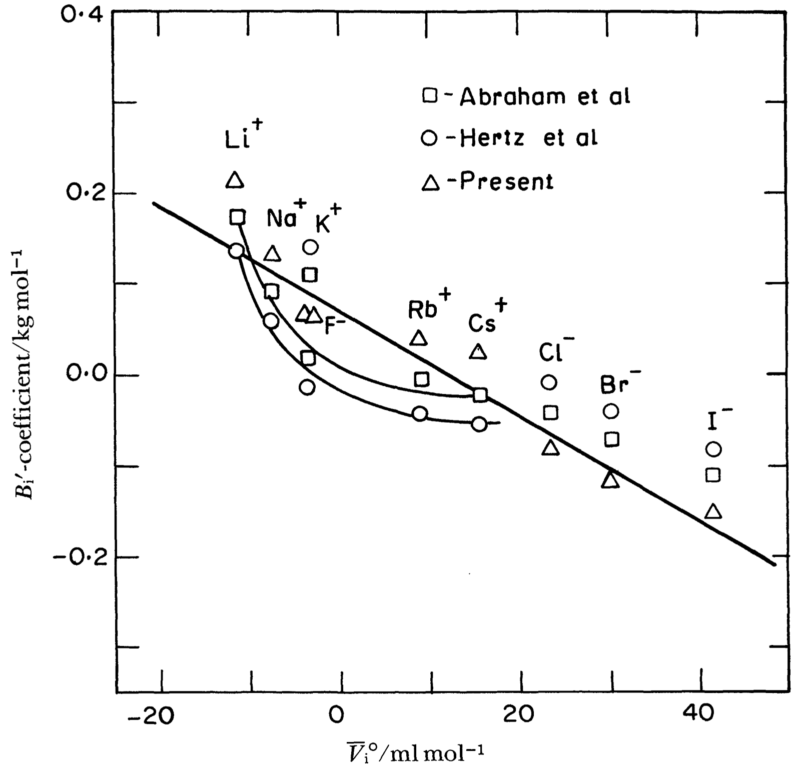

Fig. 2. Comparison of NMR B_i' versus $\overline{V}_i^\circ$ plots for monovalent monoatomic ions between the present work and those obtained by (i) Hertz and co-workers (ii) Abraham and co-workers for aqueous system.

correspondence plots between the two parameters. In the present case, where the ionic B or B'-values are derived by an entirely different approach, any quantitative correlation between the derived B'-values and the entropy parameter ($\Delta S_{\mathrm{I,II}}$) should demonstrate the better applicability of the present method of division.

Partial Molal Volume of Ions ($\overline{V}_i^\circ$). Figure 2 illustrates the comparison of the various B_i' versus $\overline{V}_i^\circ$ plots obtained by using the single ion B'-values by different methods, viz., Hertz and co-workers,[6] Abraham and co-workers[11] as well as the present method for aqueous solutions. Apart from the Li^+ ion, the B_i'-$\overline{V}_i^\circ$ plots for all the inorganic ions studied in this work show an excellent linear correlation as anticipated, and the regression data are shown in Table 2. In comparison to this, the B_i'-values by Hertz and co-workers show a U-shaped curve indicating that the assumption $B'_{K^+}=B'_{Cl^-}$ is not satisfactory for aqueous system. Although the nonlinearity is considerably reduced in the case of B_i'-values derived by Abraham and co-workers,[11] it still deviates from the linearity shown by the present work. Exactly the same observation was also obtained in the case of viscosity B_i-$\overline{V}_i^\circ$ plot obtained by the present method[12] in aqueous system, indicating the close similarity of the two coefficients. Moreover, the $\overline{V}_i^\circ$ values of K^+ and F^- ions obtained by the UVP method in water are almost identical, as is similarly obtained for both the B' and B-coefficient for the same ions following the present method (Table 1).

It is striking to note that contrary to what is observed for aqueous system, the B_i'-values obtained in this work and those by Abraham and coworkers[11] are quite close in almost all the nonaqueous solvents studied here.

the B_i'-$\overline{V}_i^\circ$ plots for all the non-aqueous solvent excepting NMF have also been studied taking different derived B_i'-values. The various $\overline{V}_i^\circ$ values required for these plots were compiled from the UVP method for methanol[16] and ethylene glycol,[17] Mukerjee's method[20] for formamide and those reported by Abraham et al.[11] for DMSO. A comparison of B_i'-$\overline{V}_i^\circ$ plots in methanol and formamide obtained by using B_i'-values of this work with those of Abraham et al.[11] clearly shows that the quantitative correlations are quite similar, as is evident from Table 2.

In DMSO, such comparison is made with the two different sets of B_i'-values derived by Sacco and coworkers[9] using two different reference electrolytes,[10,21] as very few data were reported by Abraham et al. in this solvent. While the B_i'-values of Sacco et al. following Lawrence et al.'s method[21] fail to correlate well with the $\overline{V}_i^\circ$, the other set of B_i'-values[10] show comparable linear correlation with those obtained by this work (Table 2). Also, the B_i'-values of only three ions as reported by Abraham et al.[11] in this solvent are quite close to the present values.

Table 2. Regression Data for Various NMR B_i' vs. $\overline{V}_i^\circ$, NMR B_i' vs. $\Delta S_{I,II}$ and Viscosity B_i^* vs. $\Delta S_{I,II}$ Linear Plots for Simple Inorganic Ions in Various Solvents Obtained by Computerized Least Square Method

	Abraham et al.	This work
Water	—	$B'=-0.0062\overline{V}_i^\circ+0.089$ ±0.001 ±0.016
	$B'=-0.0053\Delta S_{I,II}+0.016$ ±0.002 ±0.015	$B'=-0.0068\Delta S_{I,II}+0.021$ ±0.008 ±0.029
		$B^*=-0.0060\Delta S_{I,II}+0.019$ ±0.004
Methanol	$B'=-0.0029\overline{V}_i^\circ+0.084$ ±0.002	$B'=-0.0034\overline{V}_i^\circ+0.088$ ±0.0016 ±0.007
	$B'=-0.0051\Delta S_{I,II}+0.005$ ±0.0008 ±0.003	$B'=-0.0060\Delta S_{I,II}+0.016$ ±0.0007 ±0.006
Formamide	$B'=-0.0033\overline{V}_i^\circ+0.124$ ±0.0043 ±0.016	$B'=-0.0036\overline{V}_i^\circ+0.132$ ±0.0036 ±0.013
	$B'=-0.0032\Delta S_{I,II}+0.0016$ ±0.0015	$B'=-0.0044\Delta S_{I,II}+0.02$ ±0.0003
DMSO	[a] $B'=-0.0024\overline{V}_i^\circ+0.117$ ±0.001 ±0.004	$B'=-0.0018\overline{V}_i^\circ+0.108$ ±0.001 ±0.0034
	[a] $B'=-0.0032\Delta S_{I,II}+0.005$ ±0.0004 ±0.009	$B'=-0.0024\Delta S_{I,II}+0.022$ ±0.0003
NMF	$B'=-0.0032\Delta S_{I,II}+0.0076$ ±0.0006 ±0.005	$B'=-0.0025\Delta S_{I,II}+0.02$ ±0.0003 ±0.004
Ethylene glycol		$B'=-0.0029\overline{V}_i^\circ+0.073$ ±0.003 ±0.019

a) Sacco et al.[9)]

Electrostatic Entropy of Solvation of Ions ($\Delta S_{I,II}$). It is interesting to note that contrary to what is observed for B_i'-$\overline{V}_i^\circ$ plots in aqueous system, the B_i'-values of all the inorganic ions including Li^+ derived by the two methods give good linear correlation with the ionic entropy of solvation as shown in Table 2. A comparison of the regression data for the two linear relations, however, indicates that the Abraham et al.'s correspondence method makes the smaller ions less structure makers and the larger ions less structure breakers in water than the present method. Table 2 also reveals that the B_i'-$\Delta S_{I,II}$ correlations for the various non-aqueous systems studied here obtained by the two methods, are almost similar. However, the corresponding correlations between the viscosity-B_i versus $\Delta S_{I,II}$ also shown in Table 2 are even better than the same for the NMR B_i'-coefficient.

The striking similarity between the B_i'-values by the two methods in the nonaqueous solvents can now be explained as follows. According to Abraham et al.,[11)] the entropy calculations either by one layer or two layer model in aprotic solvents result in the same value and these agree well also with the experimental values. However, this is not true in the case of hydrogen-bonded solvents, where a disordered second layer of solvation makes the calculations rather more complicated. For DMSO, NMF, methanol, and formamide, there is either no such disordered region, or the effect due to this is quite insignificant. As a result, the estimated entropy values are of the right order of magnitude. However, water being a predominantly structured solvent is also known to be highly susceptible to structure-breaking in presence of larger inorganic ions.[22)] It is perhaps due to encroaching of this disordered region into the first layer that the estimated entropy values as given by Abraham et al. do not reflect satisfactorily the effective picture of ion-solvent interaction in water.

Table 3. Ionic B'-Coefficient of Higher Valent Cation and Polyatomic Anions in Aqueous Solution at 25 °C

Ion	Pauling radius	B_i'	Ion	Pauling radius	B_i'
	Å	kg mol^{-1}		Å	kg mol^{-1}
Ba^{2+}	1.43	0.33	SCN^-	2.34	−0.145
Sr^{2+}	1.27	0.38	ClO_3^-	2.58	−0.155
Ca^{2+}	1.06	0.42	BrO_3^-	2.69	−0.135
Mg^{2+}	0.78	0.65	IO_3^-	2.79	−0.055
Pb^{2+}	1.32	0.35	NO_3^-	2.49	−0.125
CO_3^{2-}	2.48	0.10	$Hg(CN)_4^{2-}$	4.68	−0.26
SO_3^{2-}	2.54	0.07	CdI_4^{2-}	4.75	−0.24
SO_4^{2-}	2.89	−0.03	HgI_4^{2-}	4.85	−0.21
$S_4O_6^{2-}$	3.6	−0.10	WO_4^{2-}	3.35	+0.02

Table 4. Ratio of Rotational Correlation Times of Simple Inorganic Ions for Different Hydration Numbers by This Work as Also from Hertz et al.[6,13)] (within Parentheses) in Aqueous Solution at 25 °C

Ion	Hydration numbers			
	4	6	8	10
Li^+	3.9	2.9	2.5	2.2
	(2.9)	(2.3)	(2.0)	(1.8)
Na^+	2.8	2.2	1.9	1.7
	(1.8)	(1.6)	(1.4)	(1.3)
K^+	1.9	1.6	1.4	1.3
	(0.8)	(0.9)	(0.9)	(0.9)
Rb^+	1.5	1.3	1.2	1.2
		(0.6)	(0.7)	(0.8)
Cs^+	1.3	1.2	1.2	1.1
		(0.5)	(0.7)	(0.7)
F^-	1.9	1.6	1.4	1.3
	(2.9)	(2.3)	(2.0)	(1.8)
Cl^-	—	0.2	0.4	0.6
	(0.8)	(0.9)	(0.9)	(0.9)
Br^-	—	—	0.2	0.4
	(0.4)	(0.6)	(0.7)	(0.8)
I^-	—	—	—	0.2
	—	(0.3)	(0.4)	(0.6)

Crystal Ionic Radii (r). Engel and Hertz[6] deduced the NMR B'-coefficient as a function of ionic radius by the following equation,

$$B'^{\pm}=K(ar^2-b|Z|e+cZ^2e^2/r^2), \tag{4}$$

where K, a, b, and c are constants, $|Z|e$ is the charge on the ion.

Equation 4 can be conveniently written as

$$B'^{\pm}=A_1r^2-A_2|Z|e+A_3Z^2e^2/r^2, \tag{5}$$

where A_1, A_2, and A_3 are the products of the various constants.

Equation 5 is a parabolic equation such that the B_i'-coefficient has high values both for smaller and higher ionic radii and a minimum in between. The expression for $r_{\min}$ can easily be obtained by equating the first derivative of B' in Eq. 5 to zero

$$r_{\min}=(A_3/A_1)^{1/4}\,(|Z|e)^{1/2} \tag{6}$$

and by substituting $r_{\min}$ in Eq. 5 one obtains

$$B'^{\pm}_{\min}=|Z|e\,[2(A_1A_3)^{1/2}-A_2]. \tag{7}$$

Thus for a change in $|Z|e$ values, both $r_{\min}$ and $B'^{\pm}_{\min}$ should change by $\sqrt{|Z|e}$ and $|Z|e$ fold respectively.

Figure 3 illustrates two smooth parabolic curves of B_i' versus r_i plots, one for the monovalent ions and the other for the divalent ions. The different B'-values for various ions for aqueous solution are derived by the present method from those reported by Hertz and co-worker,[6] and are included in Table 3. The noticeable feature is that both the cations and anions of the same valence fall on the same line of the curve. This is contrary to what was demonstrated earlier by Engel and Hertz[6] showing two separate curves for the cations and anions with the B_i'-values derived on the basis of $B'_{K^+}=B'_{Cl^-}$. It is now known that the cation-solvent and anion-solvent interactions are very similar in aqueous as also in many nonaqueous solutions.[16,23] Figure 3 also reveals that while the increase in $B'^{\pm}_{\min}$ for $Z=2$ is in accordance with Eq. 7, the same for $r_{\min}$ is slightly larger than that predicted by Eq. 6.

Rotational Correlation Times and the Hydration Number. Equation 2 gives the values of $(\tau_c^{\pm}/\tau_c^{\circ})$ for various ions provided the hydration number ($n_h^{\pm}$) is known with certainty. According to Engel and Hertz,[6,13] if $\tau_c^{\pm}/\tau_c^{\circ}>1$, then the ion is structure forming and for $\tau_c^{\pm}/\tau_c^{\circ}<1$, the ion is structure breaking. Table 4 compares such values for simple inorganic ions calculated with B_i'-values derived by the two methods, viz., Hertz and co-workers and the present method, assuming arbitrary values of n_h=4,6,8, and 10. The interesting feature of Table 4 is that only the present method rules out the possibility of hydration

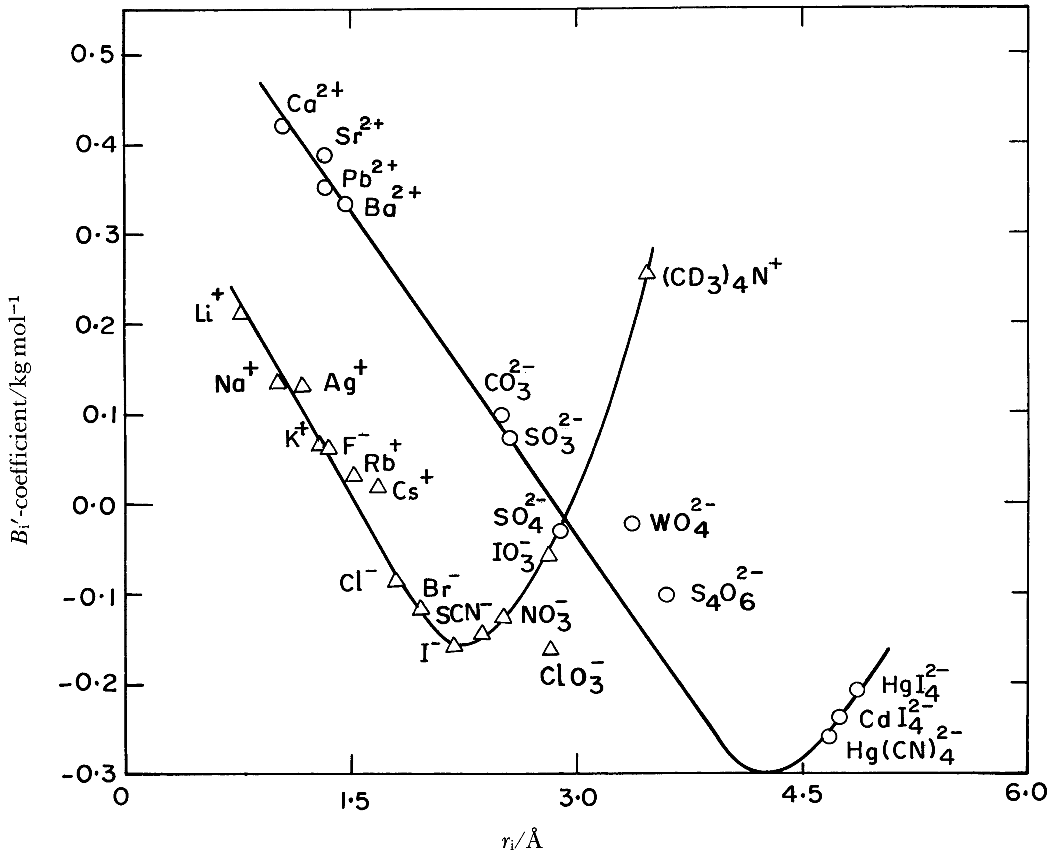

Fig. 3. Variation of ionic NMR B'-values with crystal ionic radii at 25 °C for aqueous system.

number equal to 4 for Cl^- because of the negative value obtained for $(\tau_c^{\pm}/\tau_c^{\circ})$, and agree with a value of 6 instead, which is confirmed by definitive experimental studies.[24]

Moreover, Hertz and co-workers[13] also estimated the correlation time for fluoride ion (τ_c^-) in aqueous solution, considering the unsymmetrical arrangement of water molecule in the hydration sphere (nonrigid) of the ion and the values are $\tau_c^- \approx 1\times10^{-11}$ s for $n_h=4$ and $\tau_c^- \approx 0.5\times10^{-11}$ s for $n_h=6$. The corresponding values from the proton relaxation data derived by the present method are 0.5×10^{-11} s and 0.4×10^{-11} s respectively. The fair agreement between the values in the case of $n_h=6$ thus strongly favors the latter as the hydration number for F^- ion.

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