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A New Estimate of Ionic Values of Viscosity *B*-Coefficient, NMR *B′*-Coefficient and the Ion–Solvent Interactions at Extended Temperatures in Aqueous Solutions

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Synopsis. New estimates of ionic viscosity *B*-coefficient and NMR *B′*-coefficient have been obtained in aqueous solutions over the temperature range 0 to 95 °C by a recently developed method. The derived values for the alkali metal and halide ions have been compared with the existing ones and the discrepancies discussed. Temperature effect on the two coefficients for the simple inorganic ions has been satisfactorily discussed using the concept of the Frank and Wen model. Energy of activation for viscous flow has also been calculated using the Eyring model and three different values are obtained for each ion over the temperature range studied.

Recently, a non-thermodynamic method has been reported from this laboratory for the splitting of electrolyte properties and applied successfully to both the viscosity *B* and the NMR *B′*-coefficients in different solvents, albeit at a single temperature.[1,2] The study of ion–solvent interaction at room temperature only is utterly incomplete unless it is studied in a wide range of temperatures. It is the purpose of the present work to estimate the ionic values of the two coefficients mentioned, by the present method at various temperatures between 0 and 95 °C. These not only permit us to compare the present estimates of ionic values with those of the earlier ones[3,4] but also throw new light on the complicated nature of ion–solvent interactions and the solvent structure. Moreover, since both the ionic *B*-coefficient and the ionic NMR *B′*-coefficient are measure of ion solvent interactions,[5,6] the study of these two coefficients together with the ionic partial molal volumes provide us a complementary view point of the problem under consideration.

Method of Division

The mechanics of splitting by the present method has been described in details elsewhere.[1,2] We have procured very precise viscosity *B*-coefficient data for the alkali metal halides in aqueous solution each at 10 °C intervals over the temperature range 5—95 °C as reported by Out and Los,[7] and applied the present method of division. The thus derived ionic values for the alkali metal and halide ions together with the different estimated values (correction term) at various temperatures are included in Table 1.

In the case of NMR *B′*-coefficient, Hertz et al.[6,8] reported the corresponding data for the alkali metal halides in aqueous solution at four temperatures, viz., 0°, 25°, 50°, and 80 °C. The same method has also been adopted for the resolution of the *B′*-coefficient and the derived ionic *B′*-values together with the estimated correction terms at the specified temperatures are also shown in Table 1.

Discussion

In our earlier communications we have introduced the empirical correction term[1,2] which was believed to be constant for all values of temperatures (range studied 25—42.5 °C) in aqueous solutions. However in the present case when an extended range of temperature (5—95 °C) has been studied, it is seen that the correction term is no longer constant but depends upon temperature. In fact, we got two different values of the correction term for the viscosity *B* coefficient in aqueous solutions, one for the temperature range 5—55 °C and the other for 65—95 °C (Table 1).

It appears that the B_i values of the structure making or breaking ions change significantly with temperature at the lower temperature range (0—55 °C) in comparison to the same at the higher temperature (55—95 °C). As a result the B_i values of the two classes of ions come somewhat closer at the higher temperature range than those at the lower temperature, thereby leading to a slightly different lower value of the correction term at high temperatures (Table 1). Thus, the effect of pre-

Table 1. Single Ion Values of Viscosity B_i-Coefficient (kg mol^{-1}), NMR B_i-Coefficient (kg mol^{-1}) within Parentheses for Monovalent Ions together with the Correction Terms at Various Temperatures in Aqueous Solutions

Ions	0 °C	5 °C	15 °C	25 °C		35 °C	45 °C	50 °C	55 °C	65 °C	75 °C	80 °C	85 °C	95 °C
Li^+	(0.285)	0.2176	0.2050	(0.215)	0.2015	0.1870	0.1811	(0.20)	0.1769	0.1622	0.1605	(0.170)	0.1587	0.1566
Na^+	(0.155)	0.127	0.1350	(0.135)	0.1383	0.1349	0.1335	(0.14)	0.1333	0.1226	0.1251	(0.120)	0.1253	0.1266
K^+	(0.055)	0.011	0.031	(0.065)	0.045	0.0561	0.0675	(0.08)	0.0717	0.0654	0.0699	(0.080)	0.0757	0.0794
Rb^+	(0.025)			(0.035)	0.022[a]	0.036[a]	42.5 °C 0.038[a]	(0.07)				(0.08)		
Cs^+	(0.015)			(0.025)	0.011[a]	0.022[a]	42.5 °C 0.026[a]	(0.07)				(0.08)		
F^-	(0.055)			(0.065)	0.0445			(0.08)				(0.08)		
Cl^-	(−0.155)	−0.093	−0.073	(−0.085)	−0.059	−0.0479	−0.0395	(−0.08)	−0.0323	−0.0146	−0.010	(−0.06)	−0.0043	−0.0006
Br^-	(−0.185)	−0.132	−0.1085	(−0.115)	−0.094	−0.0781	−0.0658	(−0.10)	−0.0561	−0.0363	−0.0294	(−0.08)	−0.0251	−0.0189
I^-	(−0.255)	−0.1819	−0.1538	(−0.155)	−0.1205	−0.1186	−0.1061	(−0.14)	−0.0987	−0.0778	−0.0681	(−0.11)	−0.0626	−0.0557

Correction term for viscosity: 0—55 °C, 0.052; 65—95 °C, 0.040. Correction term for NMR *B′*-coefficient: 0 °C, 0.105; 25 °C, 0.075; 50 °C, 0.080; 80 °C, 0.070. a) Ref. 18.

vailing water structure and the consequent ion–solvent interaction at the two range of temperatures is duly reflected in the values of the correction term.

In the case of the NMR B'-coefficient, the correction term has been found to be much more sensitive to temperature and as such four different values have been obtained at the four different temperatures over the temperature range 0—80 °C in aqueous solution. Moreover, we have shown earlier[1,2] that the correction terms are also dependent on the nature of solvent.

The present scale of division shows positive values of both the ionic B coefficient and the NMR B'-coefficient (first layer only) for K^+, Rb^+, and Cs^+ ions (Table 1) in aqueous solution at room temperature contrary to the negative values obtained by Kaminsky[3] on the basis of ion-conductance equality of K^+ and Cl^- ions. Abraham et al.[4] also reported positive values of the two coefficients for K^+ and slightly negative values for Rb^+ and Cs^+ ions in aqueous solution derived by correspondence plots with the electrostatic entropy of solvation. Very recently, Nakahara et al.'s[9] reported positive values of orientational correlation times coefficient (α) for K^+ and Cs^+ ions in dilute aqueous solutions support our derived positive viscosity B_i-values for the same ions as the two quantities are directly related.[10]

It is however to be noted that the positive values of the coefficients for the ions mentioned do not deter them to act as structure breakers. As is well known, the temperature coefficient of the B-coefficient is much more important than the B_i-value itself to decide whether an ion would behave like structure breaker or promoter.[3,11] Since all the ions have positive temperature coefficient, these are all termed as net structure breakers in spite of the positive B_i-values. This fact, therefore, does not contradict the earlier views about these ions.

Temperature Variation of B and B'-Coefficients. Figure 1 illustrates the temperature variation of the viscosity B and the NMR B'-coefficients for the alkali metal and halide ions. For Li^+ ion the curves show a gradually decreasing trend though the NMR B_i' curve runs higher and is also slightly steeper than the corresponding curve for the B coefficient. In the case of the Na^+ ion the two curves almost merge with each other above 15 °C and the same thing happens for the larger cations at still higher temperature. However for the halide ions the two curves gradually diverge with the increase of temperature.

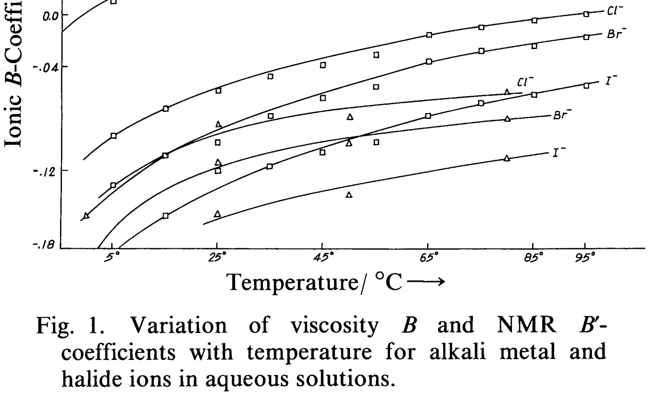

Fig. 1. Variation of viscosity B and NMR B'-coefficients with temperature for alkali metal and halide ions in aqueous solutions.

The fact that the viscosity B-coefficient reflects the contributions from all the three concentric layers of solvation as described in the Frank and Wen's model[12,13] results in a lower value of the absolute magnitude of the B-coefficient than the NMR B'-coefficient (first layer only) for the alkali metal ions at the lower temperature range. At higher temperature, the highly organized first layer becomes much more susceptible to temperature than the other layers, so that the two coefficients for these ions gradually approach each other under the condition. Since the temperature has no significant effect on the disordered first layer for structure breaking ions, and also the B-coefficient includes contribution from the bulk water which has marked temperature effect, the difference therefore gradually increases with temperature because of diminishing contribution from the bulk layer. It does also indicate that the structure disruption brought about by the larger ions in their cospheres is far more effective than that caused even by the vigorous thermal agitation under the condition.

Energy of Activation for Viscous Flow. Considering the viscous flow as a rate process, Eyring et al.[14] deduced an equation for the energy of activation for viscous flow (ΔE) by applying the absolute reaction rate theory. Following this one can obtain Eq. 1 in the case of solution:

$$\ln\frac{\eta}{\eta_o}=\ln\frac{k}{k_o}+\frac{\Delta E-\Delta E_o}{RT}, \tag{1}$$

where η, η_o, k, k_o, and ΔE, ΔE_o are respectively the viscosities, constants, and activation energies for solution and solvent. The Jones–Dole equation[15] for the relative viscosity:

$$\frac{\eta}{\eta_o}=1+A\sqrt{c}+Bc. \tag{2}$$

Neglecting the small contribution from the ion–ion interaction term ($A\sqrt{c}$), one gets Eq. 3 at c=1 molal[16] by comparing it with Eq. 1.

$$\ln(1+B)=\ln\left(\frac{k}{k_o}\right)+\frac{\Delta E-\Delta E_o}{RT} \tag{3}$$

Thus, a plot of $\ln(1+B)$ versus $1/T$ should be a straight line, the slope of which gives the energy of activation for viscous flow. The constant in the equation, though not strictly constant, is actually a function of molar volume and entropy parameters.[14]

Figure 2 illustrates the variation of $\ln(1+B_\pm)$ versus $1/T$ for the different structure making and breaking ions in aqueous solution over the temperature range 5—95 °C. The interesting feature of the plots is marked by three distinct breaks in all the curves, resulting in three different values of $\Delta E_\pm$ for each ion over the stated

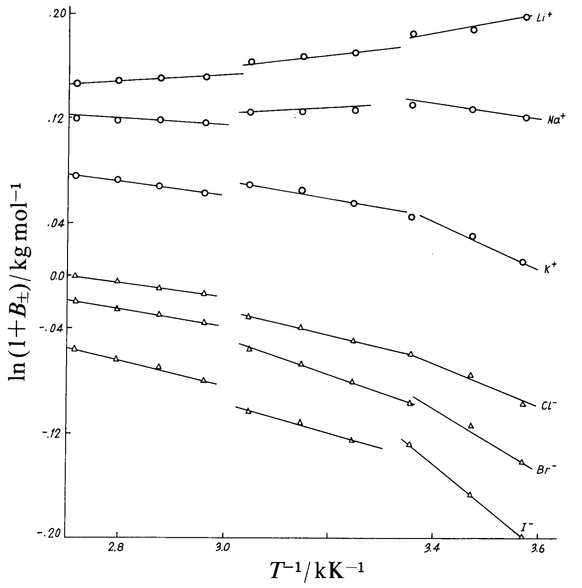

Fig. 2. Variation of $\ln(1+B_{\pm})$ with $1/T$ for alkali metal and halide ions in aqueous solutions.

range of temperature.

Table 2 contains the three numerical values of energy of activation for viscous flow for each ion obtained from the slopes of the $\ln(1+B_{\pm})$ versus $1/T$ by means of computerised least square method. The magnitudes of $\Delta E_{\pm}$ indicate that between 0—25 °C, either the structure makers or the structure breakers perturb the water structure to the maximum as expected. This effect then sharply decreases in the next range of temperature, i.e., between 25—65 °C and still further in the highest temperature range. At the highest temperature range, where the breakdown of water structure is thought to be almost complete as due to vigorous thermal motion, the negative $\Delta E_{\pm}-\Delta E_0$ values for the structure breaking ions indicate that water still retains some sort of structure even at this stage as discussed earlier. In the case of the NMR B'-coefficient, similar plots of $\ln(1+B_{\pm}')$ versus $1/T$ with only four points between 0—80 °C show similar breaks in the curve.

Partial Molal Volume of Ions ($\overline{V}_i^\circ$). Both the viscosity B_i and the NMR B_i'-coefficient are also quantitatively related to the ionic partial molal volumes at the extended temperatures, as we observed in our previous works and are shown in Table 3. The $\overline{V}_i^\circ$ values used here were obtained from those reported by Takenaka et al.[17] The noticeable feature is that the slopes of such curves as well as the intercepts increase with temperature in aqueous solutions. Similar changes in the slopes and intercepts are observed in non-aqueous systems if one passes from water to formamide and then to methanol (Table 3). The similarity is interesting and is perhaps due to decreasing H-bonding in the two cases.

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Table 2. $(\Delta E-\Delta E_0)$ Values in kJ mol^{-1} for the Simple Inorganic Ions in Aqueous Solutions

	5—25 °C	35—55 °C	65—95 °C
Li^+	0.460	0.355	0.163
Na^+	−0.343	0.059	−0.113
K^+	−1.142	−0.615	−0.460
Cl^-	−1.272	−0.678	−0.498
Br^-	−1.477	−0.992	−0.594
I^-	−2.489	−0.937	−0.795

Table 3. Values of the Parameters a and b at Various Temperatures and Solvents in Equation $B_i=a\overline{V}_i^\circ+b$ Calculated by Computerised Least Square Method

	a	b
	25 °C	
($Na^+,K^+,Rb^+,Cs^+,$ F^-,Cl^-,Br^-,I^-)	$-0.0052^{a)}\pm0.002$	0.075 ± 0.015
	$-0.0045^{b)}\pm0.0003$	0.255 ± 0.005
	$-0.0042^{c)}\pm0.001$	0.388 ± 0.009
	15 °C	
Na^+,K^+,Cl^-,Br^-,I^-	$-0.0058^{a)}\pm0.004$	0.071 ± 0.018
	35 °C	
	$-0.0053^{a)}\pm0.002$	0.089 ± 0.014
	45 °C	
	$-0.0051^{a)}\pm0.001$	0.095 ± 0.015

a) Water. b) Formamide. c) Methanol.

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