Solvent Isotope Effect on the Viscosity Coefficient B for Monovalent Ions in Water at 25 and 40 °C

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Dedicated to Dr. Karl Heinzinger on the occasion of his 60th birthday

For heavy water solutions of LiCl, NaCl, KCl and CsCl at 25 and 40 °C and KI at 25 °C the values of $B(M^+)$ and $B(X^-)$ in the equation $\eta/\eta^0 = 1 + A\sqrt{c} + [B(M^+) + B(X^-)]\,c$ were determined under the conventional assumption $B(K^+) = B(Cl^-)$. Here η^0 is the viscosity of the solvent and c the molarity. The solvent isotope effect on the B values was found to be small. The B values for the medium-sized ions K^+, Cs^+, Br^-, and I^- were systematically more negative in heavy water than in light water. This is consistent with the idea that negative B values indicate the ability of the ion to break the structure of the water, the structure of heavy water being more developed than that of light water. For the tetraalkylammonium ions, Me_4N^+, Pr_4N^+, and Bu_4N^+, on the other hand, the solvent isotope effect was small and random irrespective of the ion size. The temperature coefficients of B for the monatomic ions in heavy water were the same as for those in light water.

Introduction

For the viscosity of aqueous electrolyte solutions Jones and Dole [1] introduced the empirical equation

$$\eta/\eta^0 = 1 + A\sqrt{c} + B\,c, \quad (1)$$

where η and η^0 are the viscosity of the solution and the pure solvent, respectively, and c is the molarity of the electrolyte (mol/dm^3). The coefficient A, associated with the ion-ion interaction, is always positive. Falkenhagen and co-workers [2–4] investigated it in terms of the relaxation of the ionic atmosphere. The coefficient B is associated with ion-solvent interactions and either positive or negative, depending on the type of electrolyte. In water B is negative for medium-sized ions like Cs^+ or I^- and positive for small ions like Li^+ and large hydrophobic ions like tetraalkylammonium ions.

Recently we have put forward a theory [5, 6] for B, starting from the electrohydrodynamic equation of motion developed by Hubbard and Onsager [7, 8] originally for ion migration as an extension of the Navier-Stokes equation for uncharged systems, and tested our dielectric friction theory based on the continuum model against experiment [5, 6, 9]. However, the agreement of theory and experiment is not good at present, in contrast to the case of ionic conductance [10, 11], although our dielectric friction theory can explain [6, 9] qualitatively the solvent polarity dependence of B in contrast to the Einstein theory [12], where only the exclusion volume of a spherical solute is taken into account with the charge effect completely neglected. Thus more theoretical and experimental work is required.

In the beginning of this century, water was considered to be polymerized to some extent to account for its anomalous properties and Applebey [13] interpreted the decrease of the viscosity on addition of electrolyte to water as indicating a depolymerization of the solvent by weakly hydrated ions. Essentially this interpretation conforms with the present more detailed knowledge of the water structure from X-ray and neutron diffraction studies and computer simulations [14]. B has been widely used as a measure of the breaking (loosening) or making (tightening) effect of ions on the structure of water in their vicinity (called co-sphere in the Gurney model [15], and A and B regions in the Frank-Wen model [16]) under the great influence of the Bernal-Fowler model [17] of the water structure, which induced the development of the structursim in solution chemistry. However, the effect of the structure on B has not been thoroughly understood even in a phenomenological sense.

Hoping that studies of the solvent effect on B leads to a better understanding of B, we have measured the viscosities of electrolyte – acetonitrile solutions [18]. This solvent is one of the simplest polar aprotic solvents that have no hydrogen-bonded structure. In the present paper we examine the solvent isotope effect on the viscosity of aqueous electrolytes; there exist stud-

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ies on the solvent isotope effect on the translational [19] and rotational [20] mobilities of ions in water. Heavy water (D_2O) is chosen for such studies because it is more structured than light water, has almost the same dielectric constant as light water and supposedly the same long-range electrostatic effect on B. Attention has been paid to the sign of B and its temperature coefficient [21]. We examine here whether B for medium-sized ions becomes more negative in heavy water than in light water, whether for small ions and bulky hydrophobic ions it becomes more positive and whether the temperature coefficient of a negative B becomes more positive in heavy water.

Experimental

Heavy water (CEA, 99.8%) was once distilled under nitrogen atmosphere. The density at 25 °C (1.1042 ±0.0008 g cm^{-3}) was in good agreement with the literature value (1.1044 g cm^{-3}). The physical properties of the light and heavy water [18] used in the present work are listed in Table 1.

Commercially available salts of high purity were used without further purification. LiCl (Nakaai Tesque, atomic absorption analysis reagent), CsCl (Nakaai Tesque, equilibrium density graduation centrifugal analysis reagent), NaCl (Nagamatsu, 99.99%), and KCl and KI (Merck, suprapur) were dried for several days at 150 °C. All the solutions were prepared by vacuum corrected weight; the molarity concentration c ($M = mol\ dm^{-3}$) was then calculated from the independently measured density. The densities (ϱ) of the solutions were measured to 0.0001 g cm^{-3} with a vibration densitometer (Kyoto Electronics, DA-200).

The kinematic viscosities of the dilute solutions were measured with an automatic viscosimeter, the glass part of which is of the Ubbelohde type (Shibayama Scientific Instrument, SS-290S); the viscosimeter is equipped with an optical detection system. The flow time of the viscosimeter for light water was about 570 s at 25 °C, and its uncertainty was 0.03 s.

The kinematic viscosity ν and the dynamic viscosity η are given by the equations

$$\nu = C\,t - K/t, \quad \eta = \nu\,\varrho, \tag{2), (3}$$

where t is the flow time and C and K are the cell constants. The cell constants were assumed to be independent of temperature and calibrated using light water at 25, 30, 35, and 40 °C. Typical values for C and K are $1.569 \times 10^{-5}\ cm^2\ s^{-2}$ and $7.259 \times 10^{-3}\ cm^2$, respectively. The temperature of the water bath was controlled within 0.01 °C. The viscosity of each solution was determined in this way within an error of 0.1%.

Table 1. Physical properties of light and heavy water.

Properties[a]	H_2O		D_2O	
	25 °C	40 °C	25 °C	40 °C
ϱ^0 (g cm^{-3})	0.9970	0.9922	1.1044	1.1001
η^0 (cP)	0.8903	0.653	1.097	0.785
ε_0	78.3	73.2	78.1	72.8
ε_∞	4.2	4.2	3.9	3.5
τ_D (ps)	8.2	5.8	10.3	7.3
R_{HO} (Å)	1.50	1.51	1.51	1.54

[a] ϱ^0 is the density, η^0 the viscosity, ε_0 the static dielectric constant, ε_∞ the high-frequency dielectric constant, τ_D the dielectric relaxation time, and R_{HO} the Hubbard-Onsager radius for monovalent ions. R_{HO} is a solvent parameter introduced in the dielectric friction theory and defined by the equation

$$R_{HO} = [e^2(\varepsilon_0 - \varepsilon_\infty)\,\tau_D/16\,\pi\,\eta^0\,\varepsilon_0^2]^{1/4},$$

where e is the ionic charge.

Results and Discussion

Table 2 shows the densities and relative viscosities of some electrolyte heavy water-solutions at 25 and 40 °C.

We obtained B from the viscosity data using (1) and A calculated by the following equation derived by Falkenhagen and Vernon [4]:

$$A = \frac{0.2577\,(\lambda_+^0 + \lambda_-^0)}{\eta^0\,(\varepsilon_0\,T)^{1/2}\,\lambda_+^0\,\lambda_-^0}\left[1 - 0.6863\left(\frac{\lambda_+^0 - \lambda_-^0}{\lambda_+^0 + \lambda_-^0}\right)^2\right], \tag{4}$$

where T is the absolute temperature, ε_0 the static dielectric constant, and λ_+^0 and λ_-^0 are the limiting molar conductances of the ions. The coefficients A at 40 °C were obtained from those 10 and 25 °C, using the limiting molar conductances by Broadwater and Kay [22], and then extrapolating to 40 °C. The coefficients A and B thus determined are listed in Table 3. Our value for KI at 25 °C is in agreement with that of Bare and Skinner [23] within the experimental uncertainty.

As shown in Table 3, A increases with decreasing cation size in the homologous series of alkali chlorides. This is due to the factor $(\lambda_+^0 + \lambda_-^0)/\lambda_+^0\,\lambda_-^0$ in (4) with λ_-^0 fixed for the chloride ion.

B of completely dissociated electrolytes is controlled exclusively by interactions between the ions and the solvent. We split B into the ionic components,

$$B(MX) = B(M^+) + B(X^-), \tag{5}$$

Table 2. Densities and relative viscosities of electrolyte solutions in heavy water at 25 and 40 °C.

$c \times 10^2$ (mol dm^{-3})	ϱ (g cm^{-3})	η/η^0	$c \times 10^2$ (mol dm^{-3})	ϱ (g cm^{-3})	η/η^0
LiCl 25 °C			LiCl 40 °C		
0	1.1042	–	0	1.0993	–
0.3909	1.1043	1.001	0.3892	1.0995	1.001
1.577	1.1047	1.003	1.570	1.0999	1.003
2.953	1.1051	1.005	2.940	1.0002	1.005
4.906	1.1056	1.008	4.885	1.1008	1.008
9.787	1.1067	1.015	9.743	1.1018	1.015
NaCl 25 °C			NaCl 40 °C		
0	1.1043	–	0	1.0998	–
0.4051	1.1045	1.001	1.613	1.1004	1.002
1.619	1.1049	1.002	3.031	1.1007	1.003
3.045	1.1056	1.003	5.042	1.1018	1.005
5.062	1.1063	1.004	10.04	1.1037	1.010
10.08	1.1083	1.008			
KCl 25 °C			KCl 40 °C		
0	1.1034	–	0	1.0990	–
0.4065	1.1035	1.000	0.4049	1.0992	1.000
1.639	1.1041	1.000	1.632	1.0998	1.001
2.994	1.1044	0.999	2.982	1.1000	1.000
5.126	1.1059	0.999	5.106	1.1015	1.001
9.963	1.1084	0.999	9.922	1.1039	1.003
CsCl 25 °C			CsCl 40 °C		
0	1.1041	–	0	1.0998	–
1.608	1.1062	0.999	1.602	1.1017	1.000
3.016	1.1080	0.998	3.004	1.1035	0.999
5.018	1.1104	0.997	4.998	1.1059	0.999
10.05	1.1168	0.994	10.01	1.1121	0.998
KI 25 °C					
0	1.1049	–			
0.6279	1.1057	1.000			
1.639	1.1067	0.998			
3.116	1.1085	0.997			
5.255	1.1111	0.995			
9.626	1.1162	0.991			

Table 3. The coefficients $A/\mathrm{M}^{-1/2}$ and B/M^{-1} for alkali halides in heavy water at 25 and 40 °C.

Elec.	25 °C			40 °C		
	$A \times 10^3$	B	$\sigma_B \times 10^2$ [a]	$A \times 10^3$	B	$\sigma_B \times 10^2$
LiCl	7.29	0.13	0.4	8.00	0.13	0.8
NaCl	5.99	0.06	0.7	6.22	0.08	0.7
KCl	4.97	−0.03	1.7	5.30	0.00	1.1
CsCl	4.85	−0.09	1.4	5.21	−0.05	1.4
KI	4.93	−0.12	1.2	–	–	–

[2] σ_B is the root mean square deviation of B.

Table 4. B/M^{-1} for monovalent ions in heavy and light water at 25 and 40 °C.

Ions	25 °C		40 °C	Ions	25 °C	
	H_2O	D_2O	D_2O		H_2O	D_2O
Li^+	0.150	0.15	0.13	Me_4N^+	0.12	0.13
Na^+	0.086	0.08	0.08	Et_4N^+	0.38	–
K^+	−0.007	−0.02	0.00	Pr_4N^+	0.86	0.84
Cs^+	−0.045	−0.07	−0.05	Bu_4N^+	1.28	1.31
Cl^-	−0.007	−0.02	0.00			
Br^-	−0.032	−0.05	–			
I^-	−0.069	−0.10	–			

and use the conventional assumption [15]

$$B(\mathrm{K}^+) = B(\mathrm{Cl}^-). \tag{6}$$

Using our B values and those in the literature we have determined $B(\mathrm{M}^+)$ and $B(\mathrm{X}^-)$ as listed in Table 4 and partly illustrated in Figure 1; the B values for tetraalkylammonium bromides and iodides were taken from Kay et al. [24] and divided into the ionic values using our $B(\mathrm{I}^-)$ value. $B(\mathrm{M}^+)$ and $B(\mathrm{X}^-)$ values for light water at 25 °C are also listed in Table 4 as taken from Kaminsky [21] for the alkali metal and halide ions, and from Kay et al. [24] for the tetraalkylammonium ions.

An inspection of Table 4 tells us the following: 1) the solvent isotope effect on the ionic B values is small, 2) the absolute values of the negative B's are larger in heavy water than in light water, 3) these differences are largest for Cs^+ and I^- in the series of the alkali metal and halide ions, respectively, and 4) the solvent isotope effect on the ionic B values for the tetraalkylammonium ions is unexpectedly small and random.

First we attempt to explain point 1). The viscosity of pure D_2O is 23% larger than that of pure H_2O at 25 °C, as shown in Table 1. The isotope effects of the B values, however, are much smaller because they depend on the much smaller isotope effect of η/η^0. The electrical conductance, however, depends directly on η [10, 11] and shows a large solvent isotope effect for light and heavy water [19, 22]. In addition, since the two solvents have almost the same dielectric constant and HO radius, no difference in the long-range electrostatic effect on the ionic B coefficient is expected according to the dielectic friction theory, which neglects the solvent structure.

The points 2) and 3) mentioned above concern the structure breaking ability of ions with negative B. This ability increases from K^+ to Cs^+ and from Cl^- to I^-, and since heavy water is more structured than light water [19, 20], the breaking effect is more pronounced in heavy water. Also in the studies [25, 26] on the viscosity of concentrated solutions, whose concentrations are too high to give B coefficients, the relative viscosities of RbCl and CsCl solutions are reported to

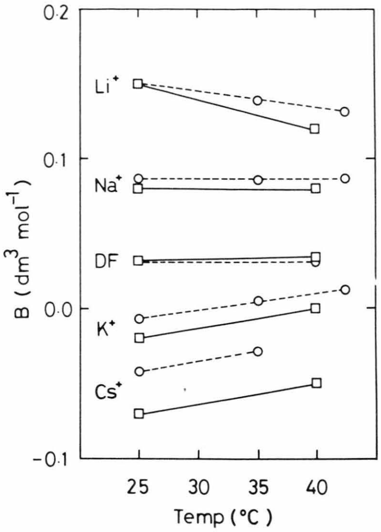

Fig. 1. Temperature dependence of *B* for the alkali metal ions in heavy (□) and light (○) water. DF indicates the predictions of the dielectric friction theory for the lip at the boundary.

be smaller than unity and to be smaller in heavy water than in light water. This is consistent with the *B* coefficients for CsCl given in Table 3. A negative *B* coefficient is not predicted by any continuum model and not observed for acetonitrile, which is polar but not hydrogen-bonded [18]. Thus we can conclude that negative *B*'s are characteristic of water.

Contrary to the structure-breaking ions, we do not see any systematic solvent isotope effect on the *B* coefficients for structure-making ions, such as Li^+ or the larger tetraalkylammonium ions. At present we do not know why a corresponding solvent isotope effect (a more positive *B* in heavy water) is not observed for the electrostrictive (Li^+) and hydrophobic (R_4N^+) ions in water. This suggests doubts about the applicability of the ionic *B* coefficient as a general measure of the effect of the ion on the structure of water.

In Fig. 1 we show the temperature dependence of *B* for the alkali metal ions in heavy and light water. The experimental values for light water are taken from Kaminsky [21] except for the Cs^+ ion at 35 °C [27]. The predictions of the dielectric friction theory are also depicted. The theory predicts almost the same *B* values for all the ions indicated here, the *B* values being also almost independent of temperature and solvent because of the negligible dependence of the HO radius on temperature and the isotopic compositions of the solvent. Thus the theory is not successful in explaining the experimental results.

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