Thermochimica Acta, 84 (1985) 157–174
Elsevier Science Publishers B.V., Amsterdam – Printed in The Netherlands

THERMODYNAMICS AND FREE VOLUME OF VARIOUS ALKALI HALIDES IN AQUEOUS D-MANNITOL SOLUTION

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(Received 22 August 1984)

ABSTRACT

Ultrasonic, density and viscometric investigations have been conducted on several alkali halides in 0.4 M aqueous D-mannitol solution at four different temperatures: 25, 30, 35 and 40°C. Free volumes, internal pressures, ionic viscosity coefficients, and hydration numbers have been calculated. Activation parameters of viscous flow were also calculated and all these properties were discussed in terms of structure-making or -breaking properties of electrolytes in aqueous D-mannitol solutions. Results show that in addition to viscometric properties, the temperature dependency of free volumes and internal pressures is found to be a powerful tool in elucidating the structure-making or -breaking properties of the electrolyte solutions.

INTRODUCTION

This paper continues our investigation of the physico-chemical properties of aqueous ternary systems of alkali metal halides [1–3]. The effects of sugars and polyols on the solvent properties of water and the interactions of such solutes with electrolytes and non-electrolytes is of biological and thermodynamic importance. In recent years, active interest has been shown in solute–solvent and solute–solute interactions, which were determined by the chemical structure of solute and solvent molecules. Ultrasonic studies are mostly limited in obtaining hydration numbers [4–6]. However, recently, it is shown that ultrasonic velocity measurements, along with viscosity and density values, can be used to calculate important factors such as free volumes (V_f) and internal pressures (Π) [7]. Free volume is a fundamental property to be considered when explaining the variation in physico-chemical properties of liquid mixtures and aqueous electrolyte solutions [8,9].

In the present communication we report the results of ultrasonic velocity and density measurements of LiCl, CSCl, RbCl, sodium and potassium

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halides in aqueous D-mannitol solutions. Viscosity measurements were carried out on aqueous D-mannitol solutions of lithium, rubidium and cesium chlorides at four different temperatures. Using our experimental data along with the viscosity measurements of Vishnu and Misra [10], the free volume and internal pressure of various alkali metal halides in aqueous D-mannitol have been calculated at four different temperatures. Viscosity data were analyzed in terms of different viscosity equations to obtain information about ionic interactions prevalent at such high concentrations of electrolytes. Various thermodynamic parameters of viscous flow were also determined.

EXPERIMENTAL

Analytical reagent grade samples of alkali metal halides and D-mannitol, obtained from B.D.H. or Merck, were employed for the present work, and were used without further purification. All solutions were prepared by molar basis in nanopure water (sp. conductivity $\approx 8 \times 10^{-7}$ mhos). A 0.4 M D-mannitol solution was used as a stock solution. Viscosity and density, and ultrasonic velocity measurements were obtained by the methods and with the apparatus described previously [1,2].

RESULTS AND DISCUSSION

It has been shown that the viscosity B coefficient is a valuable tool in understanding the structure-making (SM) or structure-breaking (SB) properties of solute molecules [11,12]. Viscosity B coefficients were obtained by three different procedures. The Jones–Dole equation [13], modified for higher concentration

$$\eta_{\mathrm{rel}} = 1 + BC \tag{1}$$

was used to calculate B values from the relative viscosity data for all electrolyte solutions. B values were obtained employing the least-squares method. Viscosity data in the entire concentration range were fitted into the Goldsack–Franchetto equation [14]

$$\ln[\eta_{\mathrm{rel}}(1 + XV)] = XE \tag{2}$$

where E and V are parameters characteristic of the electrolytes and X is the mole fraction of the electrolyte in solution. E and V were obtained by solving eqn. (2) by a non-linear least-squares method using an HP 3000 computer. A typical fit of the equation for the chlorides of an alkali metal is presented in Fig. 1. The approximate values for B coefficients were obtained using the relation

$$B = (E - V)/55.51 \tag{3}$$

Vishnu and Misra [10] have calculated B coefficients using Breslau and Miller's equation [15] for sodium and potassium halides

$$V_e = \frac{-2.5C + \left[(2.5C)^2 - 40.20C^2(1-\eta_{\text{rel}})\right]^{1/2}}{20.10C^2} \tag{4}$$

and the average $\overline{V}_e$ values thus obtained were fitted into the following equation

$$B = 2.90\overline{V}e - 0.018 \tag{5}$$

for 1 : 1 electrolytes. B coefficients for lithium, rubidium and cesium chloride in 0.4 M D-mannitol solution were also calculated using the Breslau–Miller equation. All these values are presented in Table 1. B coefficients obtained for Na and K halides by Vishnu and Misra are also included in the table for comparison. The values of B coefficients obtained by the three different procedures do not agree very well, although they are of the same order of magnitude. Since different approximations were involved in the derivation of these equations, the observed differences in the values of B coefficients is not

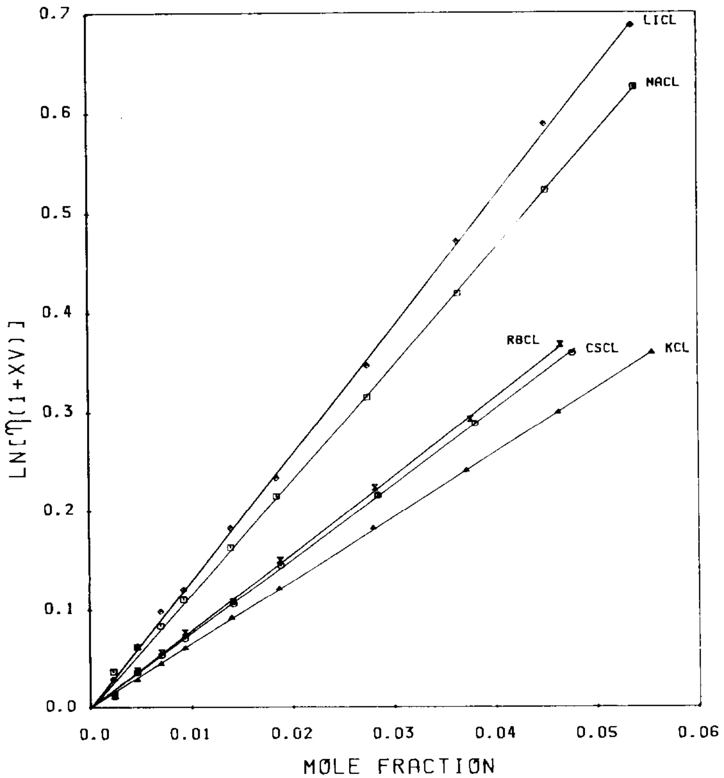

Fig. 1. Test for eqn. (2).

TABLE 1

B-values of alkali metal halides in 0.4 M aqueous D-mannitol solution

Salt	Jones–Dole's equation: T(K) =				Breslau–Miller's equation: T(K) =				Goldsack–Franchetto equation: T(K) =			
	298	303	308	313	298	303	308	313	298	303	308	313
LiCl	0.1644	0.1625	0.1583	0.1533	0.1415	0.1415	0.1467	0.1235	0.1456	0.1431	0.1412	0.1100
NaCl	0.0889	0.1018	0.1040	0.1078	0.1008	0.0769	0.0601	0.0451	0.0901	0.0440	0.0691	0.0586
NaBr	0.0695	0.0686	0.0706	0.0689	0.0703	0.0464	0.0379	0.0165	0.0604	0.0440	0.0397	0.0214
NaI	0.0353	0.0363	0.0449	0.0369	0.0311	0.0082	−0.0069	−0.0192	0.0214	0.0083	0.0012	−0.0162
KCl	0.0080	0.0094	0.0135	0.0240	−0.0268	−0.0324	−0.0380	−0.0464	−0.0113	−0.0143	−0.0209	−0.0216
KBr	−0.0274	−0.0176	−0.0129	−0.0128	−0.0537	−0.0647	−0.0695	−0.0744	−0.0436	−0.0505	−0.0513	−0.0560
KI	−0.0640	−0.0391	−0.0376	−0.0256	−0.0852	−0.0955	−0.0984	−0.0107	−0.0439	−0.0800	−0.0807	−0.0853
RbCl	−0.0216	−0.0090	0.0048	0.0184	−0.0517	−0.0515	−0.0236	−0.0260	−0.0696	−0.0622	−0.0347	−0.0475
CsCl	−0.0404	−0.0363	−0.0237	0.0141	−0.0667	−0.0706	−0.0237	−0.0189	−0.0857	−0.0861	−0.0328	−0.0392

TABLE 2

Values of ionic parameters [a]

Ion	V^0	$T = 298$ K			$T = 303$ K			$T = 308$ K			$T = 313$ K		
		$B_{\pm}$	$V_{\pm}$	N_B	$B_{\pm}$	$V_{\pm}$	N_B	$B_{\pm}$	$V_{\pm}$	N_B	$B_{\pm}$	$V_{\pm}$	N_B
Li^+	0.54	0.1604	64.16	9.61	0.1578	63.12	9.45	0.1515	60.62	9.07	0.1413	56.52	8.46
Na^+	2.16	0.0849	33.96	4.80	0.0971	38.84	5.54	0.0972	38.90	5.55	0.0958	38.32	5.46
K^+	5.93	0.0040	1.60	−0.654	0.0047	1.88	−0.61	0.0067	2.70	−0.49	0.0120	4.80	−0.17
Rb^+	8.17	−0.0256	−10.24	−2.78	−0.0146	−5.84	−2.12	−0.0019	−0.76	−1.35	0.0064	2.56	−0.85
Cs^+	12.16	−0.0444	−17.76	−4.52	−0.0410	−16.40	−4.31	−0.0304	−12.56	−3.73	0.0021	0.84	−1.71
Cl^-	14.94	0.0040	1.60	−2.02	0.0047	1.88	−1.97	0.0067	2.70	−1.85	0.0120	4.80	−1.53
Br^-	18.68	−0.0314	−12.56	−4.72	−0.0223	−8.92	−4.17	−0.0196	−7.86	−4.01	−0.0248	−9.92	−4.32
I^-	25.39	−0.0680	−27.20	−7.94	−0.0438	−17.52	−6.48	−0.0443	−17.74	−6.52	−0.0376	−15.04	−6.11

[a] Values of $B_{\pm}$ in l mol^{-1} and $V_{\pm}$ in cm^3 mol^{-1}.

unexpected. Also, for eqns. (2) and (4), the entire concentration range was utilized in the calculation of B coefficients. This could explain the difference in the trend of dependency of B values on temperature.

It has been shown [16] that the B coefficient may be considered as being formed by two contributions: one positive and one negative. The former comes from the tendency of the ions to attract the solvent molecules around it centro-symmetrically, while the latter stems from the fact that the structure of the solvent itself goes against this tendency, so that these two opposing influences can cause breakdown in the solvent structure beyond the first solvation shell.

Generally, the positive contribution prevails over the negative one, producing an increase in the viscosity of the solution with respect to that of the solvent. Only for solvents with extended three-dimensional structure, due to hydrogen bonds [17,18], does the negative contribution dominate for ions with low charge density, with negative B-values and a relative decrease in viscosity of the solution with respect to that of the solvent can be found. Following the above lines, one can discusss the variation of B coefficients in terms of viscosity effects. In a given series of alkali metal halides, e.g., chlorides, the charge density decreases in the order: $Li^+ > Na^+ > K^+ > Rb^+ > CS^+$ and one can expect that B-values vary in the order $LiCl > NaCl > KCl > RbCl > CSCl$.

In order to distinguish the effect each single ion has in an aqueous 0.4 M D-mannitol solution, viscosity B-coefficient values were split into ionic contributions on the hypothesis that $B(K^+) = B(Cl^-) = B(KCl)/2$ as already reported [17]. $B_\pm$ values calculated according to the procedures of Kaminsky [17] are presented in Table 2. According to Gurney [19] $dB_\pm/dT$ is either negative or near zero for structure-making ions and positive for structure-breaking ions. Examination of Table 2 reveals that Li^+ and Na^+ are definitely structure-making ions and all the other ions are structure-breaking. Positive $dB_\pm/dT$ values for anions could be due to the interaction of the ion with water molecules through hydrogen bonding. Slightly positive values of $dB_\pm/dT$ for Na^+ ions initially may be due to carbohydrate–salt interactions involving the hydroxyl groups of D-mannitol and the ions [20].

Using ionic $B_\pm$ values and assuming that the ions behave like a rigid sphere, one can calculate the ionic molar volumes of ions ($\bar{V}_\pm$) according to Einstein's equation [21]

$$B_\pm = 2.5\bar{V}_\pm \tag{6}$$

where 2.5 is the shape factor for a sphere. Hydration numbers (N_B) of ions can be obtained from the equation

$$\bar{V}_\pm = \bar{V}^0_{ion} + N_B\bar{V}^0_s \tag{7}$$

where $\bar{V}^0_{ion}$ is the free ionic volume calculated from the equation $\bar{V}^0_{ion} = 2.52r^3$ (r = ionic radius) and $\bar{V}^0_s$ is the molar volume of water equal to 6.62 cm^3

mol^{-1}. The values of N_B are presented in Table 2. According to Millero [22] and Curthoys and Mathieson [23] positive hydration numbers and negative dN_B/dT and $dV_{\pm}/dT$ are characteristics of structure-making ions, whereas structure-breaking ions normally have negative hydration numbers and positive dN_B/dT and $dV_{\pm}/dT$. One can conclude from the examination of Table 2, that Li^+ and Na^+ ions are structure-makers and K^+, Rb^+, Cs^+, Cl^-, Br^- and I^- ions are structure-breakers in aqueous 0.4 M D-mannitol solutions.

According to Krestov [24], depending on the sign of the charge, a linear relationship exists between hydration number and entropy change in aqueous electrolyte solutions with ionic radius. When N_B is plotted against ionic radii or $B_{\pm}$ we observed different linear relationships for positive and negative ions (Figs. 2 and 3).

This supports the idea [25,26] that Li^+ and Na^+ are electrostrictive structure-making ions with positive ionic volumes and hydration numbers, whereas K^+, Rb^+, Cs^+, Cl^-, Br^- and I^- are structure-breaking ions with negative ionic volumes and hydration numbers. Probably the structure-breaking ions in solution disrupt the water structure by pushing water

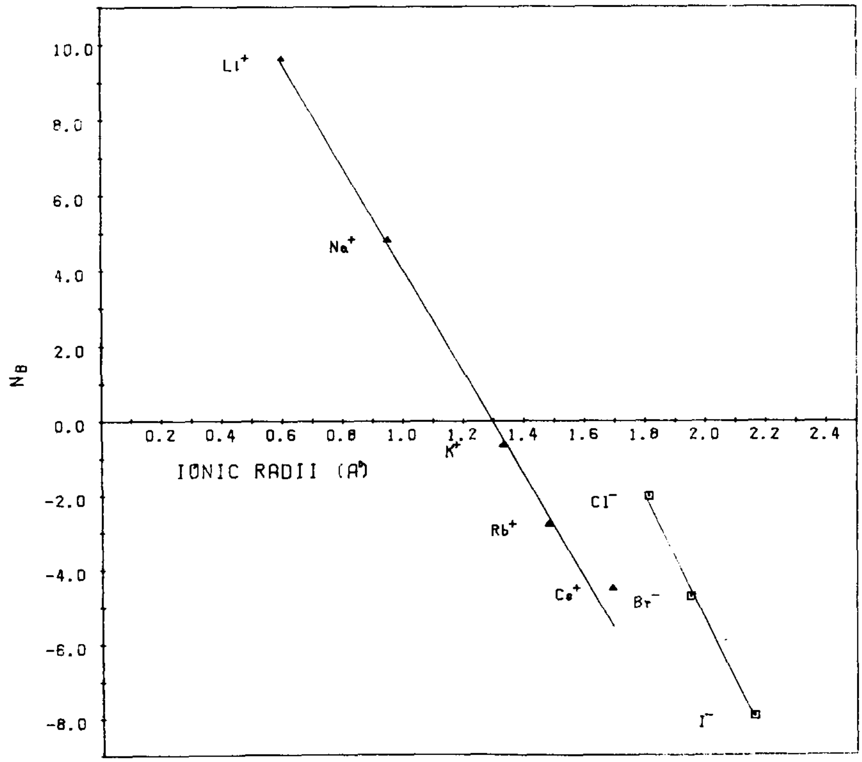

Fig. 2. Plot of hydration number versus Pauling's ionic radii for alkali and halide ions in aqueous D-mannitol solution at 25°C.

molecules apart in both primary and secondary hydration spheres. From the magnitude of hydration numbers, one can conclude that the structure-breaking ability of various ions in aqueous D-mannitol solution at 298 K is in the order: $I^- > Br^- > Cs^+ > Rb^+ > Cl^- > K^+ > Na^+ > Li^+$.

From the variation of viscosity with temperature, values of thermodynamic activation parameters of viscous flow were calculated [27]. The values are presented in Tables 3–5. From the dependency of thermodynamic parameters of viscous flow (ΔH^*, ΔS^* and ΔG^*) on concentration, one can divide the results into three types. In structure-making electrolytes, like LiCl and NaCl, the ΔH^* of viscous flow remains constant with an increase in concentration of the electrolyte within the experimental error, ΔS^* decreases and ΔG^* increases slightly. An increase in electrolyte concentration in these cases leads to an increased order in the activated state which thus becomes less favourable, compared to the unactivated state in aqueous D-mannitol solutions.

For structure-breakers, like CSCl, RbCl and KI, the ΔH^* and ΔS^* values decrease with an increase in concentration of the electrolytes, and ΔG^* remains constant. One can conclude that for structure-breakers, the activated

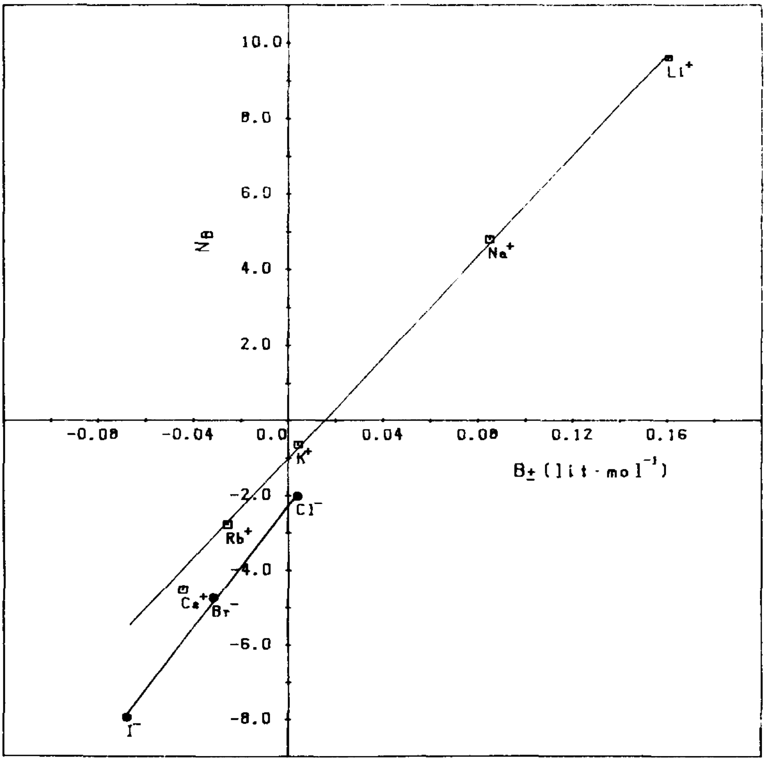

Fig. 3. Plot of hydration number versus ionic *B* coefficients for various alkali and halide ions in aqueous D-mannitol solution at 25°C.

TABLE 3

Thermodynamic properties of viscous flow of electrolytes in 0.4 M aqueous D-mannitol solution

Concentration (M)	Sodium chloride			Sodium bromide			Sodium iodide		
	ΔH(kJ)	ΔS(J)	ΔG(kJ)	ΔH(kJ)	ΔS(J)	ΔG(kJ)	ΔH(kJ)	ΔS(J)	ΔG(kJ)
0.125	17.92 ± 0.47	26.47 ± 1.5	10.03 ± 0.66	17.63 ± 0.40	25.57 ± 1.3	10.01 ± 0.56	17.61 ± 0.61	25.56 ± 2.0	10.00 ± 0.85
0.250	17.75 ± 0.34	25.81 ± 1.1	10.06 ± 0.47	17.58 ± 0.27	25.28 ± 0.89	10.04 ± 0.38	17.43 ± 0.32	24.88 ± 1.1	10.02 ± 0.45
0.375	17.42 ± 0.22	24.66 ± 0.70	10.08 ± 0.36	17.57 ± 0.34	25.20 ± 1.1	10.06 ± 0.48	17.64 ± 0.32	25.51 ± 1.0	10.04 ± 0.44
0.500	17.26 ± 0.42	24.04 ± 1.4	10.10 ± 0.59	17.36 ± 0.25	24.45 ± 0.83	10.08 ± 0.36	17.41 ± 0.36	24.70 ± 1.2	10.05 ± 0.50
0.750	17.27 ± 0.31	23.84 ± 1.0	10.16 ± 0.44	17.44 ± 0.28	24.57 ± 0.92	10.12 ± 0.39	17.32 ± 0.28	24.27 ± 0.93	10.09 ± 0.40
1.000	17.25 ± 0.33	23.57 ± 1.1	10.22 ± 0.46	17.27 ± 0.36	23.83 ± 1.2	10.17 ± 0.51	17.19 ± 0.22	23.71 ± 0.72	10.13 ± 0.31
1.500	17.07 ± 0.32	22.56 ± 0.06	10.35 ± 0.45	17.26 ± 0.43	23.40 ± 1.4	10.28 ± 0.60	17.00 ± 0.16	22.74 ± 0.54	10.22 ± 0.23
2.0	17.07 ± 0.32	22.09 ± 1.0	10.48 ± 0.45	17.11 ± 0.35	22.61 ± 1.2	10.38 ± 0.50	16.84 ± 0.22	21.85 ± 0.73	10.33 ± 0.31
2.5	17.08 ± 0.39	21.65 ± 1.3	10.63 ± 0.54	16.96 ± 0.33	21.65 ± 1.1	10.50 ± 0.46	16.79 ± 0.22	21.24 ± 0.73	10.46 ± 0.31
3.0	17.24 ± 0.41	21.70 ± 1.3	10.78 ± 0.57	16.94 ± 0.45	21.16 ± 1.5	10.63 ± 0.63	16.54 ± 0.35	19.95 ± 1.2	10.60 ± 0.49

TABLE 4

Thermodynamic properties of viscous flow of electrolytes in 0.4 M aqueous D-mannitol solution

Concentration (M)	Potassium chloride			Potassium bromide			Potassium iodide		
	ΔH(kJ)	ΔS(J)	ΔG(kJ)	ΔH(kJ)	ΔS(J)	ΔG(kJ)	ΔH(kJ)	ΔS(J)	ΔG(kJ)
0.125	17.13 ± 0.33	24.02 ± 1.1	9.97 ± 0.47	17.18 ± 0.36	24.21 ± 1.2	9.97 ± 0.50	17.34 ± 0.30	24.75 ± 0.97	9.96 ± 0.41
0.250	17.01 ± 0.14	23.62 ± 0.44	9.98 ± 0.19	17.02 ± 0.40	23.69 ± 1.3	9.96 ± 0.56	17.11 ± 0.36	23.99 ± 1.2	9.96 ± 0.50
0.375	16.91 ± 0.21	23.25 ± 0.70	9.98 ± 0.30	16.98 ± 0.35	23.56 ± 1.1	9.96 ± 0.48	16.86 ± 0.32	23.14 ± 1.0	9.97 ± 0.45
0.500	16.82 ± 0.22	22.93 ± 0.71	9.98 ± 0.38	16.92 ± 0.30	23.88 ± 1.1	9.96 ± 0.41	16.61 ± 0.23	22.42 ± 0.77	9.93 ± 0.33
0.750	16.54 ± 0.30	21.99 ± 0.99	9.99 ± 0.42	16.59 ± 0.33	22.27 ± 1.1	9.95 ± 0.46	16.02 ± 0.29	20.50 ± 0.96	9.92 ± 0.41
1.000	16.17 ± 0.36	20.70 ± 1.2	10.00 ± 0.50	16.09 ± 0.33	20.63 ± 1.1	9.94 ± 0.46	16.05 ± 0.31	20.58 ± 1.0	9.91 ± 0.43
1.500	15.77 ± 0.49	19.30 ± 1.6	10.02 ± 0.68	15.45 ± 0.27	18.46 ± 0.88	9.95 ± 0.37	15.61 ± 0.29	18.92 ± 0.95	9.97 ± 0.43
2.000	15.29 ± 0.38	17.59 ± 1.2	10.25 ± 0.53	14.87 ± 0.29	16.39 ± 0.95	9.98 ± 0.40	14.99 ± 0.50	16.76 ± 1.6	9.99 ± 0.70
2.500	14.87 ± 0.34	16.07 ± 1.1	10.08 ± 0.47	14.43 ± 0.26	14.86 ± 0.85	10.00 ± 0.36	14.16 ± 0.54	13.89 ± 1.8	10.02 ± 0.75
3.000	14.41 ± 0.44	14.39 ± 1.4	10.12 ± 0.61	14.07 ± 0.26	13.45 ± 0.85	10.06 ± 0.36	13.66 ± 0.43	12.01 ± 1.4	10.68 ± 0.59

TABLE 5

Thermodynamic properties of viscous flow of electrolytes in 0.4 M aqueous D-mannitol solution

Concentration (M)	Lithium chloride			Rubidium chloride			Cesium chloride		
	ΔH(kJ)	ΔS(J)	ΔG(kJ)	ΔH(kJ)	ΔS(J)	ΔG(kJ)	ΔH(kJ)	ΔS(J)	ΔG(kJ)
0.125	16.70 ± 0.28	22.40 ± 0.91	10.03 ± 0.39	16.26 ± 0.22	22.07 ± 0.72	9.69 ± 0.31	15.85 ± 0.47	20.69 ± 1.6	9.68 ± 0.67
0.250	16.74 ± 0.22	22.33 ± 0.73	10.08 ± 0.31	16.02 ± 0.25	21.22 ± 0.82	9.70 ± 0.35	15.63 ± 0.49	19.95 ± 1.6	9.68 ± 0.68
0.375	16.74 ± 0.23	22.16 ± 0.74	10.14 ± 0.32	15.77 ± 0.16	20.40 ± 0.52	9.69 ± 0.22	15.10 ± 0.54	18.22 ± 1.8	9.67 ± 0.75
0.500	16.46 ± 0.30	21.08 ± 0.97	10.18 ± 0.42	15.60 ± 0.54	19.86 ± 1.8	9.68 ± 0.76	15.17 ± 0.43	18.46 ± 1.4	9.66 ± 0.60
0.750	16.67 ± 0.23	21.46 ± 0.74	10.27 ± 0.32	15.28 ± 0.43	18.85 ± 1.4	9.66 ± 0.60	14.06 ± 0.76	14.85 ± 0.25	9.64 ± 1.1
1.000	16.63 ± 0.22	21.10 ± 0.72	10.34 ± 0.31	15.00 ± 0.42	17.88 ± 1.4	9.67 ± 0.58	13.90 ± 0.76	14.29 ± 0.25	9.64 ± 1.1
1.500	16.90 ± 0.19	21.41 ± 0.61	10.53 ± 0.26	13.99 ± 0.47	14.50 ± 1.6	9.67 ± 0.66	13.87 ± 0.29	14.15 ± 0.94	9.65 ± 0.40
2.000	16.73 ± 0.18	20.10 ± 0.60	10.74 ± 0.25	13.55 ± 0.43	12.98 ± 1.4	9.68 ± 0.60	12.80 ± 0.30	10.50 ± 0.99	9.67 ± 0.42
2.500	16.70 ± 0.18	19.32 ± 0.60	10.94 ± 0.26	12.68 ± 0.45	9.97 ± 1.5	9.71 ± 0.62	12.49 ± 0.27	9.36 ± 0.90	9.70 ± 0.38
3.000	16.43 ± 0.67	17.85 ± 0.22	11.11 ± 0.93	–	–	–	–	–	–

state becomes more orderly and the energy required to break the bonds in the activated state decreases with an increase in concentration.

For the rest of the electrolytes the observed behaviour falls in between the above two cases. In these cases the structure-breaking ability of the anions dominates at higher concentration. ΔH^* and ΔS^* of viscous flow decrease with an increase in electrolyte concentration and the dependency of ΔG^* on concentration varies from Cl^- to I^-. For the structure-breaking electrolytes, ΔG^* is independent of electrolyte concentration and it could be attributed to the fact that the effect of ions in this group is relatively non-specific, a response which is expected from a common disrupting force on bulk water [28].

The limiting values of activation parameters at infinite dilution of the electrolytes were obtained according to the procedures of Feakins et al. [29] and are presented in Table 6. According to these authors, the chemical potential change ($\Delta\mu_2^{0\#}$) is greater than that of pure solvent ($\Delta\mu_1^{0\#}$) for net structure-makers. From the data of Table 6, one can conclude that LiCl, KCl and sodium halides are acting as structure-makers and the remaining electrolytes as structure-breakers at infinite dilution. From the dependency of $\Delta\mu_2^{0\#}$ on temperature, $\Delta S_2^{0\#}$ values and $\Delta H_2^{0\#}$ values were computed. Except for lithium ions the values of $T\Delta S_2^{0\#}$ and $\Delta H_2^{0\#}$ are negative, indicating that the formation of the activated complex is associated with bond making and an increase in order. For the lithium ions the transition is accompanied by bond breaking and a decrease in order. This suggests that the slip-plane is somewhere in the region of centro-symmetric order for lithium ions and in the disordered region for the remaining ions in aqueous D-mannitol solutions. A plot of $\Delta H_2^{0\#}$ against $T\Delta S_2^{0\#}$ indicates a linear relationship between these two parameters (Fig. 4) and the linearity depended on the ability of structure-making or -breaking properties of the ions.

Free volumes at all concentrations and temperatures were calculated using

TABLE 6

Thermodynamic parameters of activation of flow at infinite dilution [a]

Salt	$\Delta\mu_2^{0\#}$	$T\Delta S_2^{0\#}$	$\Delta H_2^{0\#}$	Ions	$T\Delta S_2^{0\#}$	$\Delta H_2^{0\#}$
LiCl	31.52	24.9	56.4	Li^+	54.8	89.1
NaCl	21.78	−32.2	−10.4	Na^+	−2.3	12.3
NaBr	19.56	−41.0	−21.4	K^+	−29.9	−22.7
NaI	17.50	−44.1	−26.6	Rb^+	−74.5	−72.7
KCl	12.55	−57.9	−45.4	Cs^+	−116.6	−116.1
KBr	8.90	−66.7	−57.8	Cl^-	29.9	−22.7
KI	6.36	−94.2	−87.8	Br^-	26.8	−35.1
RbCl	9.07	−104.4	−95.4	I^-	−64.3	−55.1
CsCl	7.71	−146.5	−138.8			

[a] Values in kJ mol^{-1}. $\Delta\mu_1^{0\#} = 9.80$ kJ mol^{-1}.

the following formula [7]

$$V_f = (\overline{M}U/K\eta)^{3/2} \tag{8}$$

where $\overline{M}$ is the average molecular mass, U is the ultrasound velocity, η is the viscosity of the solution and K is a constant equal to 4.28×10^5.

Internal pressures (Π) were calculated from the following equation [7]

$$\Pi = bRT/V_m^{2/3}V_f^{1/3} \tag{9}$$

where b is the packing factor in liquids (equal to 2 for cubic packing), and V_m is the molar volume of the media. Computed values are presented in Tables 7–14. Representative diagrams of free volumes against concentration at four different temperatures are presented in Figs. 5 and 6. Adiabatic compressibilities were also calculated and are included in the tables. Examination of Tables 7–14 indicates that the free volume dependency on concentration of the electrolyte depends on the type of the electrolytes. For net structure-makers like sodium and lithium chlorides, the free volume decreases with an increase in concentration of the electrolyte at all four temperatures. One can conclude that the high charge density of Li^+ and Na^+ dominate the structure-breaking properties of the Cl^- ions in these electrolytes, resulting in the ordering of the solution and a decrease in free

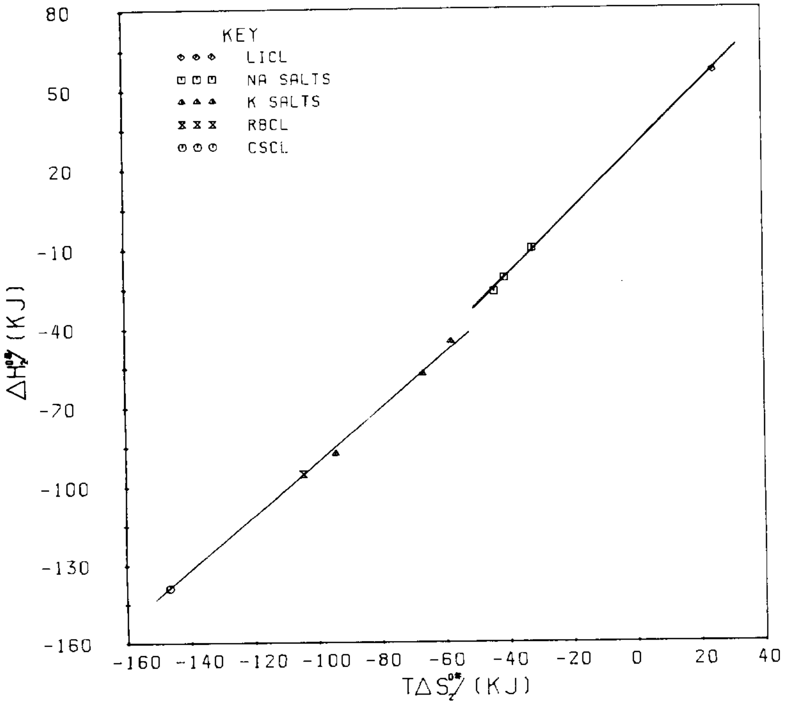

Fig. 4. The relationship between $\Delta H_2^0\#$ and $T\Delta S_2^0\#$ at 25°C.

volume. For all other electrolytes the structure-breaking properties of the anions dominate, resulting in an increase in free volume with an increase in concentration of the electrolytes. Similar behaviour is observed in the case of alkali metal halides in aqueous dimethyl formamide, aqueous urea and aqueous xylose systems (refs. 8, 2 and 3, respectively).

Internal pressure values show that, except for lithium and sodium chlorides, the values decrease with an increase in concentration at all temperatures. In a given series, internal-pressure values vary in the order: $Li^+ > Na^+ > K^+ > Cs^+$ and $Cl^- > Br^- > I^-$. Higher values of internal pressure can be attributed to the electrostriction of the ions in solution. Adiabatic compressibility values decrease in all cases with an increase in concentration at all temperatures.

TABLE 7

LiCl system

Temp. (K)	Molarity	U (m s^{-1})	$\kappa \times 10^6$ (bar^{-1})	$V_f \times 10^2$ (cm^3)	P (atm)
298	0.125	1529.5	4.17	1.518	27902
	0.250	1536.8	4.12	1.485	28118
	0.500	1550.2	4.02	1.437	28432
	0.750	1565.1	3.92	1.382	28798
	1.000	1576.6	3.85	1.347	29054
	2.000	1631.0	3.52	1.148	30367
	3.000	1674.1	3.28	0.988	32138
303	0.125	1540.5	4.11	1.829	26647
	0.250	1546.6	4.07	1.785	26869
	0.500	1559.7	3.98	1.695	27341
	0.750	1574.1	3.88	1.660	27523
	1.000	1584.7	3.81	1.615	27791
	2.000	1637.7	3.49	1.377	29294
	3.000	1680.1	3.26	1.175	30810
308	0.125	1549.6	4.07	2.150	25637
	0.250	1555.7	4.03	2.106	25808
	0.500	1568.1	3.94	2.034	26114
	0.750	1581.9	3.85	1.953	26467
	1.000	1592.5	3.78	1.898	26742
	2.000	1643.6	3.48	1.632	28083
	3.000	1684.9	3.25	1.382	29629
313	0.125	1557.0	4.04	2.563	24534
	0.250	1563.2	4.00	2.505	24723
	0.500	1575.4	3.91	2.387	25126
	0.750	1588.6	3.83	2.319	25373
	1.000	1599.2	3.75	2.253	25630
	2.000	1648.5	3.46	1.912	27063
	3.000	1690.1	3.23	1.627	28515

TABLE 8

NaCl system

Temp. (K)	Molarity	U (m s^{-1})	$\kappa \times 10^6$ (bar^{-1})	$V_f \times 10^2$ (cm^3)	P (atm)
298	0.125	1528.6	4.17	1.512	27927
	0.250	1536.1	4.11	1.512	27930
	0.500	1551.1	3.99	1.512	27930
	0.750	1565.6	3.88	1.499	27996
	1.000	1579.8	3.78	1.484	28084
303	0.125	1539.3	4.11	1.856	26518
	0.250	1546.8	4.06	1.847	26548
	0.500	1561.3	3.94	1.848	26542
	0.750	1574.9	3.84	1.820	26674
	1.000	1588.9	3.74	1.801	26756
308	0.125	1548.8	4.07	2.234	25305
	0.250	1556.1	4.01	2.216	25377
	0.500	1569.9	3.91	2.192	25456
	0.750	1583.0	3.81	2.166	25553
	1.000	1596.5	3.71	2.149	25608
313	0.125	1556.4	4.04	2.633	24312
	0.250	1563.5	3.98	2.618	24357
	0.500	1576.8	3.88	2.585	24449
	0.750	1589.8	3.78	2.553	24549
	1.000	1602.9	3.69	2.524	24633

TABLE 9

NaBr system

Temp. (K)	Molarity	U (m s^{-1})	$\kappa \times 10^6$ (bar^{-1})	$V_f \times 10^2$ (cm^3)	P (atm)
298	0.125	1524.3	4.17	1.536	27762
	0.250	1527.4	4.12	1.544	27694
	0.500	1535.4	4.00	1.573	27487
	0.750	1542.4	3.90	1.590	27350
	1.000	1547.9	3.80	1.597	27279
303	0.125	1535.1	4.12	1.880	26389
	0.250	1538.0	4.07	1.883	26335
	0.500	1544.7	3.96	1.911	26179
	0.750	1551.2	3.86	1.932	26051
	1.000	1556.7	3.76	1.944	25972
308	0.125	1544.5	4.08	2.249	25215
	0.250	1547.2	4.02	2.243	25240
	0.500	1552.8	3.92	2.266	25109
	0.750	1558.7	3.83	2.230	24964
	1.000	1564.1	3.73	2.307	24906
313	0.125	1552.4	4.04	2.656	24229
	0.250	1554.8	3.99	2.667	24167
	0.500	1559.4	3.90	2.692	24072
	0.750	1564.8	3.80	2.718	23966
	1.000	1570.0	3.71	2.717	23930

TABLE 10

NaI system

Temp. (K)	Molarity	U (m s^{-1})	$\kappa \times 10^6$ (bar^{-1})	$V_f \times 10^2$ (cm^3)	P (atm)
298	0.125	1519.6	4.18	1.561	27585
	0.250	1517.4	4.14	1.582	27403
	0.500	1518.1	4.03	1.620	27087
	0.750	1518.0	3.94	1.696	26563
	1.000	1516.7	3.85	1.746	26204
303	0.125	1530.7	4.12	1.991	26212
	0.250	1529.9	4.08	1.935	26042
	0.500	1527.7	3.99	2.001	25655
	0.750	1526.9	3.89	2.060	25306
	1.000	1525.3	3.81	2.110	25004
308	0.125	1540.1	4.08	2.304	25005
	0.250	1539.0	4.04	2.297	24947
	0.500	1536.2	3.95	2.386	24566
	0.750	1534.5	3.86	2.446	24259
	1.000	1532.3	3.78	2.512	23950
313	0.125	1547.5	4.05	2.687	24113
	0.250	1546.3	4.01	2.731	23921
	0.500	1543.0	3.90	2.814	23596
	0.750	1540.6	3.84	2.896	23270
	1.000	1538.0	3.76	2.964	22998

TABLE 11

KCl system

Temp. (K)	Conc. (M)	U (m s^{-1})	$\kappa \times 10^6$ (bar^{-1})	$V_f \times 10^2$ (cm^3)	P (atm)
298	0.125	1527.6	4.17	1.580	27502
	0.250	1533.8	4.11	1.603	27353
	0.500	1546.2	4.01	1.653	27013
	0.750	1558.8	3.90	1.704	26688
	1.000	1567.7	3.83	1.753	26339
303	0.125	1538.5	4.12	1.914	26212
	0.250	1544.6	4.06	1.933	26103
	0.500	1556.6	3.96	1.989	25803
	0.750	1568.5	3.86	2.049	25502
	1.000	1577.8	3.78	2.106	25177
308	0.125	1547.8	4.06	2.279	25166
	0.250	1553.9	4.02	2.305	24992
	0.500	1565.3	3.92	2.371	24707
	0.750	1576.9	3.82	2.435	24445
	1.000	1585.0	3.75	2.488	24180
313	0.125	1555.3	4.04	2.686	24122
	0.250	1561.3	3.99	2.717	24028
	0.500	1572.6	3.89	2.781	23784
	0.750	1583.7	3.80	2.842	23565
	1.000	1591.7	3.73	2.891	23346

TABLE 12

KBr system

Temp. (K)	Conc. (M)	U (m s^{-1})	$\kappa \times 10^6$ (bar^{-1})	$V_f \times 10^2$ (cm^3)	P (atm)
298	0.125	1523.1	4.18	1.588	27430
	0.250	1525.6	4.12	1.631	27152
	0.500	1529.7	4.02	1.712	26634
	0.750	1533.9	3.93	1.793	26145
	1.000	1537.7	3.84	1.892	25597
303	0.125	1534.1	4.12	1.927	26144
	0.250	1536.4	4.07	1.985	25839
	0.500	1539.9	3.97	2.074	25392
	0.750	1543.5	3.88	2.172	24925
	1.000	1547.0	3.79	2.267	24495
308	0.125	1543.6	4.08	2.306	24994
	0.250	1545.3	4.03	2.359	24768
	0.500	1548.6	3.94	2.465	24332
	0.750	1551.8	3.85	2.573	23914
	1.000	1554.7	3.76	2.676	23527
313	0.125	1551.3	4.04	2.706	24050
	0.250	1552.7	4.00	2.768	23834
	0.500	1555.8	3.90	2.891	23440
	0.750	1558.5	3.79	3.008	23049
	1.000	1561.3	3.74	3.114	22699

TABLE 13

KI system

Temp. (K)	Conc. (M)	U (m s^{-1})	$\kappa \times 10^6$ (bar^{-1})	$V_f \times 10^2$ (cm^3)	P (atm)
298	0.125	1519.2	4.18	1.603	27322
	0.250	1519.2	4.14	1.666	26808
	0.500	1513.7	4.04	1.789	26144
	0.750	1508.1	3.97	1.915	25389
	1.000	1504.2	3.89	2.032	24749
303	0.125	1530.1	4.12	1.948	26024
	0.250	1529.5	4.09	2.027	25516
	0.500	1523.8	3.99	2.153	24978
	0.750	1517.0	3.93	2.295	24299
	1.000	1512.9	3.85	2.435	23690
308	0.125	1539.3	4.09	2.330	24874
	0.250	1538.6	4.05	2.411	24449
	0.500	1532.3	3.96	2.560	23919
	0.750	1525.2	3.89	2.702	23350
	1.000	1520.1	3.82	2.863	22785
313	0.125	1546.9	4.05	2.747	23901
	0.250	1545.6	4.02	2.836	23510
	0.500	1538.9	3.93	2.997	23046
	0.750	1531.6	3.87	3.148	22532
	1.000	1526.1	3.80	3.336	21978

TABLE 14

CsCl system

Temp. (K)	Molarity	U (m s^{-1})	$\kappa \times 10^6$ (bar^{-1})	$V_f \times 10^2$ (cm^3)	P (atm)
298	0.125	1514.4	4.20	1.604	27341
	0.250	1509.5	4.16	1.644	27070
	0.500	1509.5	4.04	1.772	26294
	0.750	1505.2	3.95	1.893	25622
	1.000	1514.9	3.80	2.026	24946
303	0.125	1525.3	4.15	1.939	26060
	0.250	1521.1	4.11	1.988	25795
	0.500	1521.6	3.99	2.131	25088
	0.750	1514.2	3.91	2.275	24471
	1.000	1523.9	3.76	2.429	23851
308	0.125	1534.6	4.11	2.246	25196
	0.250	1529.5	4.07	2.295	24965
	0.500	1527.8	3.96	2.445	24342
	0.750	1522.0	3.88	2.588	23783
	1.000	1532.3	3.73	2.749	23221
313	0.125	1541.9	4.07	2.651	24196
	0.250	1537.1	4.04	2.703	23989
	0.500	1534.5	3.94	2.866	23432
	0.750	1528.8	3.86	2.967	23058
	1.000	1538.2	3.71	3.167	22466

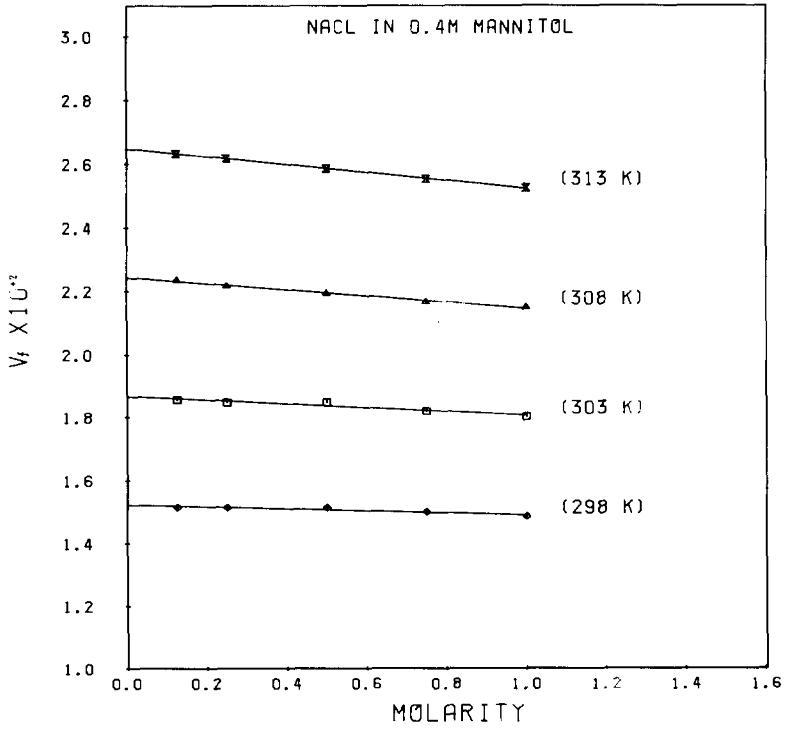

Fig. 5. Plot of V_f against molarity of NaCl in aqueous D-mannitol solution.

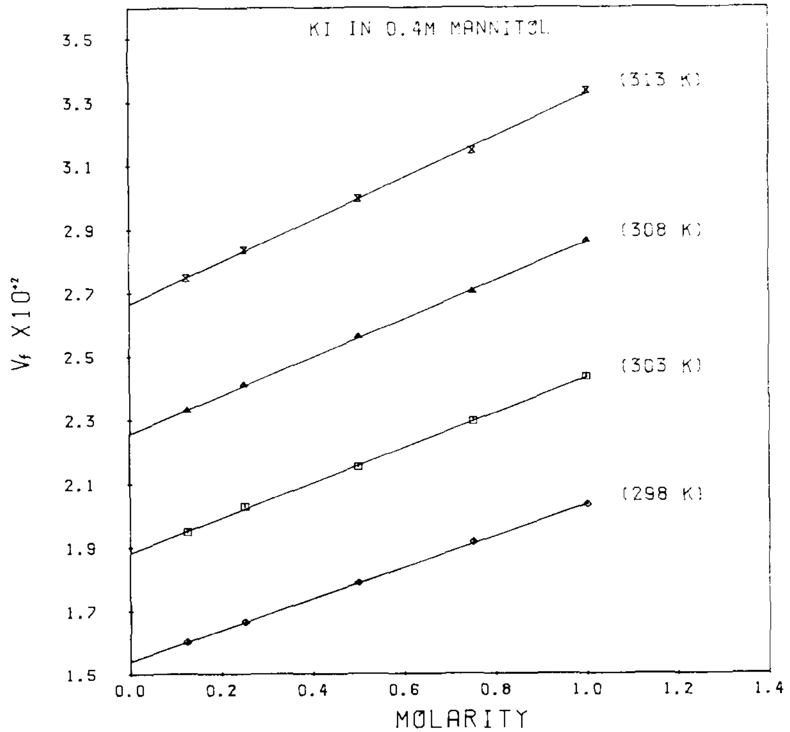

Fig. 6. Plot of V_f against molarity of KI in aqueous D-mannitol solution.

In conclusion, thermodynamic activation parameters of viscous flow, *B* coefficients, hydration numbers and their dependency on temperature are found to be very valuable in differentiating the structure-making and -breaking properties of the electrolytes in solution. Also, by coupling the viscosity values with ultrasonic velocity measurements, one can obtain two valuable parameters, namely free volume and internal pressure. It is found that the dependency of these parameters on concentration further throws light in terms of structure-making or -breaking properties of the electrolytes in solution.

ACKNOWLEDGEMENTS

The financial support of the National Science and Engineering Research Council of Canada and C.E.R.P. (U.C.C.B.) is greatly appreciated. Also, the authors wish to acknowledge the grant provided by Employment and Immigration of Canada under the Canada Works program (H.M.) and to the Cape Breton Development Corporation for providing the summer research stipend (G.M.).

REFERENCES

1 R. Palepu, R. Johnson and W. Rolls, Electrochim. Acta, in press.
2 R. Palepu, C. Fidgen and K. Hennessey, Z. Phys. Chem. (Leipzig), accepted.
3 R. Palepu and H. MacDonald, Thermochim. Acta, submitted.
4 H. Shiio, J. Am. Chem. Soc., 80 (1958) 70.
5 J. Stuher and E. Yeager, in R. Mason (Ed.), Physical Acoustics, Vol. II, Part A, Academic Press, New York, 1965.
6 F.I. BraginsKaya and S.Kh. Sadikhova, Biofizika, 20 (1975) 20.
7 C.V. Suryanarayana, J. Acoust. Soc. India, 7 (1979) 107.
8 S.O. Pillai, S. Natarajan and P.K. Palanisami, J. Acoust. Soc. Am., 73 (1983) 1616.
9 C.V. Suryanarayana and J. Kuppusami, J. Acoust. Soc. India, 4 (1976) 75.
10 Vishnu and V.P. Misra, Carbohydr. Res., 63 (1978) 29.
11 R.L. Kay, Trace Inorganics in Water, Advances in Chemistry Series No. 15, The Chemical Society, London, 1968, p. 73.
12 E.R. Nightingale, in B.E. Conway and R. Barradas (Eds.), Chemical Physics of Ionic Solutions, Wiley, New York, 1966, p. 87.
13 D. Jones and M. Dole, J. Am. Chem. Soc., 51 (1929) 2950.
14 S.W. Goldsack and R. Franchetto, Can. J. Chem., 55 (1977) 1062.
15 B.R. Breslau and I.F. Miller, J. Phys. Chem., 74 (1970) 1056.
16 D. Feakins and K.G. Lawrence, J. Chem. Soc. A, (1966) 212.
17 M. Kaminsky, Discuss. Faraday Soc., 2 (1957) 171.
18 K. Crickard and J.K. Skinner, J. Phys. Chem., 73 (1969) 2060.
19 R.W. Gurney, Ionic Processes in Solution, McGraw-Hill, New York, 1953.
20 S.P. Moulik and A.K. Mitra, Carbohydr. Res., 23 (1972) 65.
21 A. Einstein, Ann. Phys., 19 (1906) 289.
22 F.J. Millero, Chem. Rev., 71 (1971) 147.
23 G. Curthoys and J.G. Mathieson, Trans. Faraday Soc., 66 (1970) 43.
24 G.A. Krestov, Zh. Strukt. Khim., 8 (1962) 402.
25 O.Ya. Somoilov, in R.A. Horne (Ed.), Water and Aqueous Solution, Wiley Interscience, New York, 1972.
26 C.A. Engel and E.J. Sare, J. Chem. Phys., 52 (1969) 1058.
27 S. Gladstone, K.J. Laidler and H. Eyring, The Theory of Rate Processes, McGraw-Hill, New York, 1941.
28 W. Wood, Electrochim. Acta, 9 (1964) 203.
29 D. Feakins, D.J. Freemantle and K.G. Lawrence, J. Chem. Soc., Faraday Trans. 1, 70 (1974) 795.