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PHYSICOCHEMICAL PROPERTIES OF CONCENTRATED SOLUTIONS OF SOME ALKALI METAL HALIDES IN AQUEOUS THIOUREA SOLUTIONS

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ABSTRACT

Viscosity, density and ultrasonic velocity measurements of some alkali metal halides in 1 M thiourea solution at four different temperatures have been determined. The viscosity data are analysed in terms of various viscosity equations to obtain *B* coefficients. Ionic viscosity coefficients, hydration numbers, apparent partial molar volumes and free volumes are calculated and discussed in terms of solute–solvent interactions. Activation parameters of viscous flow are calculated and discussed in terms of structure-breaking or making properties of the electrolyte solutions.

INTRODUCTION

This paper is part of a series on the physicochemical properties of aqueous ternary systems of alkali metal halides [1–4]. The aim of the present investigation was to measure the density, viscosity and ultrasonic velocities of some alkali metal halides in aqueous thiourea solutions in the range 298–313 K. The results of such measurements may constitute a basis for discussion of the effect of electrolytes on the structure of the solvent. Free volume is a fundamental property to be considered when explaining the variation in physicochemical properties of aqueous electrolyte mixtures [5,6]. Ultrasonic velocity measurements, along with viscosity and density values, can be used to calculate free volumes (V_f).

EXPERIMENTAL

Analytical reagent grade samples of alkali metal halides were obtained from B.D.H. and Merck and were dried at 383 K for 5 h before being used.

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Thiourea was crystallised from ethanol and then dried under vacuum at 333 K. All solutions were prepared on a molar basis in degassed nanopure water (specific conductivity 8×10^{-7} mhos). A 1.0 M thiourea solution was used as a stock solution. Viscosity, density and ultrasonic velocity measurements of various electrolyte solutions in the concentration range 0.05–2.5 M were obtained by the methods and with the equipment described previously [1,2]. Apparent partial molar volumes of the electrolytes at 298 K were calculated from the densities, measured with a Sodev densimeter Model 03D. The temperature of the cell compartment was controlled at ± 0.001 K with a Sodev circulating waterbath model CTL. Since all solutions must be free of large particles, before measurement solutions were filtered through Millipore filters (type HA, pore size 0.45 μm).

RESULTS AND DISCUSSION

Viscosity B coefficients have been found to be valuable in measuring the size and shape effect of the solute as well as structural modification induced by solute–solvent interaction [7,8]. Viscosity B coefficients were obtained by three different procedures. A modified Jones–Dole equation [9]

$$\eta_{\mathrm{rel}} = 1 + BC + DC^2 \tag{1}$$

for higher concentrations of the solute was used to calculate B coefficients from experimental relative viscosities, using the least-squares method. Viscosity data were fitted into the Goldsack–Franchetto equation [10]

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

where E and V are parameters characteristic of the electrolytes and X is the mole fraction of the electrolyte. The values of E and V were obtained by means of non-linear least-squares methods and approximate values of B coefficients were obtained using the relation

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

The B coefficient values were also obtained following the procedures of the Breslau–Miller equation [11]

$$V_{\mathrm{e}} = \frac{-2.5C + \left[(2.5C)^2 - 40.2C^2(1 - \eta_{\mathrm{rel}})\right]^{1/2}}{20.10C^2} \tag{4}$$

and the average $\overline{V}_{\mathrm{e}}$ values thus obtained were fitted into the following equation for 1 : 1 electrolytes

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

TABLE 1

B values of alkali halides in 1.0000 M aqueous thiourea solution

Salt	Eqn. (1) [a]		Eqn. (2) [b]	Eqn. (3) [c]	Eqn. (1)		Eqn. (2)	Eqn. (3)
	B	D	B	B	B	D	B	B
	$T = 298$ K				$T = 303$ K			
LiCl	0.1357	0.0166	0.1309	0.1272	0.1344	0.0158	0.1336	0.1316
NaCl	0.0925	0.0165	0.0927	0.0978	0.0915	0.0179	0.0916	0.1003
NaBr	0.0573	0.0190	0.0526	0.0598	0.0662	0.0159	0.0649	0.0704
NaI	0.0429	0.0023	0.0422	0.0317	0.0714	0.0050	0.0695	0.0620
KF	0.1331	0.0144	0.1319	0.1320	0.1276	0.0231	0.1231	0.1161
KCl	0.0194	0.0004	0.0186	0.0039	0.0235	0.0050	0.0228	0.0117
KBr	−0.0295	0.0104	−0.0258	−0.0258	−0.0159	0.0093	−0.0241	−0.0345
KI	−0.0476	0.0102	−0.0496	−0.0669	−0.0378	0.0087	−0.0390	−0.0533
RbCl	−0.0244	0.0118	−0.0269	−0.0352	0.0013	0.0040	0.0005	−0.0129
CsCl	−0.0461	0.0095	−0.0506	−0.0530	−0.0018	0.0095	−0.0135	−0.0223
	$T = 308$ K				$T = 313$ K			
LiCl	0.1360	0.0153	0.1351	0.1307	0.1370	0.0153	0.1357	0.1337
NaCl	0.0911	0.0142	0.0876	0.0908	0.0909	0.0190	0.0859	0.0913
NaBr	0.0981	0.0140	0.0929	0.0922	0.0916	0.0204	0.0914	0.0986
NaI	0.0989	0.0088	0.0887	0.0919	0.1241	0.0138	0.1173	0.1065
KF	0.1227	0.0314	0.1230	0.1213	0.0998	0.0450	0.0992	0.1169
KCl	0.0328	0.0013	0.0313	0.0207	0.0434	0.0030	0.0414	0.0322
KBr	0.0013	0.0055	0.0062	0.0116	0.0077	0.0108	0.0097	0.0224
KI	−0.0154	0.0023	−0.0150	−0.0344	−0.0179	0.0033	−0.0167	−0.0269
RbCl	0.0181	0.0017	0.0174	0.0044	0.0227	0.0021	0.0191	0.0045
CsCl	0.0118	0.0018	0.0117	−0.0017	0.0132	0.0074	0.0122	0.0143

[a] Eqn. (1), Jones–Dole equation.
[b] Eqn. (2), Goldsack–Franchetto equation.
[c] Eqn. (3), Breslau–Miller equation.

All these values are presented in Table 1. Slight differences in the values of B coefficients could be attributed to different approximations involved in the derivation of these equations.

The coefficient D in the modified Jones–Dole equation includes solute–solute interactions and also those solute–solvent interactions that were not accounted for by the BC term in the Jones–Dole equation at higher concentrations [12]. The values of D are in general higher in the ternary systems compared to the corresponding values in aqueous systems. It has been shown that an estimate of the influence of long-range Coulombic forces on D can be obtained from conductivity measurements [13]. The contribution is of the order of 0.003 to the value of D and is certainly not negligible with alkali halide solutions in our investigations. The values of B coefficients of the electrolytes in general are slightly higher than in pure water and this could be attributed to the structure-breaking properties of the co-solute thiourea [14].

TABLE 2

Values of ionic parameters [a] of alkali halides in 1.0000 M aqueous thiourea solution

Ion	298 K			303 K			308 K			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^+	0.1260	50.40	7.53	0.1226	49.06	7.33	0.1196	47.84	7.15	0.1153	46.12	6.89
Na^+	0.0828	33.12	4.68	0.0798	31.90	4.49	0.0747	29.88	4.19	0.0692	27.68	3.85
K^+	0.0097	3.88	−0.31	0.0118	4.70	−0.19	0.0164	6.56	0.10	0.0217	8.68	0.42
Rb^+	−0.0341	−13.64	−3.29	−0.0104	−4.18	−1.87	0.0017	0.68	−1.13	0.0010	0.40	−1.17
Cs^+	−0.0558	−22.32	−5.21	−0.0236	−9.42	−3.26	−0.0046	−1.84	−2.11	−0.0194	−7.76	−3.01
F^-	0.1234	49.36	6.50	0.1158	46.34	6.04	0.1063	42.52	5.47	0.0781	31.24	3.76
Cl^-	0.0097	3.88	−1.67	0.0118	4.70	−1.55	0.0164	6.56	−1.27	0.0217	8.68	−0.95
Br^-	−0.0392	−15.68	−5.19	−0.0276	−11.06	−4.49	−0.0151	−6.04	−3.73	−0.0140	−5.60	−3.67
I^-	−0.0573	−22.92	−7.30	−0.0496	−19.82	−6.83	−0.0046	−1.84	−4.11	−0.0085	−3.40	−4.35

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

Ionic $B_{\pm}$ coefficients at various temperatures were calculated according to the procedures described by Kaminsky [15] and are presented in Table 2. The high values of the $B_{\pm}$ coefficients found for Li^+, Na^+ and F^- ions with $dB_{\pm}/dT < 0$ show that the ions are strongly solvated in aqueous thiourea solutions and behave as structure-makers. In contrast, the low $B_{\pm}$ coefficient values with $dB_{\pm}/dT > 0$ for K^+, Rb^+, Cs^+, Cl^-, Br^- and I^- ions show that they interact weakly with the solvent molecules and act as structure-breakers. Ionic molar volumes $V_{\pm}$ can be obtained from the $B_{\pm}$ values by employing Einstein's equation [16]

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

and the hydration number N_B can be calculated [17] from the equation

$$\bar{V}_{\pm} = \bar{V}^{\ominus}_{\text{ion}} + N_B\bar{V}^{\ominus}_{s} \tag{7}$$

The values of N_B and $\bar{V}_{\pm}$ are presented in Table 2. According to Millero [17] and Curthoys and Mathieson [18], structure-makers are characterised by $dN_B/dT < 0$ and structure-breakers by $dN_B/dT > 0$; one can conclude from an examination of Table 2, that Li^+, Na^+ and F^- are structure-makers and K^+, Rb^+, Cs^+, Cl^-, Br^- and I^- are structure-breakers in aqueous thiourea solutions. The negative hydration numbers for the structure-breaking ions could be attributed to the ability of these ions in solution to disrupt the water structure by pushing the water molecules apart in both primary and secondary hydration spheres around them [19,20].

According to Krestov [21], a linear relationship exists between hydration number and ionic radius. The linearity depends on the charge of the ions involved. Different linear relationships are observed when N_B is plotted against ionic radius or $B_{\pm}$ coefficients (Figs. 1 and 2). From the magnitude of hydration numbers, one can conclude that the structure-breaking ability of various ions in aqueous thiourea solutions at 298 K is in the order $I^- > Br^- > Cs^+ > Rb^+ > Cl^- > K^+ > Na^+ > F^- > Li^+$.

The Gibbs energy of activation $\Delta G^{\#}_{\text{vis}}$ flow of a solution for a given composition can be calculated using the equation of Eyring and co-workers [22]

$$\Delta G^{\#}_{\text{vis}} = RT \ln(v\eta/hN) \tag{8}$$

The $\Delta G^{\#}_{\text{vis}}$ values thus determined at different temperatures for a given composition were fitted

$$\Delta G^{\#}_{\text{vis}} = a + bT + cT^2 \tag{9}$$

The entropy and enthalpy of activation ($\Delta S^{\#}_{\text{vis}}$ and $\Delta H^{\#}_{\text{vis}}$, respectively) were then obtained according to

$$\Delta S^{\#}_{\text{vis}} = -\frac{\partial}{\partial T}(\Delta G^{\#}_{\text{vis}}) \tag{10}$$

$$\Delta H^{\#}_{\text{vis}} = \Delta G^{\#}_{\text{vis}} + T\Delta S^{\#}_{\text{vis}} \tag{11}$$

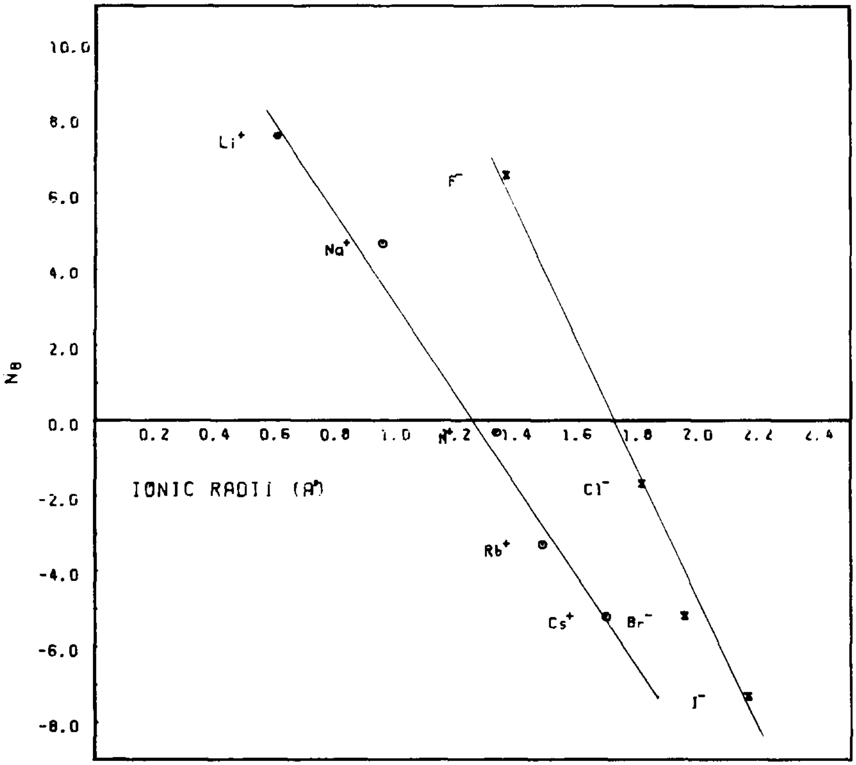

Fig. 1. Plot of hydration number versus Pauling's radii for alkali metal halides in 1 M aqueous thiourea solution at 298 K.

The dependencies of these thermodynamic parameters on composition were fitted into the following empirical equation as suggested by Tamamushi and Isono [23]

$$\Delta Y^{\#}_{\text{vis}} = \Delta Y^{\ominus}_{\text{vis}} + \beta_y X + \gamma_y X^2 \qquad (y = G,\ H \text{ and } S) \tag{12}$$

where $\Delta Y^{\ominus}$ is the activation parameter for the solvent and X is the mol fraction of the solute. The relationship among β_y and γ_y is given by

$$\beta_G = \beta_H - T\beta_S \qquad \gamma_G = \gamma_H - T\gamma_S \tag{13}$$

Then coefficients were determined by least-squares methods and are presented in Table 3. Initial effects of solutes on the activation parameters for viscous flow can be discussed in terms of β_y coefficients. The initial increase in the activation parameters $\Delta Y^{\#}_{\text{vis}}$ with an increase in concentration is represented by positive values for β_y coefficients. A positive β_H means an initial increase in $\Delta H^{\#}_{\text{vis}}$ with increasing concentration resulting from an increase in the degree of bonding or association around the solute in solution, and a positive β_S may be due to the appearance of local structural order in the solution [24,25]. It is observed that normally for structure-break-

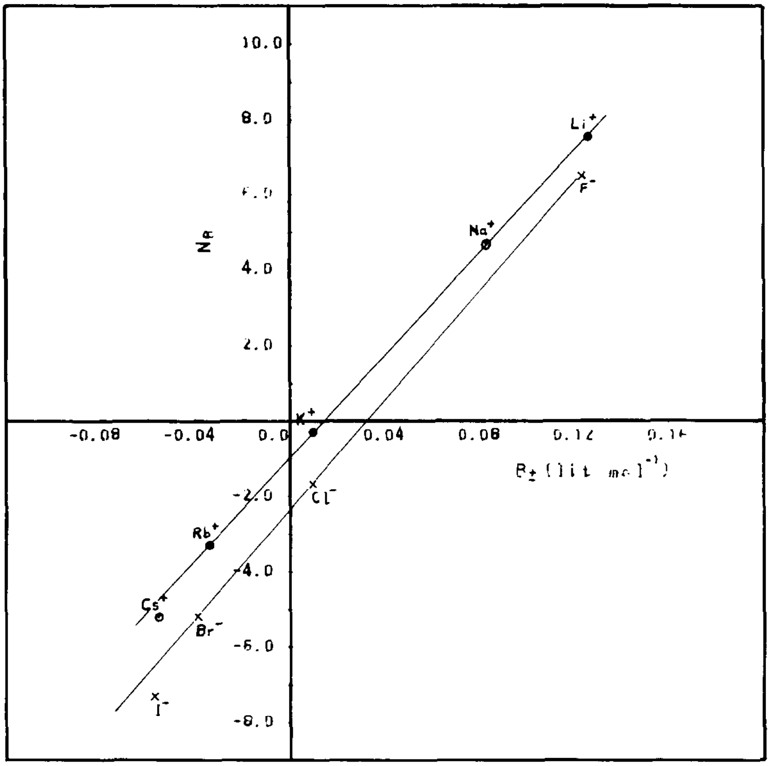

Fig. 2. Plot of hydration number versus ionic *B* coefficients for alkali metal halides in 1 M aqueous thiourea solution at 298 K.

ing ions the values of β_G, β_H and β_S are negative and for the structure-making ions $\beta_G > 0$ and β_H and $\beta_\gamma < 0$.

One can also classify the behavior of electrolytes from the dependence of

TABLE 3

Values of β and γ coefficients of alkali metal halides in 1.0000 M aqueous thiourea solution at 298 K [a]

Salt	β_G	γ_G	β_H	γ_H	β_S	γ_S
LiCl	18.4	44.5	−1.5	152.2	−0.07	0.40
NaCl	12.8	76.4	−14.4	47.2	−0.09	−0.09
NaBr	9.1	103.2	−151.7	1489.2	−0.54	4.67
NaI	8.4	20.9	−258.6	520.5	−0.90	1.67
KF	21.9	−0.3	27.8	−252.3	0.07	−8.06
KCl	3.9	8.3	9.3	−64.7	−0.23	−0.01
KBr	−1.4	74.3	−109.6	961.2	−0.36	2.97
KI	−2.7	82.2	−116.4	1548.3	−0.38	4.91
RbCl	−0.7	84.8	−107.0	991.7	−0.36	3.10
CsCl	−2.7	131.6	−176.0	2489.1	−0.58	7.97

[a] Values of ΔG, ΔH in kJ mol^{-1}, and ΔS in kJ mol^{-1} K^{-1}.

TABLE 4

Thermodynamic parameters of activation of flow at infinite dilution of alkali halides in 1.0000 M aqueous thiourea solution [a]

Salt	$\Delta\mu_2^{\ominus\#}$	$T\Delta S_2^{\ominus\#}$	$\Delta H_2^{\ominus\#}$	Ions	$T\Delta S_2^{\ominus\#}$	$\Delta H_2^{\ominus\#}$
LiCl	27.06	−10.67	16.39	Li^+	18.78	39.29
NaCl	21.70	−19.78	1.92	Na^+	9.68	24.82
NaBr	17.76	−69.10	−51.34	K^+	−29.46	−22.90
NaI	16.52	−82.86	−66.34	Rb^+	−103.22	−101.18
KF	30.56	64.93	95.49	Cs^+	−125.84	−125.85
KCl	13.11	−58.91	−45.80	F^-	94.38	118.39
KBr	7.91	−108.23	−100.32	Cl^-	−29.46	−22.90
KI	6.45	−122.00	−115.55	Br^-	−78.76	−77.42
RbCl	8.59	−132.67	−124.08	I^-	−92.54	−92.65
CsCl	6.54	−155.29	−148.75			

[a] Values in kJ mol^{-1}; (solvent = 9.32 kJ mol^{-1}).

thermodynamic properties of viscous flow on concentration. It is observed [1–4] that normally for all structure-making electrolytes, $\Delta H^{\#}_{\text{vis}}$ is independent of concentration whereas $\Delta S^{\#}_{\text{vis}}$ decreases and $\Delta G^{\#}_{\text{vis}}$ increases with concentration. For structure-breaking electrolytes $\Delta G^{\#}_{\text{vis}}$ remained constant within experimental error up to high concentrations. This effect is probably due to complete compensation for change in $\Delta H^{\#}_{\text{vis}}$ with concentration by the $\Delta S^{\#}_{\text{vis}}$.

The limiting values of the activation parameters at infinite dilution of the electrolytes were calculated according to the procedures of Feakins et al. [26] and are presented in Table 4. According to the authors, the free energy change in $\Delta\mu_2^{\ominus\#}$ is always greater than that of the pure solvent $\Delta\mu_1^{\ominus\#}$ for structure-makers. From the data of Table 4, one can conclude that LiCl, KCl, KF and sodium halides are acting as structure-makers at infinite dilution. This may be due to dominance of the structure-making ability of cations over anions like Br^- and I^- at infinite dilution. Except for Li^+, Na^+ and F^-, the values of $T\Delta S_2^{\ominus\#}$ and $\Delta H_2^{\ominus\#}$ are negative, indicating that formation of the activation complex is associated with bond making and increase in order. A plot of $\Delta H_2^{\ominus\#}$ versus $T\Delta S_2^{\ominus\#}$ indicates a linear relationship between these parameters and the linearity depended on the ability of structure-making or -breaking properties (Fig. 3).

The apparent molal volumes of electrolytes have been calculated for several concentrations of electrolyte solutions from the corresponding densities using [27]

$$\phi_v = \frac{1000\,(d_0 - d)}{m d d_0} + \frac{M_2}{d} \tag{14}$$

The apparent partial molal volume ($\phi_v^{\ominus}$) at infinite dilution is obtained

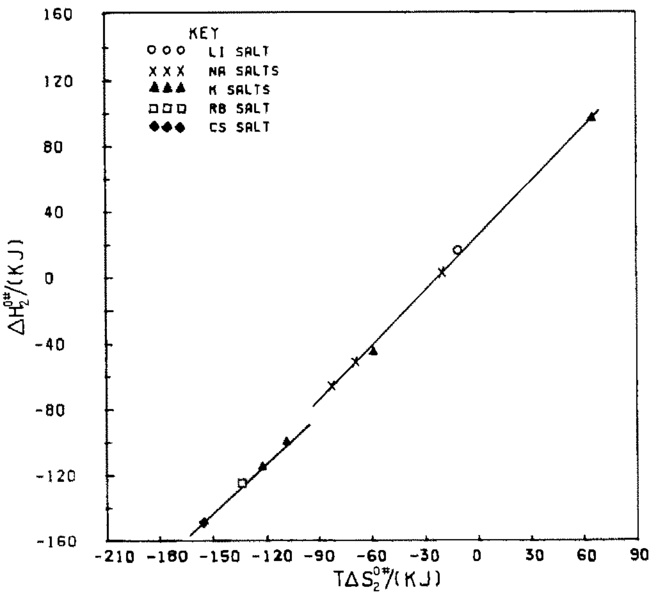

Fig. 3. The relationship between $\Delta H_2^{\ominus\#}$ and $T\Delta S_2^{\ominus\#}$ at 298 K.

using Masson's equation [28]

$$\phi_v = \phi_v^{\ominus} + S_v(m)^{1/2} \tag{15}$$

where m is the molality and S_v is the experimental slope. The values obtained are listed in Table 5. The values of $\phi_v^{\ominus}$ and S_v are in general higher than in pure water and the values are indicative of solute–solvent interaction and ion–ion interaction respectively [27].

TABLE 5

Values of partial molal volume $\phi_v^{\ominus}$ and the experimental slope S_v of alkali halides in 1.000 M aqueous thiourea solution at 298 K

Salt	$\phi_v^{\ominus}$ (ml mol^{-1})	S_v
LiCl	21.04	0.9424
NaCl	17.77	1.6177
KCl	27.95	1.7435
RbCl	33.43	1.2524
CsCl	40.78	1.2310
NaBr	24.70	1.3374
KBr	34.94	1.3687
NaI	36.25	0.9823
KI	46.31	1.1460

TABLE 6

Values of sound velocity, compressibility and free volume of alkali halides in 1.0000 M aqueous thiourea solution at 298 K

Electrolyte	Conc. (M)	U (m s^{-1})	$\beta_s \times 10^{+6}$ (bar)	$V_f \times 10^{-2}$ (cm^3)
LiCl	0.10	1528.4	4.20	2.004
	0.20	1534.0	4.16	1.980
	0.50	1549.3	4.06	1.906
	0.75	1561.4	3.96	1.830
	1.00	1575.1	3.87	1.771
NaCl	0.10	1530.2	4.18	2.010
	0.20	1537.7	4.13	2.010
	0.50	1552.1	4.00	1.980
	0.75	1566.0	3.90	1.970
	1.00	1580.8	3.79	1.930
NaBr	0.10	1524.7	4.19	2.030
	0.20	1528.4	4.14	2.050
	0.50	1536.1	4.01	2.080
	0.75	1542.5	3.91	2.090
	1.00	1549.8	3.81	2.090
NaI	0.10	1520.9	4.20	2.047
	0.20	1520.7	4.16	2.064
	0.50	1520.1	4.04	2.149
	0.75	1518.9	3.95	2.206
	1.00	1519.3	3.86	2.286
KF	0.10	1530.4	4.17	2.012
	0.20	1537.2	4.12	2.019
	0.50	1559.0	3.95	1.998
	0.75	1577.1	3.82	1.985
	1.00	1593.0	3.70	1.959
KCl	0.10	1524.9	4.21	2.038
	0.20	1533.7	4.14	2.067
	0.50	1547.7	4.01	2.127
	0.75	1559.0	3.91	2.178
	1.00	1570.6	3.82	2.230
KBr	0.10	1524.0	4.19	2.057
	0.20	1525.9	4.15	2.101
	0.50	1531.3	4.03	2.229
	0.75	1535.0	3.93	2.327
	1.00	1539.0	3.84	2.437
KI	0.10	1521.1	4.20	2.074
	0.20	1518.9	4.16	2.125
	0.50	1514.6	4.05	2.279
	0.75	1512.2	3.95	2.411
	1.00	1509.3	3.87	2.543
CsCl	0.10	1520.7	4.19	2.077
	0.20	1520.6	4.14	2.136
	0.50	1518.1	4.01	2.306
	0.75	1515.7	3.92	2.442
	1.00	1513.8	3.82	2.578

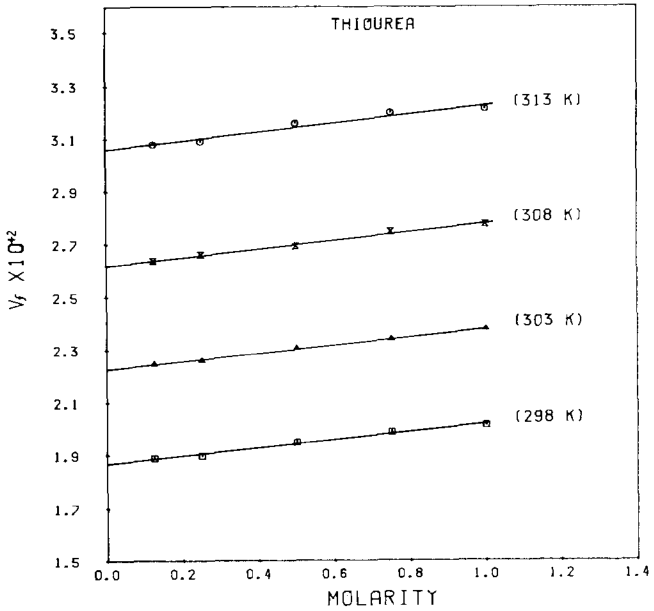

Fig. 4. Plot of V_f versus molarity of thiourea in aqueous solution at different temperatures.

Free volumes at all concentrations and temperatures were calculated using [29]

$$V_f = (\overline{M}U/K\eta)^{3/2} \tag{16}$$

where $\overline{M}$ is the average molecular mass, U is the ultrasonic velocity, η is the viscosity of the solution and K is a constant equal to 4.28×10^5; computed V_f values are represented in Table 6. Adiabatic compressibilities (β_S) were also calculated and are included in Table 6. Examination of Table 6 indicates that the free volume dependence on concentration depends on the type of electrolyte. For net structure-makers like LiCl, NaCl, and KF, the free volume decreases with an increase in concentration of the electrolyte at all temperatures. One can conclude that the high charge density of structure-making ions dominates in the ordering of the solution resulting in a decrease in free volume. In the case of other electrolytes, the structure-breaking properties of the ions dominate, resulting in an increase in free volume with increase in concentration of electrolytes. Free volumes of thiourea in aqueous solutions were also determined and the values increase with increase in concentration of thiourea indicating that thiourea is acting as a structure-breaker in aqueous solutions (Fig. 4).

CONCLUSIONS

Thermodynamic activation parameters of viscous flow, B coefficients, hydration numbers and their dependence on temperature are found to be very valuable in differentiating the structure-making and structure-breaking properties of electrolytes in solution. From the measured viscosity and ultrasonic velocity values one can obtain free volumes (V_f). It is found that the dependence of this parameter on concentration further elucidates the structure-making or structure-breaking properties of the electrolytes in solution.

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