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THERMODYNAMICS AND FREE VOLUME OF SODIUM AND POTASSIUM HALIDES IN AQUEOUS XYLOSE SOLUTION

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ABSTRACT

Thermodynamic properties of viscous flow have been calculated from the dependency of viscosity data as a function of temperature. The B coefficients obtained from the analysis of viscosity data were used to calculate the activation parameters at infinite dilution and the results were discussed in terms of structure-making or -breaking properties of the electrolytes in aqueous xylose solution. Also, ionic $B_{\pm}$ coefficients and hydration numbers have been calculated and discussed. Free volumes and internal pressure values were calculated and the dependency of these two parameters on concentration and temperature is found to be a valuable tool in elucidating structure-making and -breaking properties of the electrolyte solution.

INTRODUCTION

The present paper continues our investigation of physico-chemical properties of aqueous ternary systems of alkali metal halides [1,2]. 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) [3]. Free volume is an important factor to be considered when explaining the variation in physico-chemical properties of liquid mixtures and aqueous electrolyte solutions [4,5].

In the present investigation, we report the results dealing with the dependency of free volume and internal pressure on both concentration and temperature of alkali metal halides in aqueous D-xylose solution. Viscosity measurements of alkali halides in aqueous D-xylose were taken from Vishnu and Misra [6]. The data were analyzed in terms of various viscosity equations to obtain information about ionic interactions prevalent at such high concentrations of electrolytes. Also, various thermodynamic properties of viscous flow were determined.

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EXPERIMENTAL

Analytical reagent grade samples of alkali metal halides were obtained from BDH and Merck and were dried at 110°C for 5 h before being used. D-Xylose was recrystallized and dried in vacuo at room temperature. All solutions were prepared by molar basis in nanopure water (sp. conductivity $\approx 3 \times 10^{-7}$ mhos). D-Xylose (0.4 M) was used as a stock solution. Density and ultrasonic velocity values were determined, at specified temperatures, using the apparatus described previously [1,2].

RESULTS AND DISCUSSION

Viscosity B coefficient studies have been found to be a valuable tool in understanding the structure-making (SM) and structure-breaking (SB) of solute molecules [7,8]. The relative viscosity data for all electrolyte solutions have been utilized to calculate B coefficients from the Jones–Dole equation [9], modified for higher concentrations

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

B values were obtained employing the least-squares method. The viscosity data were fitted into the Goldsack–Franchetto equation [10] deducted from the absolute rate theory (Fig. 1)

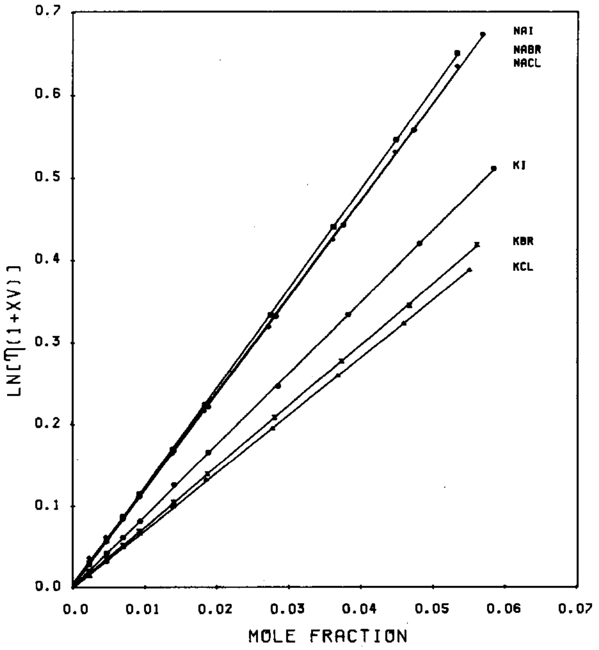

Fig. 1. Test of eqn. (2).

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

where X is the mole fraction, E and V are parameters characteristic of the electrolytes. The values of E and V were obtained by solving the equation by a non-linear least-squares method. The approximate B coefficients obtained were calculated using the relation

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

Values of B coefficients are presented in Table 1, along with B values obtained from Breslau and Miller's equation [6]. The B coefficients obtained employing the various equations are of the same order. Since different assumptions were made in the derivation of these equations, exact agreement among the B coefficients obtained should not be expected. Also, different concentration ranges were used in the calculation of B coefficients from these equations. Dependency of B values of the electrolytes in aqueous D-xylose solution on temperature varied with the type of equation and the concentration range used in the calculations. B values are slightly higher than in pure water and lower than in aqueous urea solutions [1]. According to Stokes and Mills [11], the viscosity B coefficients are due to three contributions: η^{E} (the positive increase due to shape and size of the ion), η^{A} (the increase due to the alignment or orientation of polar molecules by the ionic field) and η^{D} (the decrease in viscosity due to the distortion of the solvent structure by the ions). Therefore, the variation of B coefficients can be discussed in terms of viscosity effects. The B coefficient of KCl is found to be less than that of NaCl. Ions with a lower charge density would have a weak orientation effect in the first layer, therefore η^{E} and η^{A} will be small. A considerable amount of distortion exists in the vicinity of such ions due to competition between the ionic field and bulk structure. Consequently, η^{D} will be large. Thus B values will be smaller for K^+ salts than for Na^+ salts and the order of ion solvent interaction is $\text{K}^+ > \text{Na}^+$. Ionic $B_\pm$ coefficients, at various temperatures, were calculated according to the procedure described by Kaminsky [12] and are presented in Table 2. According to Gurney [13], $\text{d}B_\pm/\text{d}T$ is either negative or nearly zero for structure-making ions and positive for structure-breaking ions. Positive values of $\text{d}B_\pm/\text{d}T$ for K^+, Br^-, Cl^-, and I^- indicate interaction between the ions and the solvent molecules. For the anions, the interaction with the water dipole is through hydrogen bonding. The positive values show that the anions have a firm layer of water molecules in their cosphere. Slightly positive values for $\text{d}B_\pm/\text{d}T$ for Na^+ in aqueous D-xylose may be due to xylose–salt interactions involving hydroxyl groups of the D-xylose and the ions [14].

Ionic molar volumes ($\overline{V}_\pm$) can be obtained from the ionic $B_\pm$ coefficient employing the relation

$$B_\pm = 2.5\overline{V}_\pm \tag{4}$$

TABLE 1

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

Salt Temp. (K) =	Jones–Dole equation				Breslau–Miller equation				Goldsack–Franchetto equation			
	289	303	308	313	298	303	308	313	298	303	308	313
NaCl	0.0965	0.1014	0.1049	0.1065	0.095	0.071	0.058	0.042	0.0860	0.0742	0.0698	0.0590
NaBr	0.0678	0.0708	0.0699	0.0706	0.058	0.041	0.029	0.008	0.0528	0.0405	0.0376	0.0235
NaI	0.0346	0.0407	0.0502	0.0510	0.022	0.008	−0.010	−0.023	0.0134	0.00724	−0.0020	−0.0170
KCl	0.0033	0.0059	0.0103	0.0213	−0.022	−0.023	−0.032	−0.042	−0.0110	−0.0117	−0.0112	−0.0097
KBr	−0.0217	−0.0136	−0.0104	0.0056	−0.049	−0.051	−0.052	−0.060	−0.0395	−0.0402	−0.0365	−0.0323
KI	−0.0640	−0.0488	−0.0104	−0.0149	−0.083	−0.084	−0.086	−0.087	−0.0790	−0.0750	−0.0708	−0.0698

TABLE 2

Values of ionic parameters ($B_{\pm}$ in 1 mol^{-1}, V^0 and $V_{\pm}$ in cm^3 mol^{-1})

Ion	298 K				303 K			308 K			313 K		
	V^0	$B_{\pm}$	$V_{\pm}$	N_B	$B_{\pm}$	$V_{\pm}$	N_B	$B_{\pm}$	$V_{\pm}$	N_B	$B_{\pm}$	$V_{\pm}$	N_B
Na^+	2.16	0.0950	38.0	5.41	0.0984	39.4	5.62	0.0998	39.9	5.70	0.0959	38.4	5.47
K^+	5.93	0.0016	0.6	−0.80	0.0030	1.2	−0.71	0.0051	2.0	−0.59	0.0106	4.2	−0.26
Cl^-	14.94	0.0016	0.6	−2.17	0.0030	1.2	−2.08	0.0051	2.0	−1.95	0.0106	4.2	−1.62
Br^-	18.68	−0.0234	−9.4	−4.24	−0.0160	−6.4	−3.79	−0.0155	−6.2	−3.75	−0.0050	−2.0	−3.12
I^-	25.39	−0.0650	−26.0	−7.76	−0.0518	−20.7	−6.96	−0.0344	−13.8	−5.92	−0.0255	−10.2	−5.38

and the hydration number (N_B) of ions can be calculated from the equation

$$\bar{V}_{\pm} = \bar{V}^0_{\mathrm{ion}} + N_B \bar{V}^0_S \tag{5}$$

where $\bar{V}^0_{\mathrm{ion}}$ is the free ionic volume calculated from the relation $\bar{V}^0_{\mathrm{ion}} = 2.52r^3$ (r = ionic radius) and $\bar{V}^0_S$ is the volume of water equal to 6.62 cm^3 mol^{-1}. The results are presented in Table 2. $V_{\pm}$ values and N_B values increase with temperature for K^+, Cl^-, Br^- and I^-, and are slightly positive for Na^+ ions. Thus, our results agree with Millero [15] and Curthoys and Mathieson [16] thereby confirming the structure-breaking properties of K^+, Cl^-, Br^-, and I^- and the structure-making properties of Na^+ ions. This agrees well with the general relation that a positive hydration number indicates a structure-maker (e.g., Na^+) and negative hydration numbers indicate structure-breakers (e.g., K^+, Cl^-, Br^-, I^-). Almost all the structure-breaking ions disrupt the water structure by pushing the water molecules apart in both the primary and secondary hydration spheres around them. Thus the magnitude of the hydration number suggests that the structure-breaking ability in aqueous D-xylose is in the order: $I^- > Br^- > Cl^- > K^+ > Na^+$.

Values of free energy ($\Delta G^*_{\mathrm{visc}}$), enthalpy ($\Delta H^*_{\mathrm{visc}}$) and entropy of activation ($\Delta S^*_{\mathrm{visc}}$) were calculated [18] and are presented in Tables 3 and 4. From the dependency of thermodynamic properties of viscous flow on concentration, one can classify sodium chloride as a structure-making electrolyte. In this case, $\Delta H^*_{\mathrm{visc}}$ remains constant within the experimental errors, whereas $\Delta S^*_{\mathrm{visc}}$ decreases and $\Delta G^*_{\mathrm{visc}}$ increases with an increase in electrolyte concentration [1]. In the other sodium halides and potassium chloride, the structure-breaking ability of the anions dominates at higher concentrations. In these cases both $\Delta H^*_{\mathrm{visc}}$ and $\Delta S^*_{\mathrm{visc}}$ decrease with an increase in electrolyte concentration and the dependency of $\Delta G^*_{\mathrm{visc}}$ on concentration varies from Cl^- to I^-. Potassium bromide and potassium iodide can be classified as structure breakers. The structure-breaking properties of Br^- and I^- dominate, even at low concentrations. In these cases, $\Delta G^*_{\mathrm{visc}}$ remains constant (except at high concentration of the electrolyte), and both $\Delta H^*_{\mathrm{visc}}$ and $\Delta S^*_{\mathrm{visc}}$ decrease with an increase in electrolyte concentration. In the case of structure breakers, $\Delta G^*_{\mathrm{visc}}$ remains constant and essentially identical with that for 0.4 M D-xylose solution and independent of the concentration. This shows 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 [19].

The limiting values of the activation parameters at infinite dilution of the electrolytes were calculated according to the procedures of Feakins et al. [20] and are presented in Table 5. Normally for the net structure-makers in solution, the free energy change ($\Delta\mu_2^{0\#}$) is always greater than that of the pure solvent ($\Delta\mu_1^{0\#}$). Examination of Table 4 suggests that sodium halides and KCl are acting as net structure makers at infinite dilution. This can be attributed to the dominance of the structure-making ability of the cations over the anions at infinite dilution. Potassium bromide and potassium iodide

TABLE 3

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

Conc. (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	17.53±0.16	26.00±1.37	9.78±0.58	17.17±0.22	24.85±0.73	9.76±0.31	17.08±0.32	24.62±1.06	9.75±0.45
0.250	17.35±0.14	25.33±1.17	9.80±0.50	17.01±0.26	24.25±0.87	9.78±0.37	16.69±0.20	23.25±0.67	9.76±0.28
0.375	17.18±0.21	24.70±0.70	9.82±0.30	16.96±0.26	24.02±0.84	9.80±0.36	17.24±0.35	25.01±1.13	9.78±0.48
0.500	16.74±0.17	23.12±0.54	9.85±0.23	16.88±0.27	23.64±0.89	9.84±0.38	17.04±0.38	24.29±1.24	9.80±0.53
0.750	16.55±0.16	22.29±0.53	9.90±0.22	16.73±0.24	23.04±0.78	9.86±0.33	17.05±0.25	24.21±0.81	9.84±0.35
1.00	16.35±0.18	21.40±0.60	9.97±0.26	16.69±0.38	22.73±1.26	9.92±0.54	16.81±0.24	23.25±0.80	9.88±0.34
1.50	16.19±0.27	20.47±0.89	10.09±0.38	16.92±0.33	23.13±1.07	10.03±0.46	16.50±0.19	21.90±0.63	9.97±0.27
2.00	16.09±0.45	19.69±1.50	10.23±0.64	17.07±0.38	23.33±1.25	10.12±0.53	16.43±0.17	21.29±0.55	10.09±0.24
2.50	16.78±0.21	21.50±0.70	10.37±0.30	17.15±0.49	23.19±1.61	10.23±0.68	16.46±0.31	20.92±1.01	10.23±0.43
3.00	16.19±0.44	19.05±1.44	10.52±0.61	17.71±0.51	24.65±1.67	10.37±0.71	16.59±0.52	20.86±1.70	10.37±0.72

TABLE 4

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

Conc. (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	16.83±0.22	23.82±0.71	9.73±0.30	16.44±0.13	22.58±0.41	9.71±0.18	16.78±0.33	23.70±1.07	9.72±0.45
0.25	16.66±0.08	23.21±0.27	9.74±0.11	16.55±0.28	22.91±0.90	9.73±0.38	16.66±0.28	23.33±0.92	9.71±0.39
0.375	16.55±0.22	22.85±0.70	9.72±0.31	16.38±0.23	22.35±0.75	9.72±0.32	16.29±0.36	22.13±1.00	9.70±0.42
0.5	16.43±0.19	22.43±0.61	9.74±0.26	16.33±0.26	22.20±0.85	9.72±0.36	15.86±0.25	20.68±0.82	9.70±0.35
0.75	16.23±0.21	21.74±0.69	9.75±0.29	15.89±0.36	20.72±1.17	9.71±0.50	15.56±0.37	19.75±1.21	9.67±0.51
1.0	15.85±0.25	20.46±0.82	9.76±0.35	15.53±0.32	19.49±1.06	9.72±0.45	15.28±0.25	18.83±0.83	9.67±0.35
1.5	15.29±0.09	18.47±0.31	9.78±0.13	14.91±0.35	17.38±1.14	9.73±0.49	14.12±0.22	14.92±0.72	9.67±0.31
2.0	14.95±0.07	17.21±0.22	9.82±0.09	14.33±0.44	15.36±1.45	9.75±0.62	13.83±0.28	13.82±0.96	9.71±0.39
2.5	14.62±0.12	15.98±0.38	9.86±0.16	13.81±0.41	13.49±1.33	9.79±0.57	13.33±0.28	12.01±0.92	9.75±0.39
3.0	14.39±0.16	15.02±0.52	9.92±0.22	13.56±0.71	12.47±2.32	9.84±0.99	12.97±0.29	10.53±0.96	9.84±0.41

TABLE 5

Thermodynamic parameters of activation of flow at infinite dilution (values in kJ mol^{-1}, $\Delta\mu_1^{0\#}$ (for solvent) = 9.62 kJ mol^{-1})

Salt	$\Delta\mu_2^{0\#}$	$T\Delta S_2^{0\#}$	$\Delta H_2^{0\#}$	Ions	$T\Delta S_2^{0\#}$	$\Delta H_2^{0\#}$
NaCl	22.84	−36.1	−13.3	Na^+	−24.8	−7.8
NaBr	20.46	−56.9	−36.4	K^+	−11.3	−5.4
NaI	17.51	−57.3	−37.8	Cl^-	−11.3	−5.4
KCl	11.78	−22.6	−10.8	Br^-	−56.2	−52.6
KBr	9.41	−67.5	−58.1	I^-	−115.2	−109.8
KI	5.32	−126.5	−121.2			

act as structure breakers. One can obtain values for $T\Delta S_2^{0\#}$ and $\Delta H_2^{0\#}$ for the ions assuming equality of effects for the potassium and chloride ions [12]. The $T\Delta S_2^{0\#}$ and $\Delta H_2^{0\#}$ are negative in all cases suggesting that the transition is associated with bond making and an increase in order. This suggests that the slip-plane is in the disordered region.

Free volumes and internal pressures were calculated according to the procedures described previously [2]. The computed results are presented in Tables 6–11. Representative diagrams of free volume versus concentration at

TABLE 6

NaCl 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	1524.5	4.20	1.635	27414
	0.250	1532.0	4.14	1.642	27377
	0.500	1546.2	4.01	1.636	27449
	0.750	1560.1	3.91	1.625	27498
	1.000	1574.3	3.82	1.612	27509
303	0.125	1535.2	4.14	1.999	26046
	0.250	1542.5	4.09	1.989	26088
	0.500	1556.1	3.98	1.972	26149
	0.750	1571.0	3.87	1.958	26202
	1.000	1583.6	3.80	1.939	26156
308	0.125	1544.4	4.10	2.396	24894
	0.250	1551.7	4.04	2.380	24963
	0.500	1564.6	3.94	2.354	25028
	0.750	1577.5	3.85	2.326	25118
	1.000	1591.3	3.77	2.309	25073
313	0.125	1552.1	4.07	2.819	23928
	0.250	1559.2	4.01	2.799	23991
	0.500	1571.6	3.92	2.765	24047
	0.750	1580.3	3.85	2.721	24161
	1.000	1592.2	3.78	2.689	24146

TABLE 7

NaBr 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	1515.7	4.20	1.661	27239
	0.250	1521.7	4.16	1.676	27121
	0.500	1528.8	4.08	1.700	26849
	0.750	1536.2	3.94	1.723	26832
	1.000	1542.3	3.84	1.735	26707
303	0.125	1529.8	4.16	2.017	25938
	0.250	1532.2	4.11	2.029	25861
	0.500	1539.0	4.03	2.053	25617
	0.750	1545.3	3.89	2.073	25640
	1.000	1551.0	3.81	2.089	25488
308	0.125	1539.1	4.11	2.410	24828
	0.250	1541.3	4.07	2.420	24759
	0.500	1547.3	3.99	2.447	24533
	0.750	1553.4	3.86	2.470	24545
	1.000	1558.6	3.77	2.494	24414
313	0.125	1547.2	4.08	2.841	23849
	0.250	1548.9	4.04	2.851	23766
	0.500	1554.4	3.97	2.877	23558
	0.750	1560.1	3.85	2.906	23543
	1.000	1564.7	3.78	2.931	23363

TABLE 8

NaI 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	1515.0	4.22	1.689	27069
	0.250	1514.3	4.17	1.721	26836
	0.500	1512.3	4.07	1.778	26444
	0.750	1512.1	3.98	1.837	26043
	1.000	1511.4	3.89	1.893	26654
303	0.125	1525.3	4.17	2.044	25790
	0.250	1525.1	4.11	2.074	25625
	0.500	1522.1	4.03	2.141	25241
	0.750	1521.0	3.94	2.204	24844
	1.000	1520.0	3.85	2.267	24541
308	0.125	1534.6	4.12	2.450	24669
	0.250	1533.9	4.11	2.493	24332
	0.500	1530.1	3.99	2.574	24125
	0.750	1529.0	3.90	2.642	23831
	1.000	1526.8	3.82	2.705	23521
313	0.125	1542.3	4.09	2.870	23743
	0.250	1540.4	4.08	2.925	23426
	0.500	1536.6	3.97	3.013	23186
	0.750	1536.1	3.87	3.097	22931
	1.000	1532.6	3.80	3.163	22647

TABLE 9

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	1522.1	4.21	1.695	27052
	0.250	1528.3	4.16	1.723	26847
	0.500	1540.9	4.04	1.777	26553
	0.750	1552.9	3.94	1.753	26630
	1.000	1565.6	3.88	1.889	25930
303	0.125	1533.0	4.15	2.035	25871
	0.250	1539.0	4.11	2.068	25649
	0.500	1551.3	3.99	2.128	25413
	0.750	1561.9	3.90	2.191	25103
	1.000	1574.7	3.79	2.249	24862
308	0.125	1542.3	4.11	2.438	24728
	0.250	1548.2	4.07	2.463	24573
	0.500	1560.0	3.96	2.538	24332
	0.750	1569.0	3.87	2.596	24095
	1.000	1583.0	3.76	2.660	23868
313	0.125	1550.1	4.08	2.856	23808
	0.250	1555.7	4.05	2.893	23650
	0.500	1567.1	3.93	2.957	23468
	0.750	1576.0	3.84	3.020	23265
	1.000	1585.9	3.74	3.083	23065

TABLE 10

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	1517.1	4.20	1.780	27055
	0.250	1520.0	4.17	1.750	26687
	0.500	1524.1	4.06	1.841	26193
	0.750	1528.1	3.96	1.930	25695
	1.000	1532.0	3.89	2.023	25122
303	0.125	1528.1	4.16	2.057	25763
	0.250	1530.3	4.12	2.106	25494
	0.500	1534.3	4.01	2.204	25067
	0.750	1537.7	3.92	2.299	24631
	1.000	1541.1	3.85	2.405	24100
308	0.125	1537.1	4.12	2.450	24674
	0.250	1539.7	4.07	2.505	24440
	0.500	1543.0	3.96	2.617	24061
	0.750	1546.0	3.87	2.719	23693
	1.000	1549.0	3.80	2.821	23257
313	0.125	1545.0	4.09	2.870	23739
	0.250	1547.1	4.05	2.933	23502
	0.500	1548.0	3.95	3.048	23182
	0.750	1552.7	3.86	3.154	22838
	1.000	1555.5	3.79	3.273	22402

TABLE 11

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	1512.8	4.23	1.724	25831
	0.250	1511.4	4.18	1.789	26456
	0.500	1507.3	4.10	1.926	25621
	0.750	1505.1	3.98	2.050	25079
	1.000	1502.5	3.89	2.188	24408
303	0.125	1523.7	4.18	2.078	25620
	0.250	1522.0	4.12	2.150	25292
	0.500	1517.2	4.05	2.299	24534
	0.750	1514.4	3.93	2.446	24028
	1.000	1510.2	3.86	2.574	23486
308	0.125	1533.1	4.13	2.484	24525
	0.250	1531.0	4.08	2.565	24229
	0.500	1525.7	4.01	2.716	23575
	0.750	1522.2	3.90	2.883	23089
	1.000	1517.5	3.82	3.037	22462
313	0.125	1540.8	4.10	2.905	23600
	0.250	1538.4	4.04	2.995	23350
	0.500	1532.8	3.98	3.156	22744
	0.750	1528.4	3.88	3.322	22352
	1.000	1525.6	3.79	3.506	21846

various temperatures for sodium chloride and potassium iodide are presented in Figs. 2 and 3. In the case of sodium chloride solutions, free volumes decrease with an increase in the concentration of sodium chloride at all temperatures. The observed behavior can be explained on the basis of structure-making and structure-breaking properties of the ions in solution. In the case of the aqueous D-xylose solutions of sodium chloride, the decrease in free volume can be attributed to the hydration of the ions and the action of the ionic field to produce long-range order of solvent molecules. Since the structure-breaking ability increases in the order $I^- > Br^- > Cl^-$, one can conclude that the structure-making ability of the Na^+ ions (owing to their high charge density) dominates the structure-breaking ability of the Cl^- ions at all concentrations. In all other salts, the structure-breaking ability of the anions dominates and the free volumes increase at all temperatures. In all cases, the observed temperature effect on free volume is due to the variation of viscosity with temperature and the disruption of the solvents structure due to thermal agitation.

A quick study of the internal pressure values show that, except for NaCl solutions, the internal pressure decreases with an increase in concentration at all temperatures. In a given series, internal pressure values vary in the order:

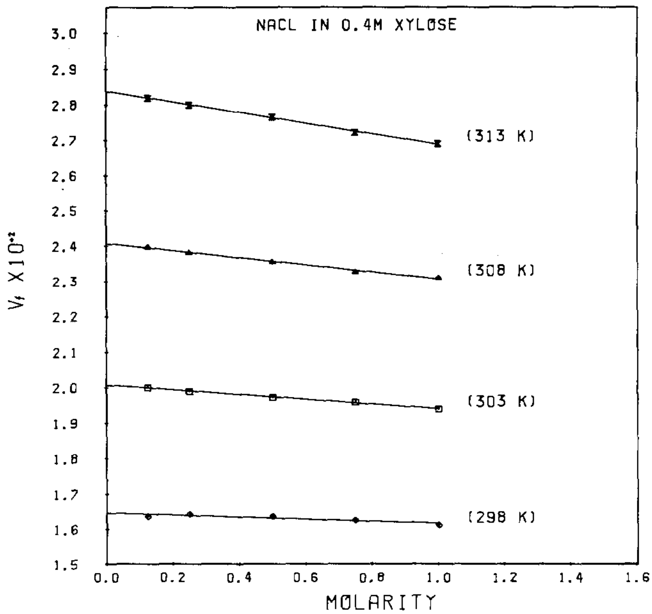

Fig. 2. Plot of V_f against molarity of NaCl in aqueous D-xylose solution.

$Cl^- > Br^- > I^-$. Higher values of internal pressure can be attributed to the electrostriction of the ions in the solution.

From the foregoing studies, one can conclude that the structure-breaking

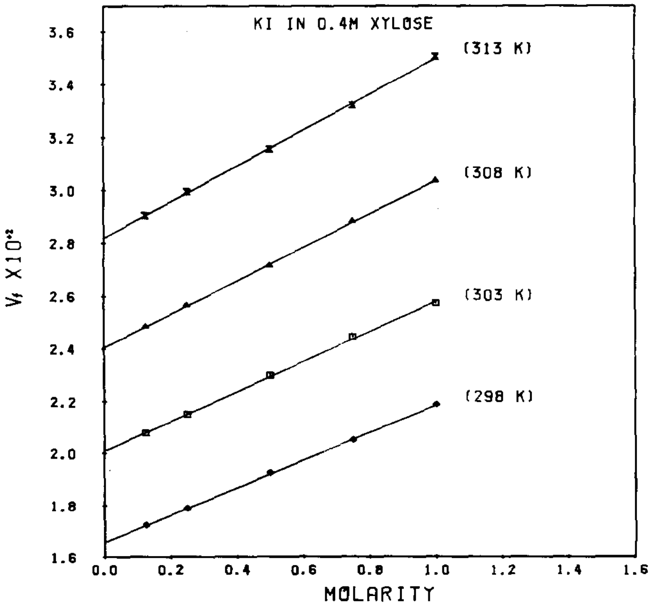

Fig. 3. Plot of V_f against molarity of KI in aqueous D-xylose solution.

ability of ions in aqueous 0.4 M D-xylose is in the following order: $I^- > Br^- > Cl^- > K^+ > Na^+$.

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