

Acoustic and viscosity studies of alkali metals and ammonium halides in aqueous dextran solutions at four different temperatures

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The density and viscosity of halides of potassium, sodium and ammonium have been measured in different aqueous solutions of dextran at 298.15, 303.15, 308.15 and 313.15 K and the ultrasonic velocity in these solutions has been measured at 298.15 K. Various parameters such as isentropic compressibility, acoustic impedance, apparent molar volume, partial molar volume, relative association and relaxation time have been calculated using experimentally determined values of ultrasonic velocity and density. The variation of these parameters has been discussed in the light of solute-solvent and solute-solute interactions. The viscosity data have been analyzed on the basis of Jones-Dole equation to interpret the ion-solvent interactions.

Keywords: Aqueous dextran solutions, Alkali metal halides, Apparent molar volumes, Isentropic compressibility

1 Introduction

Solvation dynamics^{1,2} has been the focus of intense research activities for the past few years. Experimental and theoretical studies have given rise to renewed interest in the field^{3,4}. Measurement of some bulk properties like viscosity (η), density (ρ) and ultrasonic velocity (U) provides insight into the intermolecular arrangements of the components in solutions and helps to understand the thermodynamics and acoustic properties of the solutions. Evaluations of partial molar quantities are of importance as they provide a lot of information regarding the ion-solvent interactions in various solutions. Since these quantities cannot be directly determined from the experiments, it is difficult to study the molecular interaction in ternary mixtures. However, these quantities are related to the corresponding apparent molar quantities which are directly determined.

In this paper, values of η , ρ , U and related acoustic parameters have been determined and the possible ion-ion and ion-solvent interactions for the solutions of KCl, NaCl, NH₄Cl, KBr and KI in 0.1, 0.5 and 1% (w/v) dextran in aqueous solution have been studied.

2 Theory

The apparent molar volume V_ϕ , was calculated from the density data by the standard equation⁵:

$$V_\phi = 1000 (cd_0)^{-1} (d_0 - d) + Md_0^{-1} \quad \dots (1)$$

where c is the molar concentration, d_0 is the density of the solvent, d is the density of the solution and M is the molar mass of the solute. The V_ϕ data were fitted to the Masson equation by least squares method⁵ and the limiting apparent volume, V_ϕ^0 was determined from the equation :

$$V_\phi = V_\phi^0 + S_v c^{1/2} \quad \dots (2)$$

where S_v is the slope in the V_ϕ versus $c^{1/2}$ plot.

The apparent molar expansibility E_ϕ was calculated by using the equation⁵:

$$E_\phi = \alpha_0 V_\phi + (\alpha - \alpha_0) 1000 c^{-1} \quad \dots (3)$$

The E_ϕ data were fitted into the Masson equation⁵ to get the limiting apparent expansibility (E_ϕ^0) and the slope (S_E) as follows :

$$E_\phi = E_\phi^0 + S_E c^{1/2} \quad \dots (4)$$

In Eq. (3), α and α_0 are the co-efficient of expansion of the solution and solvent, respectively, and were obtained from the usual relation^{5,6}.

The partial molar volume and partial molar expansibility have been calculated from the following equations⁵:

$$\bar{V}_2 = V_\phi + (1000 - c V_\phi) (2000 + S_v c^{3/2})^{-1} S_v c^{1/2} \quad \dots (5)$$

$$\bar{E}_2 = E_\phi + (1000 - c E_\phi) (2000 + S_E c^{3/2})^{-1} S_E c^{1/2} \quad \dots (6)$$

From the ultrasonic velocity and density data the values of adiabatic isentropic compressibility, K_s , apparent isentropic compressibility, $K_{s,\phi}$, acoustic impedance and solvation number, S_n of the solute have been calculated by using the following equations, respectively^{7,10,11}:

$$K_s = \left(\frac{1}{U^2 d} \right) \quad \dots (7)$$

where, U = ultrasonic velocity of the solution, d = density of the solution

$$K_{s,\phi} = 1000 K_s c^{-1} - K_s^0 d_0^{-1} (1000 c^{-1} d - M) \quad \dots (8)$$

$$Z = Ud \quad \dots (9)$$

$$S_n = n_1 n_2^{-1} [1 - V K_s (n_1 V_1^0 K_s^0)^{-1}] \quad \dots (10)$$

where, V = volume of the solution containing n_2 moles of the salt of molecular mass, M

V_1^0 = molar volume of the solvent,

n_1 = number of moles of the solvent

K_s^0 = the apparent isentropic molar compressibility at infinite dilution.

The molar sound velocity¹² (R), free volume (V_f), molar compressibility¹³ (W) and the increase in internal pressure (π_i) due to electrostatic field of the ion¹⁴ are also calculated by using the following equations, respectively:

$$R = \bar{M} d^{-1} U^{1/3}$$

$$V_f = V_m - b$$

$$W = K_s^{-1/7} \bar{M} d^{-1}$$

$$\pi_i = (K_s^0 - K_s)$$

$$\text{where, } \bar{M} = \frac{\sum n_i m_i}{\sum n_i}$$

$$b = \frac{\bar{M}}{d} \left[1 - \left(\frac{RT}{\bar{M}U^2} \right) \left\{ \left(1 + \frac{\bar{M}U^2}{3RT} \right)^{1/2} - 1 \right\} \right] \quad \dots (11)$$

The empirical equation of Jones-Dole¹⁵ relates the relative viscosity of an electrolytic solution to the concentration c of the electrolyte as follows :

$$\frac{\eta}{\eta_0} = 1 + A_F c^{1/2} + B_J c \quad \dots (12)$$

where, η = viscosity coefficient of the solution

η_0 = viscosity coefficient of the solvent

A_F = Falken-Halgen constant characteristic of the solute

B_J = Jones-Dole coefficient.

The constants A_F and B_J were determined from the intercept and slope of the linear plots of $(\eta/\eta_0 - 1)/c^{1/2}$ versus $c^{1/2}$. The viscosity data have been analyzed on the basis of transition state theory from the relation¹⁶:

$$\Delta\mu_2^{0*} = \Delta\mu_1^{0*} + \left(\frac{RT}{\bar{V}_1^0} \right) 1000 B_J - (\bar{V}_1^0 - \bar{V}_2^0) \quad \dots (13)$$

($\Delta\mu_2^{0*}$ = Contribution per mol of the solute to free energy of activation for viscous flow of the solution)

$$\Delta\mu_1^{0*} = 2.303 RT \log \left(\frac{\eta_0 \bar{V}_1^0}{hN} \right)$$

($\Delta\mu_1^{0*}$ = Contribution per mol of the solvent to free energy of activation for viscous flow of the solution)

$$\bar{V}_1^0 = \frac{M_{\text{solvent}}}{d} \quad \text{and} \quad \bar{V}_2^0 = V_\phi^0.$$

The viscosity relaxation time (τ) is to be computed from the relation:

$$\tau = \frac{4\eta}{3dU^2} \quad \dots (14)$$

3 Experimental Details

All chemicals used were of G R or B D H, analAR grades. Alkali metal halides were heated at 120°C for 4 h and kept along with ammonium chloride in vacuum desiccators over anhydrous calcium chloride until required. Conductivity of water (Sp. cond. $\sim 10^{-6}$ S cm⁻¹) was used for preparing water + dextran [0.1, 0.5 and 1.0%, (w/v)] mixtures. The dextran content in the mixed solvents was accurate within $\pm 0.01\%$. The salt solutions were prepared on the molal basis and conversion of molality to molarity was done by using the standard expression¹⁷ considering the density differences at the respective temperatures. Solutions were kept for 2 h in a water thermostat maintained at

the required temperature accurate to within ± 0.05 K before use for density measurements. Density measurements were done using a specific gravity bottle (25 ml capacity) as described earlier¹⁸. At least five observations were taken and differences in any two readings did not exceed $\pm 0.02\%$. Viscosity measurements were made using an Ostwald viscometer¹⁹ in a water thermostat whose temperature was controlled to ± 0.05 K. The values of viscosity so obtained were accurate to within $\pm 0.3 \times 10^{-3}$ c P. The viscosity values of water at the experimental temperatures were obtained from literature¹⁷. Ultrasonic velocity measurements on the solutions of the salts were made by using an Ultrasonic Interferometer (Mittal Enterprise, New Delhi, India) at frequency of 2 MHz at 298.15 K only. The accuracy of the ultrasonic velocity measurement is within ± 0.5 m/s. The salt content of the solutions varied over a concentration range of 4.0×10^{-3} to 8.0×10^{-2} M for all these measurements.

4 Results and Discussion

The values of V_ϕ^0 and S_v as obtained from Eq. (2) are given in Table 1. The positive and large values of S_v for alkali metals and ammonium halides in aqueous dextran solutions at the experimental temperatures indicate the presence of strong ion-ion interactions varying with change of temperature, halide salt and the solvent. The ion-ion interactions are more in aqueous dextran solutions than in water⁵. At a particular temperature S_v decreases as the dextran content in water increases and then increases with increase in dextran content in water. The V_ϕ^0 values are negative for almost all the salts in all solvents at the experimental temperatures. Since V_ϕ^0 is a measure of ion-solvent interaction, negative value indicates weak solute-solute interaction and also provides evidence of electrostriction which increases as the temperature increases for all the salts and in all the solvents. As observed, V_ϕ^0 varies similarly as S_v with the change of the dextran content in water.

The values of E_ϕ^0 and S_E as obtained from Eq. (4) are also given in Table 1. The E_ϕ^0 values are negative for all the salts in all solvents at the experimental temperatures excepting sodium chloride in 0.5% and potassium bromide in 1% dextran. Since E_ϕ^0 gives an indication of caging or packing effect¹⁴, the negative values of E_ϕ^0 suggest that the structure making effect of the salts is not favoured in aqueous dextran solutions in comparison with that in aqueous medium⁵.

Table 1 — Values of parameters, V_ϕ^0 ($\text{m}^3 \text{mol}^{-1}$), S_v ($\text{m}^{9/2} \text{mol}^{-3/2}$), E_ϕ^0 ($\text{m}^3 \text{mol}^{-1} \text{K}^{-1}$), S_E ($\text{m}^{9/2} \text{mol}^{-3/2} \text{K}^{-1}$) for KCl, NaCl, KBr, KI, and NH_4Cl in aqueous dextran solution at different temperatures

Wt % D	Temp /K	V_ϕ^0	S_v	E_ϕ^0	S_E
Potassium chloride					
0.1	298.15	-45.837	329.952	-0.029	24.292
	303.15	-6.658	302.727	-0.015	24.282
	308.15	-96.113	583.906	-0.048	24.383
	313.15	-99.601	602.619	-0.049	24.390
0.5	298.15	-38.194	243.130	-25.297	92.512
	303.15	-151.242	654.796	-25.334	92.648
	308.15	-160.517	690.819	-25.337	92.660
	313.15	-166.509	698.084	-25.339	92.662
1.0	298.15	-93.003	501.022	-21.182	81.022
	303.15	-187.566	867.094	-21.212	81.915
	308.15	-96.171	496.376	-21.183	81.796
	313.15	-228.520	1020.881	-21.225	81.964
Sodium chloride					
0.1	298.15	-34.656	214.674	-2.982	4.793
	303.15	-10.361	89.831	-2.973	4.748
	308.15	-130.584	571.168	-3.017	4.921
	313.15	-64.840	304.550	-2.993	4.825
0.5	298.15	-229.012	942.167	1.680	-2.063
	303.15	-252.668	1053.965	1.673	-2.028
	308.15	-298.970	1250.959	1.658	-1.966
	313.15	-180.064	806.872	1.696	-2.105
1.0	298.15	4.212	38.312	-2.520	7.469
	303.15	2.981	32.720	-2.520	7.467
	308.15	84.997	-267.351	-2.494	7.370
	313.15	64.618	-192.840	-2.501	7.394
Ammonium chloride					
0.1	298.15	-143.897	804.816	-22.605	63.967
	303.15	-217.872	976.684	-22.631	64.029
	308.15	-356.602	1539.264	-22.681	64.231
	313.15	-268.706	1174.247	-22.650	64.100
0.5	298.15	-102.950	505.455	-27.333	112.272
	303.15	-226.143	1015.854	-27.374	112.440
	308.15	-63.458	324.120	-27.320	112.212
	313.15	-282.227	1245.862	-27.392	112.516
1.0	298.15	-112.019	576.788	-8.622	21.262
	303.15	-143.629	693.312	-8.632	21.282
	308.15	-119.092	910.927	-8.650	21.369
	313.15	-180.986	845.129	-8.644	21.348
Potassium bromide					
0.1	298.15	168.336	-584.065	-43.585	179.752
	303.15	-41.621	285.193	-43.659	180.062
	308.15	-134.641	670.617	-43.693	180.199
	313.15	-134.360	639.244	-43.693	180.188

Contd —

Table 1 — Values of parameters, V_ϕ^0 ($\text{m}^3 \text{mol}^{-1}$), S_v ($\text{m}^{9/2} \text{mol}^{-3/2}$), E_ϕ^0 ($\text{m}^3 \text{mol}^{-1} \text{K}^{-1}$), S_E ($\text{m}^{9/2} \text{mol}^{-3/2} \text{K}^{-1}$) for KCl, NaCl, KBr, KI, and NH_4Cl in aqueous dextran solution at different temperatures — *Contd*

Wt % D	Temp /K	V_ϕ^0	S_v	E_ϕ^0	S_E
0.5	298.15	-48.725	284.141	-3.965	23.579
	303.15	-54.814	350.686	-3.967	23.601
	308.15	-7.037	171.626	-3.951	23.542
	313.15	-3.870	174.698	-3.950	23.543
1.0	298.15	21.396	47.365	1.849	-5.555
	303.15	7.189	109.207	1.845	-5.538
	308.15	-40.935	304.061	1.831	-5.483
	313.15	155.530	-409.174	1.886	-5.683
Potassium iodide					
0.1	298.15	45.949	329.952	0.004	24.292
	303.15	85.278	302.727	0.018	24.282
	308.15	-3.994	583.906	-0.014	24.383
	313.15	-7.313	602.619	-0.016	24.390
0.5	298.15	53.443	234.130	-25.267	92.512
	303.15	-59.460	654.796	-25.304	92.648
	308.15	-68.602	690.819	-25.307	92.660
	313.15	-74.426	698.084	-25.309	92.662
1.0	298.15	-293.455	1610.386	-12.133	47.521
	303.15	-374.394	1925.233	-12.156	47.610
	308.15	-318.340	1689.296	-12.140	47.543
	313.15	-291.494	1609.460	-12.132	47.521

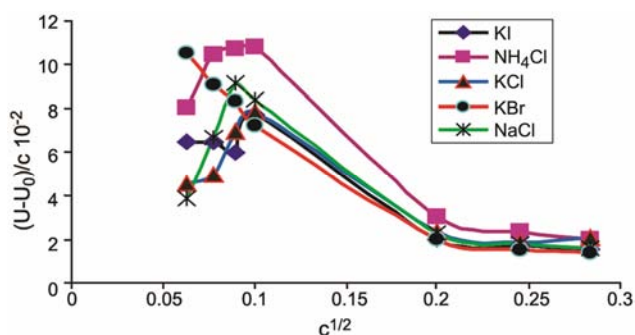


Fig. 1 — Variation of $(U - U_0)/c$ versus $c^{1/2}$ for different composition in 0.1 wt.% of dextran

A study of ultrasonic behaviour of solutions of alkali metals and ammonium halides in the mixed solvents shows that the sound velocity U increases as the proportion of dextran increases in water. The values of U were fitted to an equation of the form:

$$U = U_0 + Ac + Bc^{3/2} + Cc^2 \quad \dots (15)$$

The variation of $(U - U_0)/c$ versus $c^{1/2}$ indicates that in very low concentration of dextran is parabolic and thereafter increases linearly for three concentration of dextran 0.1, 0.5 and 1.0 wt.%. This trend fairly agrees with the Eq.(15), typical plots are shown in Fig. 1.

Table 2 — Values of parameters, A , B and C of equation (15), A' , B' , and C' of equation (16), $K_{s,\phi}^0$ ($\text{m}^3 \text{mol}^{-1} \text{Pa}^{-1}$) A'' and B'' of equation (17) and S_n^0 for KCl, NaCl, KBr, KI, and NH_4Cl in aqueous dextran solution at different temperatures

Constants	Wt % of D	KCl	NaCl	KBr	KI	NH_4Cl
$10^2 A$	0.1	6.486	6.672	17.457	10.016	13.462
$10^2 B$		-3.283	9.191	-125.606	-47.060	-45.886
$10^3 C$		-5.422	-10.888	24.411	5.603	0.850
$10^{-7} A'$		-5.388	-4.470	-7.440	-7.840	-8.755
$10^{-6} B'$		1.962	-0.241	4.172	4.308	3.008
$10^{-6} C'$		-1.562	5.818	-6.771	-7.765	-35.270
$10^{-4} K_{s,\phi}^0$		-6.608	-4.738	-7.454	-9.069	-9.318
$10^{-3} A''$	3.707	325.700	3.942	5.885	3.245	
$10^{-3} B''$	-6.277	5.296	-5.697	-12.400	2170.900	
S_n^0	53.457	59.889	70.008	65.003	86.931	
$10^2 A$	0.5	4.827	8.875	11.996	31.160	15.930
$10^2 B$		2.245	-17.572	-145.124	-229.630	-82.635
$10^3 C$		-5.611	-3.375	51.012	45.193	11.065
$10^{-7} A'$		-3.634	-5.449	-4.989	-19.570	-0.102
$10^{-6} B'$		48.360	1.084	3.171	14.080	5.425
$10^{-6} C'$		1.689	1.905	-6.221	-17.640	-7.579
$10^{-4} K_{s,\phi}^0$		-4.208	-9.009	-5.255	-20.300	-10.880
$10^{-3} A''$	1.227	4.288	3.373	14.780	5.986	
$10^{-3} B''$	-18.198	-5.162	-6.446	-28.900	-8.576	
S_n^0	52.836	80.060	47.899	141.772	95.011	
$10^2 A$	1.0	6.997	10.414	5.435	26.489	6.579
$10^2 B$		-5.800	-38.849	-19.526	-20.640	-54.699
$10^3 C$		-5.858	1.903	1.083	42.874	13.698
$10^{-7} A'$		-7.853	-8.319	-5.600	-18.124	-7.159
$10^{-6} B'$		3.885	3.855	3.650	13.876	3.973
$10^{-6} C'$		-4.998	-4.228	-7.206	-28.954	-6.255
$10^{-4} K_{s,\phi}^0$		-6.867	-5.826	-5.613	-20.273	-5.969
$10^{-3} A''$	3.437	1.507	3.840	15.800	3.107	
$10^{-3} B''$	-4.460	1.321	-7.700	33.200	-4.388	
S_n^0	77.864	83.990	63.116	137.233	68.351	

Over the concentration range studied, where U_0 is the sound velocity in pure solvent, A , B and C are the characteristic constants given in Table 2.

The values of isentropic compressibility, K_s as calculated by Eq. (7) were fitted to an equation of the form:

$$K_s = K_s^0 + A'c + B'c^{3/2} + C'c^2 \quad \dots (16)$$

where A' , B' and C' are constants and K_s^0 is isentropic compressibility of the solvent concerned.

The values of the constants A' , B' and C' are given in Table 2. As observed, the K_s value decreases as the proportion of dextran in water increases.

The values of $K_{s,\phi}$ computed by means of Eq. (8) were fitted into equation :

$$K_{s,\phi} = K_{s,\phi}^0 + A''c^{1/2} + B''c \quad \dots (17)$$

to obtain $K_{s,\phi}^0$, the limiting apparent molar isentropic compressibility and A'' and B'' are constants and are given in Table 2. As observed, the isentropic molar compressibility $K_{s,\phi}$ increases with increase in concentration of the solution. The values of $K_{s,\phi}$ and $K_{s,\phi}^0$ are negative (Table 2). The negative $K_{s,\phi}^0$ values can be explained in terms of loss of compressibility of surrounding solvent molecules due to strong electrostrictive forces in the vicinity of ions causing electrostrictive solvation of the ions. As observed, the $K_{s,\phi}^0$ values increase with increased proportion of dextran in water. This indicates that electrostrictive solvation of ions decreases as the dextran content increases. As observed, all these halides show an irregular trend of $K_{s,\phi}^0$ with increase of dextran content in water, typical plots are shown in Fig. 2.

A perusal of Table 2 shows that the values of solvation number, S_n^0 of the halides are very high in water + dextran mixtures. This is owing to the fact that the solvation layer formed around the ions is thick and/or hard in water + dextran mixtures. However, any discrepancy in the values of $K_{s,\phi}^0$ and S_n^0 may be due to characteristic structural changes. S_n^0 values for the halides are in the order: $\text{NH}_4\text{Cl} > \text{KBr} > \text{KI} > \text{NaCl} > \text{KCl}$. However, there is some discrepancy in 0.5% and 1.0% dextran solutions where KI has higher S_n^0 values than NH_4Cl .

As observed, the relative association R_A is a function of ultrasonic velocity. The relative association is influenced by two factors: (i) The breaking-up of the solvent structures on addition of solutes to it, and (ii) the solvation of solutes. The former results in decrease and the latter results in increase in R_A . The increase in R_A with concentration suggests that the solvation of the halide salts predominate over the breaking-up of the solvent structure. As observed, R_A increases linearly with concentration for all the five halides. This is depicted in Fig. 3 for 0.5% of dextran. At very dilute solution the decrease is due to breaking up of the dextran on addition of alkali halides.

A perusal of Table 3 shows that the values of A_F are negative in all cases excepting for KCl and KI in 1% and for NH_4Cl in all aqueous dextran solutions at all

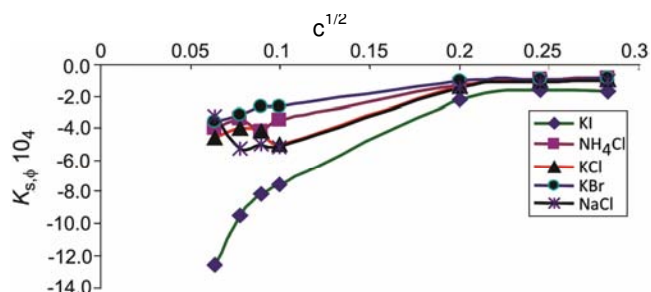


Fig. 2 — Variation of $K_{s,\phi}$ versus $c^{1/2}$ for different composition in 1.0 wt. % of dextran

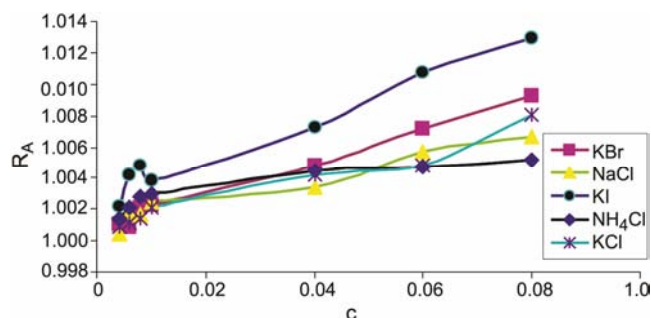


Fig. 3 — Variation of R_A versus c for different composition in 0.5 wt. % of dextran

temperatures. Since A_F is considered to be a measure of ion-ion interaction, the negative A_F values may indicate the presence of very weak ionic interactions in the solutions concerned. However, in the case of ionic interactions, it is evident that the interactions are dependent on the nature of the solute and also structure of the solvent.

The co-efficient B_j is a measure of the effective solvodynamic volume of solvated ions, and is governed by ion-solvent interactions, that is, the structural effect of the solvent in solution. It is a fact that when a solute dissolves in a solvent, some of the solvent molecules are attached to the ions (produced from the solutes) because of ion-solvent interactions, and this causes an increase in viscosity of the solution (a positive contribution to the co-efficient, B_j). On the other hand, these solvent molecules have to be wrenched out of the bulk solvent and this breaking of the solvent structure causes a decrease in viscosity of the solution (a negative contribution to B_j). Thus, the value of B_j in the solution is the resultant of these two opposing factors. The values of the coefficient B_j for all the salts are positive at all temperatures excepting a few cases indicating thereby the existence of ion-solvent interactions.

The viscosity data were also analyzed on the basis of the transition state theory for relative viscosity of the halide salt solutions as suggested by Feakins, *et al.*

Table 3 — Values of parameters, $A_F(\text{dm}^{3/2} \text{mol}^{-1/2})$ and $B_J(\text{dm}^{3/2} \text{mol}^{-1})$, of the Jones Dole equation and $\bar{V}_1^0(\text{cm}^{-3} \text{mol}^{-1})$, $\bar{V}_2^0(\text{cm}^{-3} \text{mol}^{-1})$, $\Delta\mu_1^{0*}(\text{kJ mol}^{-1})$ and $\Delta\mu_2^{0*}(\text{kJ mol}^{-1})$ of KCl, NaCl, KBr, KI, and NH_4Cl in aqueous dextran solution at different temperatures

Wt % D	Temp/ K	A_F	B_J	\bar{V}_1^0	\bar{V}_2^0	$\Delta\mu_1^{0*}$	$\Delta\mu_2^{0*}$
Potassium chloride							
0.1	298.15	-1.145	2.744	18.054	-45.837	66.328	443.023
	303.15	-0.329	1.203		-6.658	67.193	235.034
	308.15	0.745	1.207		-96.113	67.994	239.136
	313.15	-0.507	2.036		-99.601	68.900	362.289
0.5	298.15	-0.149	0.232	18.058	-38.194	66.545	98.274
	303.15	0.077	-0.550		-151.242	67.357	-9.623
	308.15	0.094	-0.487		-160.517	68.206	-1.105
	313.15	-0.191	0.197		-166.509	68.206	97.342
1	298.15	0.529	-1.445	18.063	-93.003	66.734	-131.660
	303.15	0.169	0.241		-187.566	67.522	100.979
	308.15	0.520	-1.422		-96.171	68.364	-133.465
	313.15	0.492	-1.666		-228.520	69.191	-171.212
Sodium chloride							
0.1	298.15	-1.285	4.872	18.054	-34.656	66.328	735.102
	303.15	-1.449	4.977		-10.361	67.193	761.858
	308.15	-0.835	2.811		-130.584	67.994	466.666
	313.15	-1.174	3.877		-64.840	68.900	627.887
0.5	298.15	-1.468	4.473	18.058	-229.012	66.545	680.213
	303.15	-1.274	4.021		-252.668	67.357	628.160
	308.15	-1.032	3.182		-298.970	68.206	519.247
	313.15	-1.098	3.267		-180.064	69.074	539.776
1	298.15	-0.662	2.340	18.063	4.212	66.734	387.858
	303.15	-0.407	1.329		2.981	67.522	252.920
	308.15	-0.384	1.307		84.997	68.364	253.714
	313.15	-0.221	1.086		64.618	69.191	225.676
Ammonium chloride							
0.1	298.15	0.013	-0.300	18.054	-143.897	66.328	24.994
	303.15	-0.229	0.694		-217.872	67.193	163.782
	308.15	0.418	-1.503		-356.602	67.994	-145.658
	313.15	0.012	-0.069		-268.706	68.900	58.707
0.5	298.15	0.024	-0.028	18.058	-102.950	66.545	62.606
	303.15	0.428	-1.514		-226.143	67.357	-144.136
	308.15	0.596	-2.014		-63.458	68.206	-217.525
	313.15	0.511	-1.859		-282.227	69.074	-199.172
1.0	298.15	0.430	-1.219	18.063	-112.019	66.734	-100.718
	303.15	0.768	-2.381		-143.630	67.522	-264.854
	308.15	1.143	-3.615		199.092	68.364	-444.164
	313.15	1.264	-4.173		-180.986	69.191	-532.457
Potassium bromide							
0.1	298.15	-0.671	1.833	18.054	168.336	66.328	318.177
	303.15	-0.633	1.645		-41.621	67.193	296.796
	308.15	-0.107	-0.053		-134.640	67.994	60.339
	313.15	-0.591	1.576		-134.360	68.900	295.931

Contd—

Table 3 — Values of parameters, A_F ($\text{dm}^{3/2} \text{mol}^{-1/2}$) and B_J ($\text{dm}^{3/2} \text{mol}^{-1}$), of the Jones Dole equation and \bar{V}_1^0 ($\text{cm}^{-3} \text{mol}^{-1}$), \bar{V}_2^0 ($\text{cm}^{-3} \text{mol}^{-1}$), $\Delta\mu_1^{0*}$ (kJ mol^{-1}) and $\Delta\mu_2^{0*}$ (kJ mol^{-1}) of KCl, NaCl, KBr, KI, and NH_4Cl in aqueous dextran solution at different temperatures — *Contd*

Wt % D	Temp/ K	A_F	B_J	\bar{V}_1^0	\bar{V}_2^0	$\Delta\mu_1^{0*}$	$\Delta\mu_2^{0*}$
0.5	298.15	-1.311	3.567	18.058	-48.725	66.545	556.040
	303.15	-1.140	3.247		-54.814	67.357	520.394
	308.15	-0.906	2.561		-7.037	68.206	431.511
	313.15	-1.134	3.316		-3.870	69.074	547.098
1.0	298.15	-0.236	0.493	18.063	21.396	66.734	134.391
	303.15	0.073	-0.568		7.189	67.522	10.209
	308.15	0.171	-0.833		-40.935	68.364	-49.773
	313.15	0.171	-0.505		155.530	69.191	-3.378
Potassium iodide							
0.1	298.15	-0.035	-0.212	18.054	45.949	66.328	37.199
	303.15	-0.189	0.352		85.278	67.193	116.410
	308.15	0.402	-1.792		-3.994	67.994	-186.346
	313.15	-0.060	-0.042		-7.313	68.900	62.766
0.5	298.15	-0.420	1.691	18.058	53.443	66.545	298.604
	303.15	-0.506	2.141		-59.460	67.357	366.004
	308.15	-0.510	2.159		-68.602	68.206	374.338
	313.15	-0.790	3.127		-74.426	69.074	519.685
1.0	298.15	0.290	-0.723	18.063	-293.455	66.734	-32.833
	303.15	0.622	-2.245		374.394	67.522	-245.297
	308.15	0.262	-0.708		-318.340	68.364	-32.355
	313.15	0.252	-0.464		-291.494	69.191	1.995

using Eq. (13). The values of \bar{V}_1^0 and \bar{V}_2^0 and that of $\Delta\mu_1^{0*}$ and $\Delta\mu_2^{0*}$ are presented in Table 3. The values of $\Delta\mu_2^{0*}$ indicate that the behaviour of $\Delta\mu_2^{0*}$ is quite similar to that of B_J in all cases. It follows that the formation of the transition state is accompanied by the rupture and distortion of the intermolecular forces in solvent structure

5 Conclusions

The results of the present investigation on the halides of alkali metals and ammonium reveal that the salts which show high ion-ion interaction show minimum ion-solvent interaction and vice versa. Formation of the transition state is accompanied by rupture of the intermolecular interaction.

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