Viscometric and thermodynamic studies of interactions in ternary solutions containing sucrose and aqueous alkali metal halides at 293·15, 303·15 and 313·15 K

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Abstract. Viscosities and densities of sucrose in aqueous alkali metal halide solutions of different concentrations in the temperature range 293·15 to 313·15 K have been measured. Partial molar volumes at infinite dilution (V_2^0) of sucrose determined from apparent molar volume (f_v) have been utilized to estimate partial molar volumes of transfer ($V_{2,tr}^0$) for sucrose from water to alkali metal halide solutions. The viscosity data of alkali metal halides in purely aqueous solutions and in the presence of sucrose at different temperatures (293·15, 303·15 and 313·5 K) have been analysed by the Jones–Dole equation. The nature and magnitude of solute–solvent and solute–solute interactions have been discussed in terms of the values of limiting apparent molar volume (f_v^0), slope (S_v) and coefficients of the Jones–Dole equation. The structure-making and structure-breaking capacities of alkali metal halides in pure aqueous solutions and in the presence of sucrose have been ascertained from temperature dependence of f_v^0.

Keywords. Ternary solutions; interactions of ionic and nonionic solutes; partial molar volumes; sucrose-alkali metal halide solutions.

1. Introduction

Studies on interactions of non-ionic solutes with ionic ones in different solvents are significant for investigating their physico-chemical behaviour.[1–3] The study of carbohydrates/saccharides has become a subject of increasing interest because of the multidimensional physical, biochemical and industrially useful properties of these compounds.[4–10] In addition to their importance in the food, pharmaceutical and chemical industries, simple saccharides have received considerable attention for their ability to protect biological macromolecues.[11,12] Sugars and polyols are well known stabilizing agents of proteins/enzymes[13,14] in their native state owing to their ability to enhance the structure of water. Various thermodynamic[10,15–18] and spectroscopic[19,20] studies have shown that the hydration of saccharides depends upon the number of hydroxy groups,[20,21] the potential hydrogen-bonding sites and relative positions of the next nearest neighbour hydroxy groups, within the carbohydrate molecules.[17,22]

Jha *et al*[23] have determined densities and viscosities of some alkali metal chlorides in (tetrahydrofuran + water) mixtures at different concentrations and temperatures. From the density data, apparent molar volumes have been derived and analysed using the Masson equation.[24] The limiting apparent molar volumes (f_v^0) and slopes (S_v) have been interpreted in terms of ion–solvent and ion–ion interactions respectively. The viscosity data have been analysed using the Jones–Dole equation.[25] The structure-making/breaking capacities of the salts have been inferred from the Hepler[26] and Sharma and Ahluwalia criteria.[27]

Banipal and coworkers[28] have determined apparent molar volumes of some disaccharides in water and in aqueous guanidine hydrochloride solutions at different concentrations and at 298·15 K from density measurements. Partial molar volumes at infinite dilution (V_2^0), determined from f_v values, have been utilized to estimate partial molar volumes of transfer ($V_{2,tr}^0$) of the disaccharides from water to aqueous guanidine hydrochloride solutions. The $V_{2,tr}^0$ values have been found to be positive for all the disaccharides and increase with increase in the concentration of the co-solute (guanidine) which suggests that the overall structural order is enhanced in aqueous guanidine hydrochloride solutions.

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Parmar and Dhiman[29] have recently reported studies on the determination of partial molar volumes of some mineral salts from density measurements in aqueous medium at different concentrations and temperatures. The results have been interpreted in term of ion–solvent and ion–ion interactions.

From the above survey of literature it appears that although studies of partial molar volumes and viscosities in binary systems are abundant, those on ternary systems are few. With this in view, the title study has been undertaken in the light of the following aspects.

(i) Determination of apparent molar volume (f_v) from density data as a function of molar concentration of sucrose in purely aqueous solutions and also in the presence of alkali metal halides (NaCl, KCl, KBr, KI) at different temperatures, 293·15, 303·15 and 313·15 K;

(ii) determination of limiting apparent molar volume (f_v^0) or partial molar volume at infinite dilution (V_2^0) of sucrose in purely aqueous solutions in the presence of alkali metal halides at different temperatures;

(iii) determination of partial molar volumes of transfer ($V_{2,tr}^0$) of sucrose from water to aqueous solutions of alkali metal halides at different temperature;

(iv) analysis of viscosity data of alkali metal halides in purely aqueous solutions and in the presence of sucrose at different temperatures by applying the Jones–Dole equation;[25] and

(v) ascertaining the structure-making and structure-breaking capacities of alkali metal halides in purely aqueous solutions and in the presence of sucrose from temperature dependence of f_v^0.

2. Experimental

Sucrose (Ranbaxy, India) and alkali metal halides (NaCl, KCl, KBr and KI) (AR, BDH) were dried over P_2O_5 in a vacuum desiccator for more than 48 h. The reagents were always placed in the desiccators over P_2O_5 to keep them in a dry atmosphere. Freshly prepared doubly distilled water (sp. conductivity $\sim 10^{-6}$ ohm^{-1} cm^{-1}) was used for preparing the solutions. An electrical balance with a least count of 1.0×10^{-4} g was used for measurement of mass.

Density was measured with the help of an apparatus similar to the one described by Ward and Millero[30] and followed by Parmar *et al*[31,32]. Viscosities of the solutions were measured at the desired temperature using an Ostwald's suspended level type viscometer

as per details described by Findlay.[33] Runs were repeated until three successive determinations were obtained within ± 0·1 s. Since all the flow times were greater than 100 s, kinetic energy correction was not necessary.[34]

Density and viscosity measurements were carried out in a thermostatted bath, the temperature of which was maintained within ± 0·01 K of the required value.

3. Results and discussion

Concentration variation of apparent molar volume is very useful for understanding the interactions in a system. The variation of apparent molar volume with concentration is expressed by Masson's equation,[24]

$$f_v = f_v^0 + S_v \quad C, \tag{1}$$

where f_v^0 is the limiting apparent molar volume and is equal to the partial molar volume at infinite dilution (V_2^0) of the solute and S_v is the experimental slope.

Values of f_v for sucrose in purely aqueous solutions as well as in the presence of 0·10 and 0·50 mol dm^{-3} alkali metal halides (NaCl, KCl, KBr, KI) have been determined as a function of the molar concentration of sucrose at different temperatures.

Values of limiting apparent molar volume (f_v^0) and the slopes (S_v) with respect to sucrose in purely aqueous solution as well as in 0·10 and 0·50 (mol dm^{-3}) solutions of alkali metal halides at different temperatures have been obtained from linear plots of f_v versus $\sqrt{C}$ (figures 1–3). It is seen that the value f_v^0 of sucrose in pure aqueous solution is positive and large (vide table 1) and that with rise of temperature from 293·15 to 313·15 K, f_v^0 increases sharply. In the presence of alkali metal halides, the values of f_v^0 are also positive and large. In view of the fact that f_v^0 is a measure of solute–solvent interaction,[35] it is concluded that positive and large values
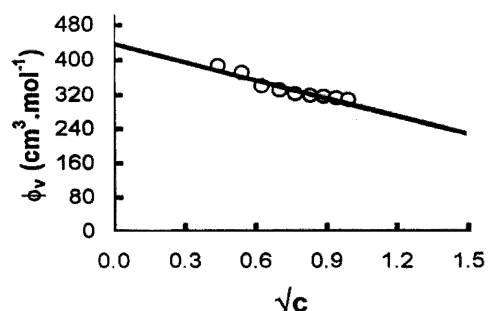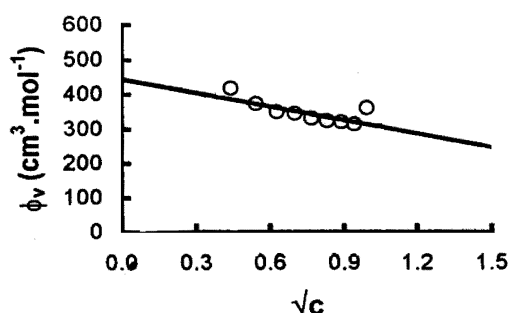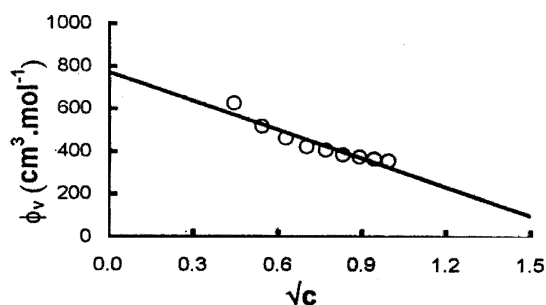

Figure 1. Variation of f_v with $\sqrt{C}$ for aqueous solution of sucrose at 293·15 K.

Table 1. Values of limiting apparent molar volume (f_v^0) and experimental slope (S_v) of sucrose in aqueous solutions of alkali halides at different temperatures.

Alkali halide	f_v^0 (cm^3 mol^{-1}) at [MX] (mol dm^{-3})			S_v (cm^3 dm$^{1/2}$ mol$^{-3/2}$) at [MX] (mol dm^{-3})		
	0·0	0·10	0·50	0·0	0·10	0·50
293×15 K						
NaCl	439·57	649·31	93·58	−140·09	−333·86	177·02
KCl	439·57	485·61	384·53	−140·09	−194·04	−237·95
KBr	439·57	520·11	1015·30	−140·09	−193·53	−646·59
KI	439·57	368·79	476·05	−140·09	−74·41	−175·23
303×15 K						
NaCl	446·93	374·73	116·09	−131·98	−358·66	156·31
KCl	446·93	451·48	374·95	−131·98	−150·19	−221·09
KBr	446·93	338·27	1097·70	−131·98	−328·66	−752·92
KI	446·93	393·61	480·69	−131·98	−97·39	−172·49
313×15 K						
NaCl	772·17	569·19	94·96	−446·52	−238·51	182·11
KCl	772·17	439·05	396·93	−446·52	−137·84	−250·63
KBr	772·17	606·77	1068·30	−446·52	−290·81	−717·11
KI	772·17	385·88	480·85	−446·52	−88·49	−176·46

Figure 2. Variation of f_v with $\sqrt{C}$ for aqueous solution of sucrose at 303·15 K.

Figure 3. Variation of f_v with $\sqrt{C}$ for aqueous solution of sucrose at 313·15 K.

of f_v^0 with respect to sucrose indicate the presence of strong solute–solvent interactions which become more pronounced at elevated temperatures. In the presence of 0·10 and 0·50 mol dm^{-3} aqueous alkali metal halides, the values of f_v^0 are also positive and large, which show that solute–solvent interactions are also strong in the presence of aqueous solutions of alkali metal halides.

A perusal of table 1 shows that the values of experimental slope S_v are negative and large both in pure aqueous solutions of sucrose as well as in the presence of 0·10 mol dm^{-3} and 0·50 mol dm^{-3} aqueous alkali metal halides except for NaCl for which the values of S_v are positive at higher concentrations. The large negative values of S_v indicate the presence of weak ion–ion interactions[29] at different temperatures.

Partial molar volume of transfer ($V_{2,\text{tr}}^0$) of sucrose from water to aqueous alkali metal halides solutions at infinite dilution has been estimated as below:

$$V_{2,\text{tr}}^0 = V_2^0 \text{ (in aqueous NaCl/KCl/KBr/KI)}$$
$$- V_2^0 \text{ (in water)}, \qquad (2)$$

The values of $V_{2,\text{tr}}^0$ of sucrose have been presented in table 2. It is seen that the values of $V_{2,\text{tr}}^0$ are positive for NaCl, KCl, and KBr but negative for KI. The positive values of $V_{2,\text{tr}}^0$ from water to aqueous NaCl, KCl and KBr solutions may be attributed to the decrease[28] in the volume of shrinkage because of stronger interactions between these alkali metal halides and the hydroxyl groups (–OH) of sucrose. The negative

Table 2. Partial molar volumes of transfer at infinite dilution ($V_{2,\text{tr}}^0$) of sucrose from water to aqueous alkali halide solutions at different temperatures.

	$V_{2,\text{tr}}^0$ (cm^3 mol^{-1})					
	[MX] = 0·10 (mol dm^{-3}) at			[MX] = 0·50 (mol dm^{-3}) at		
Alkali halide	293·15 K	303·15 K	313·15 K	293·15 K	303·15 K	313·15 K
NaCl	209·74	227·80	−202·98	−345·98	−330·84	−677·21
KCl	46·04	4·55	−333·12	−55·04	−71·98	−375·24
KBr	80·54	191·34	−165·40	575·73	650·77	296·13
KI	−70·78	−53·32	−386·29	36·48	33·76	−291·32

values of $V_{2,\text{tr}}^0$ in the case of KI may be ascribed to the interactions between iodide ion and the hydrophobic part or group of the sucrose molecule.

Viscosities of aqueous solutions of alkali metal halides have been determined as a function of their concentration in the absence and presence of 0·10 and 0·50 mol dm^{-3} sucrose at different temperatures. Viscosity data have been analysed in the light of Jones–Dole equation.[25]

$$h/h_0 = h_{\text{rel}} = 1 + A\sqrt{C} + BC$$

or

$$(h_{\text{rel}}-1)/\sqrt{C} = A + B\sqrt{C}. \qquad (3)$$

From the linear plots of $(h_{\text{rel}}-1)/\sqrt{C}$ versus $\sqrt{C}$ (presented in figures 4–6), the values of coefficients A and B of the Jones–Dole equation have been determined and the results have been presented in table 3. It is seen that the values of A are positive for all the alkali metal halides in purely aqueous solutions, which indicate the presence of strong ion–ion interactions over the concentration range 0·2 to 2·0 mol dm^{-3} On the other hand, the values of coefficient B are negative which indicate the existence of weak ion–solvent interactions. However, in the presence of sucrose, the values of coefficient A are negative and indicate the presence of weak ion–ion interactions in the presence of increasing amounts (0·10–0·50 mol dm^{-3}) of sucrose, which may be attributed to the formation of a sheath of sucrose molecules around the ions resulting in the weakening of ion–ion attraction. On the other hand, the values of B become positive in the presence of 0·10 and 0·50 mol dm^{-3} sucrose. The positive value of B may be ascribed to the increased ion–solvent interactions owing to the structure-making tendency of the sucrose molecules.
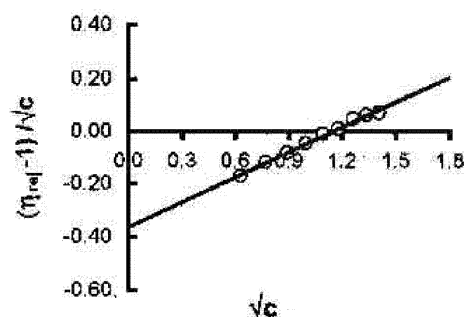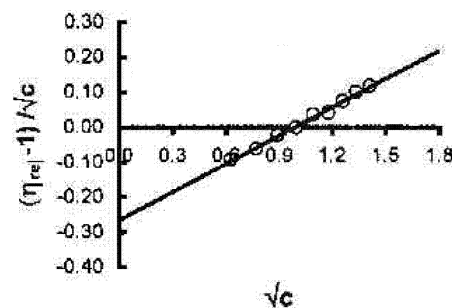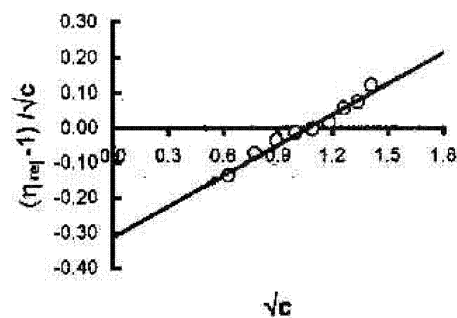

Figure 4. Variation of $(h_{\text{rel}}-1)/\sqrt{C}$ with $\sqrt{C}$ for NaCl in aqueous sucrose (0·1 M) at 293·15 K.

Figure 5. Variation of $(h_{\text{rel}}-1)/\sqrt{C}$ with $\sqrt{C}$ for NaCl in aqueous sucrose (0·1 M) at 303·15 K.

Figure 6. Variation of $(h_{\text{rel}}-1)/\sqrt{C}$ with $\sqrt{C}$ for NaCl in aqueous sucrose (0·1 M) at 313·15 K.

Table 3. Values of constants A and B of Jones–Dole equation for alkali halides in aqueous solutions of sucrose at different temperatures.

| | A (dm$^{3/2}$ mol$^{-1/2}$) | | | B (dm^3 mol^{-1}) | | |
| | [Sucrose] (mol dm^{-3}) | | | [Sucrose] (mol dm^{-3}) | | |
Alkali halide	0·0	0·10	0·50	0·0	0·10	0·50
293·15 K						
NaCl	0·0879	−0·3640	−0·0284	−0·0724	0·3159	0·0289
KCl	0·1338	−0·2463	−0·1322	−0·0860	0·0983	0·0440
KBr	0·1062	−0·2576	−0·0909	−0·0992	0·1077	0·1160
KI	0·0316	−0·3074	−0·1375	−0·0183	0·1244	0·0490
303·15 K						
NaCl	0·1468	−0·2659	−0·0721	−0·0542	0·2694	0·2073
KCl	0·2328	−0·1817	−0·1776	−0·1608	0·0894	0·0428
KBr	0·1360	−0·1679	−0·1616	−0·0903	0·0779	0·1441
KI	0·1035	−0·2080	−0·1761	−0·0674	0·0817	0·0391
315·15 K						
NaCl	0·0512	−0·3113	−0·1318	−0·1144	0·2908	0·0984
KCl	0·1277	−0·2159	−0·1635	−0·0910	0·1013	0·0643
KBr	0·1269	−0·2161	−0·1124	−0·0920	0·1010	0·0965
KI	0·0766	−0·2576	−0·1382	−0·0383	0·1123	0·0451

Table 4. Values of limiting of apparent molar volume (f_v^0) and experimental slope (S_v) of alkali halides in aqueous solutions of sucrose at different temperatures.

| | f_v^0 (cm^3. mol^{-1}) | | | S_v (cm^3 dm$^{1/2}$ mol$^{-3/2}$) | | |
| | [Sucrose] (mol dm^{-3}) | | | [Sucrose] (mol dm^{-3}) | | |
Alkali halide	0·0	0·10	0·50	0·0	0·10	0·50
293·15 K						
NaCl	−513·46	249·60	118·20	344·07	−129·36	−97·50
KCl	−499·67	218·45	134·35	343·29	−111·18	−97·55
KBr	−494·60	308·15	304·35	340·34	−148·53	−164·39
KI	−497·95	271·60	271·45	349·14	−135·39	−135·17
303·15 K						
NaCl	−400·76	260·52	167·87	253·51	−137·24	−137·69
KCl	−401·71	219·49	140·87	263·22	−110·31	−101·78
KBr	−392·91	311·15	282·63	257·66	−149·18	−148·32
KI	−376·04	282·63	275·91	250·98	−142·49	−137·69
315·15 K						
NaCl	−520·36	255·11	160·72	351·22	−133·87	−132·85
KCl	−510·24	216·44	132·90	352·63	−109·53	−96·42
KBr	−495·70	306·16	249·70	341·90	−146·19	−121·45
KI	−490·38	277·51	269·13	344·80	−138·12	−132·85

Values of f_v of alkali metal halides have been determined as a function of concentration in purely aqueous solutions as well as in the presence of 0·10 and 0·50 mol dm^{-3} sucrose at different temperatures. Values of f_v^0 and S_v have been obtained at different temperatures from the linear plots of f_v versus $\sqrt{C}$ and are presented in table 4. It is seen that values of f_v^0 are largely negative but become largely positive in the presence of 0·10 and 0·50 mol dm^{-3} sucrose. From this it is concluded that in pure aqueous solu-

Values of coefficients a_i for alkali halides in aqueous solutions of sucrose (temperature dependence of f_v^0)

| | [Sucrose] (mol dm^{-3}) | | | | | | | | |
| | 0.00 | | | 0.10 | | | 0.50 | | |
	a_0	a_1	a_2	a_0	a_1	a_2	a_0	a_1	a_2
	-145032.31	950.021516	-1.55905	-7326.6265	49.779895	-0.08165	-26585.395	174.37583	-0.2841
	-95123.57	625.445935	-1.03245	-1629.3968	12.298335	-0.020405	-6274.9812	42.398815	-0.07005
	-94334.718	619.82612	-1.0224	-3330.0885	24.122185	-0.03995	-4040.0033	31.250615	-0.05605
	-109047.57	716.570375	-1.18125	-7227.8696	49.254225	-0.08075	-4853.7002	33.95806	-0.0562

Table 6. Limiting apparent molar expansibility (f_E^0) for various alkali halides in aqueous solutions of sucrose at different temperatures.

| | f_E^0 [cm^3 mol^{-1} K^{-1}] for [sucrose] (mol dm^{-3}) | | | | | | | | |
| | 0.00 at | | | 0.10 at | | | 0.50 at | | |
Alkali halide	293.15 K	303.15 K	313.15 K	293.15 K	303.15 K	313.15 K	293.15 K	303.15 K	313.15 K
NaCl	35.9505	4.7695	-26.4115	1.9085	0.2755	-1.3575	7.8080	2.1260	-3.5560
KCl	20.1205	-0.5285	-21.1775	0.3085	-0.1005	0.5095	1.3285	-0.0725	-1.4735
KBr	20.3930	-0.0550	-20.5030	0.6995	-0.0995	-0.8985	-1.6115	-2.7325	-3.8535
KI	24.3930	0.3785	-23.2465	1.9105	0.2955	-1.3195	1.0080	-0.1160	-1.2400

tions of alkali metal halides the ion–solvent interactions are weak but are rendered stronger in the presence of 0·10 and 0·50 mol dm^{-3} sucrose. On the other hand, the values of S_v are largely positive in purely aqueous solutions of alkali halides but become largely negative in the presence of 0·10 and 0·50 mol dm^{-3} sucrose, thereby indicating the presence of strong ion–ion interactions in pure aqueous solution of alkali metal halides, which are rendered weaker in the presence of sucrose.

Thus, identical conclusions in regard to ion–ion and ion–solvent interactions are obtained from the viscometric and apparent molar volume data in respect of solutions of alkali metal halides in pure aqueous solutions as well as in aqueous sucrose solutions of different concentration.

The temperature dependence of f_v^0 follows the equation,[36]

$$f_v^0 = a_0 + a_1 T + a_2 T^2. \qquad (4)$$

Values of coefficients a_i have been calculated and are listed in table 5. Limiting apparent molar expansibility f_E^0 has been calculated from the following,[36]

$$f_E^0 = (\partial f_v^0 / \partial T)_P. \qquad (5)$$

These values are listed in table 6. It is seen that the values of f_E^0 decrease in magnitude with rise in temperature for all the alkali metal halides. This is true both in pure aqueous solutions as well as in the presence of 0·10 and 0·50 mol dm^{-3} sucrose. From this, it follows that the behaviour of alkali metal halides is like that of common salt,[37,38] NaCl.

Hepler[26] has proposed a method by which qualitative information on hydration of solutes can be obtained from thermal expansion of aqueous solution by the following relation:

$$(\partial C_P^0 / \partial P)_T = -T(\partial^2 f_v^0 / \partial T^2)_P.$$

Table 7. Values of $(\partial^2 f_v^0 / \partial T^2)_p$ for alkali halides in aqueous solutions of sucrose

| Alkali halide | $(\partial^2 f_v^0 / \partial T^2)_p$ for [sucrose] (mol dm^{-3}) | | |
	0·00	0·10	0·50
NaCl	−3·1181	−0·1633	−0·5682
KCl	−2·0649	−0·0409	−0·1401
KBr	−2·0448	−0·0799	−0·1121
KI	−2·3625	−0·1615	−0·1124

According to this the left hand side of the above equation should be positive for structure-breaking solutes, and therefore, structure-breaking solutes posses negative values of $[\partial^2 f_v^0 / \partial T^2]_P$. On the other hand, positive values of $[\partial^2 f_v^0 / \partial T^2]_P$ should be associated with structure-making solutes.

In the present studies the values of $[\partial^2 f_v^0 / \partial T^2]_P$ have been obtained from (4) and are listed in table 7. It is seen that the values are negative in pure aqueous alkali metal halide solutions as well as in the presence of sucrose solutions. Thus, NaCl, KCl, KBr and KI behave as structure-breakers in these systems.[26]

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