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Ultrasonic studies on interionic interactions of some alkali metal halides in aqueous d-glucose solution at varying molalities and temperatures

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Abstract

The present experimental investigation was carried out in order to explore the possible molecular interionic interactions of alkali metal halides namely, sodium chloride, potassium chloride, potassium bromide and potassium iodide in aqueous D-glucose solution at 303.15, 308.15K and 313.15 K. Experimental values of density (ρ), viscosity (η) and ultrasonic velocities (U) were carried out on the liquid ternary mixtures of water +D-glucose + alkali metal halides The binary solvent mixture of water + D-glucose was prepared under molality(m) basis say, at two fixed molalities (0.2 and 0.4mol.kg^{-1}). Alkali metal halides (NaCl, KCl, KBr and KI) were added under different molalities with these binary solvent mixtures. The related and relevant parameters correlated to our present study such as adiabatic compressibility (β), molal hydration number (n_H), apparent molal compressibility (φ_k), apparent molal volume (φ_v), limiting apparent molal compressibility (φ_K^0), limiting apparent molal volume (φ_V^0) and their associated constants (S_K, S_V), partial transfer volume ($\Delta_{\varphi_V^0}$) from water to aqueous solution were determined. In order to stress more on the viscometric data to substantiate its importance, the viscosity B-coefficient has been meticulously evaluated, The present investigation has exploited the possible molecular associations such as ion-ion, ion-solvent, solute-solvent, solute-solute etc., which are identified and eventually discussed about the behaviour of solutes (alkali metal halides) in the solvent mixture.

Keywords: Molal hydration number, adiabatic compressibility, structure-maker, viscosity, B- coefficient, transfer volume, limiting apparent molal volume

INTRODUCTION

Saccharides are very important for some physiological processes. They are not only the basic material for energy metabolism in organisms, but also play a significant role in the configuration of biological molecules [1,2].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 [3-9]. In addition to their importance in the food, pharmaceutical and chemical industries, simple saccharides have received considerable attention for their ability to protect biological macromolecules [10,11]. Sugars and polyols are well known stabilizing agents of proteins/enzymes [12, 13] in their native state owing to their ability to enhance the structure of water. Saccharides and their derivatives as the most abundant class of biomolecules are known to exist in wide range of forms, which is a reflection of their biological versatility and the great diversity of their biological functions such as structural, protective metabolic and recognition. The saccharide components of cell membranes are the receptors of biologically active components (enzymes, drugs, etc). Saccharides are able to stabilize the native state of proteins/enzymes [14-16]. Interactions of electrolytes with

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saccharides are very important in exploring the stability of polysaccharides in biological systems as well as in the chemical industry of saccharides. It is an essential component for maintaining cell viability, a natural cell-protecting agent, as well as an energy reservoir in many organisms [17]. It has been found that the decomposition, synthesis, metabolism and transmembrane transport of saccharides have relationships with the concentration of H+, Na+ and other metal ions in body-fluid. So the study of the interaction between alkali metal halides and aqueous D-glucose is valuable to examine the influence of electrolytes on some physiological behavior and helpful to understand the essence of some biological phenomena.

Various thermodynamic [10,18-19] and spectroscopic [20,21] studies have shown that the hydration of saccharides depends upon the number of hydroxyl groups [21,22] the potential hydrogen bonding sites and relative positions of the next nearest neighbour hydroxy groups within the carbohydrate molecules [23]. Jha et al [24] 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. Banipal and coworkers [25] 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 determined from φ_V values have been utilized to estimate partial molar volumes of transfer of the disaccharides from water to aqueous guanidine hydrochloride solutions. Parmar and Dhiman [26] have recently reported 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.

Our earlier literature survey shows that although studies of inter-ionic interactions and viscosities in binary mixtures are abundant, those of ternary systems are few. Taking this in view, we have carried out the present investigation in the light of the following aspects.

- Determination of adiabatic compressibility (β), molal hydration number (n_H) as a function of molal concentration of alkali metal halides namely NaCl, KCl, KBr and KI in aqueous D-glucose solutions at different temperatures (303.15, 308.15 and 313.15 K)

- Determination of apparent molal compressibility (φ_k), apparent molal volume (φ_v), limiting apparent molal compressibility (φ_K^0), and its related constant (S_k), limiting apparent molal volume (φ_v^0) and its related constants (S_v), partial transfer volume ($\Delta \varphi_v^0$) and

- To shed more details on the viscometric study, viscosity B-coefficient of Jones-Dole equation has also been evaluated.

EXPERIMENTAL

D-glucose (SRL, India) and alkali metal halides, namely NaCl, KCl, KBr and KI (AR, BDH) were dried over P_2O_5 in vacuum desiccators for more than 48h. The reagents were always placed in the desiccators over P_2O_5 to keep them in dry atmosphere. Freshly prepared doubly distilled water (sp. conductivity -10^{-6} ohm^{-1}cm^{-1}) was used for preparing the solutions at different concentrations. Aqueous solutions were prepared and used on the day they were prepared. The required quantity of alkali metal halide for a given molality was

dissolved in the binary mixture and similar procedure was adapted for different molalities. The chemicals were weighed in an electronic digital balance (SHIMADZU AX-200, Japan Make) with a least count of 0.0001g. The density was determined using a specific gravity bottle by relative measurement method with an accuracy of ±0.01kgm^{-3}. An Ostwald's viscometer of 10ml capacity was used for the viscosity measurement. Efflux time was determined using a digital chronometer within ±0.01s. An Ultrasonic Interferometer having the fixed frequency of 2MHz (Mittal Enterprises, New Delhi-Model: F-81) with an overall accuracy of 2ms^{-1} has been used for velocity measurement. An electronically digital operated constant temperature bath (RAAGA Industries, Chennai) has been used to circulate water through the double walled measuring cell made up of steel containing the experimental solution at desired temperature, whose accuracy is maintained at ± 0.1K.

RESULTS AND DISCUSSION

From Table 1, one can notice that in all the four alkali metal halide systems which were taken for study, the values of density increases with increase in concentration of metal halides as well as aqueous D-glucose content (0.2 mol Kg^{-1} and 0.4 mol Kg^{-1}) and the same decreases with change of temperature. But however the ultrasonic velocity found to be increasing with increase in concentration of alkali metal halides and the content of aqueous D-glucose as well as with rise in temperature. Such an observed increase in the ultrasonic velocity values which suggests that disruption of water structure is enhanced with the addition of solvent (aqueous D-glucose solution) and the solutes.(alkali metal halides). Moreover, the increase in ultrasonic velocity in these solutions further be attributed as the cohesion brought about the ionic hydration.

Table 1. Values of density (ρ), viscosity (η) and Ultrasonic velocity (U) of alkali metal halides in aqueous D-glucose solution at different temperatures.

Molality (mol.kg^{-1})	0.2 m			0.4 m			0.2 m			0.4 m			0.2 m			0.4 m		
	Temperature (K)																	
	303.15	308.15	313.15	303.15	308.15	313.15	303.15	308.15	313.15	303.15	308.15	313.15	303.15	308.15	313.15	303.15	308.15	313.15
Sodium chloride + aqueous D-glucose solution																		
0.00	1005.60	1005.01	1004.57	1012.31	1010.62	1008.13	0.9685	0.8832	0.8032	1.0343	0.9377	0.8467	1527.31	1531.96	1536.09	1538.31	1541.63	1544.58
0.05	1010.71	1009.91	1008.67	1017.94	1015.89	1013.13	0.9838	0.8976	0.8161	1.0522	0.9552	0.8683	1533.00	1538.27	1542.11	1544.94	1547.06	1550.76
0.10	1015.96	1014.97	1013.87	1022.83	1021.01	1018.33	0.9988	0.9118	0.8301	1.0686	0.9700	0.8769	1539.10	1544.31	1548.72	1550.26	1553.64	1556.12
0.15	1021.23	1020.07	1019.11	1028.17	1026.42	1023.33	1.0148	0.9262	0.8442	1.0840	0.9847	0.8907	1545.37	1556.48	1554.08	1556.37	1559.53	1562.04
0.20	1026.36	1025.26	1024.41	1033.28	1031.86	1028.73	1.0301	0.9407	0.8583	1.0999	0.9997	0.9056	1551.67	1556.63	1560.44	1562.10	1564.97	1568.33
0.25	1031.18	1030.38	1029.38	1038.56	1036.92	1034.31	1.0450	0.9557	0.8717	1.1156	1.0153	0.9200	1558.14	1562.48	1566.35	1568.04	1570.03	1572.57
0.30	1037.40	1035.99	1034.81	1043.59	1041.19	1039.28	1.0616	0.9705	0.8857	1.1313	1.0292	0.9339	1564.34	1568.54	1572.29	1574.35	1576.81	1578.91
Potassium chloride + aqueous D-glucose solution																		
0.00	1005.60	1005.01	1004.57	1012.31	1010.62	1008.13	0.9685	0.8832	0.8032	1.0343	0.9377	0.8467	1527.31	1531.96	1536.09	1538.31	1541.63	1544.58
0.05	1011.45	1010.01	1009.09	1020.81	1018.41	1017.11	1.0051	0.9296	0.8703	1.0691	1.0010	0.9288	1532.48	1536.02	1541.14	1543.01	1546.47	1549.36
0.10	1016.53	1015.13	1014.88	1025.93	1023.51	1022.31	0.9998	0.9246	0.8659	1.0645	0.9962	0.9241	1537.18	1540.84	1545.92	1547.71	1551.31	1554.14
0.15	1022.34	1020.83	1019.15	1031.78	1028.78	1027.71	0.9952	0.9201	0.8599	1.0597	0.9912	0.9195	1541.89	1545.68	1550.68	1552.43	1556.17	1558.90
0.20	1027.61	1026.18	1024.99	1037.63	1033.81	1032.34	0.9899	0.9151	0.8555	1.0560	0.9861	0.9141	1546.61	1550.51	1555.42	1557.11	1561.05	1563.65
0.25	1032.74	1030.58	1029.16	1042.51	1039.21	1038.61	0.9844	0.9091	0.8490	1.0499	0.9811	0.9096	1551.32	1555.36	1560.18	1561.82	1565.87	1568.43
0.30	1037.83	1036.12	1034.97	1046.71	1044.91	1043.18	0.9788	0.9041	0.8446	1.0439	0.9762	0.9038	1556.04	1560.20	1564.96	1566.54	1570.71	1573.19
Potassium bromide + aqueous D-glucose solution																		
0.00	1005.60	1005.01	1004.57	1012.31	1010.62	1008.13	0.9685	0.8832	0.8032	1.0343	0.9377	0.8467	1527.31	1531.96	1536.09	1538.31	1541.63	1544.58
0.05	1012.18	1010.28	1009.98	1024.77	1022.98	1020.56	0.9915	0.9254	0.8622	1.0580	0.9791	0.9068	1531.98	1535.83	1540.28	1542.76	1545.55	1548.34
0.10	1017.36	1015.59	1015.31	1029.96	1028.07	1025.78	0.9890	0.9229	0.8598	1.0556	0.9765	0.9043	1536.08	1539.75	1544.14	1546.86	1549.47	1552.36
0.15	1022.69	1020.95	1020.47	1035.05	1033.23	1031.00	0.9865	0.9204	0.8568	1.0529	0.9739	0.9017	1540.29	1543.66	1548.02	1551.06	1553.41	1556.36
0.20	1028.08	1026.29	1025.76	1040.38	1038.47	1036.24	0.9840	0.9177	0.8541	1.0505	0.9713	0.8991	1544.42	1547.59	1551.86	1555.31	1557.33	1560.47
0.25	1033.27	1031.78	1030.12	1045.44	1043.68	1041.39	0.9812	0.9152	0.8505	1.0478	0.9686	0.8962	1548.57	1551.53	1555.72	1559.70	1561.26	1564.60
0.30	1038.68	1036.62	1034.34	1050.82	1048.54	1046.61	0.9785	0.9119	0.8467	1.0453	0.9655	0.8934	1552.73	1555.44	1559.60	1564.22	1565.17	1568.71
Potassium iodide + aqueous D-glucose solution																		
0.00	1005.60	1005.01	1004.57	1012.31	1010.62	1008.13	0.9685	0.8832	0.8032	1.0343	0.9377	0.8467	1527.31	1531.96	1536.09	1538.31	1541.63	1544.58
0.05	1017.29	1014.50	1012.35	1047.86	1043.95	1040.67	0.9931	0.8975	0.8085	1.0766	0.9754	0.8855	1530.48	1534.17	1539.02	1540.47	1544.07	1547.63
0.10	1022.36	1019.83	1017.64	1052.43	1049.18	1045.58	0.9877	0.8922	0.8034	1.0710	0.9705	0.8805	1533.99	1537.70	1542.55	1543.98	1547.57	1551.14
0.15	1027.58	1025.10	1022.76	1057.22	1054.45	1051.03	0.9827	0.8871	0.7981	1.0654	0.9655	0.8757	1537.51	1541.22	1546.06	1547.49	1551.08	1554.66
0.20	1032.87	1030.21	1028.07	1062.01	1059.63	1056.07	0.9777	0.8818	0.7924	1.0599	0.9597	0.8706	1541.02	1544.73	1549.58	1551.01	1554.60	1558.17
0.25	1038.18	1035.67	1033.31	1067.14	1065.06	1061.24	0.9723	0.8766	0.7866	1.0533	0.9542	0.8639	1544.34	1548.26	1553.11	1554.53	1558.11	1561.69
0.30	1043.45	1040.32	1038.43	1071.93	1070.30	1066.41	0.9669	0.8705	0.7813	1.0477	0.9484	0.8580	1548.07	1551.80	1556.62	1558.04	1561.63	1565.22

Incidentally, the density (ρ) which is a measure of solvent-solvent and ion-solvent interactions. Increase of density with concentration indicates the increase in solvent-solvent and solute-solvent interactions, whereas the decrease in density indicates the lesser magnitude of solute-solvent and solvent-solvent interactions. Increase in density with concentration is due to the shrinkage in the volume which in turn is due to the presence of solute molecules. In other words, an increase in density may be interpreted to the structure-maker of the solvent due to the added solute and the decrease in density with concentration indicates structure-breaker of the solvent [27]. However, our present investigation finds that the increase in density and ultrasonic velocity with rise in temperature suggest that decrease in intermolecular forces due to increase in thermal energy of the system.

The perusal of Table 2 exhibits the values of adiabatic compressibility (β), which are found to be decreased with increase in molal concentration of solutes and content of D-glucose as well as rise in temperature. Such a decrease in adiabatic compressibility observed in this alkali metal halide with aqueous D-glucose in the present system clearly confirms the conclusions drawn from the ultrasonic velocity data. It is well known 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 interaction. Since, the solvent molecules are oriented in the ionic field (ie electrostatic field of ions $-CH_2OH$ and CHO). The solvent molecules are more compactly packed in the primary salvation shells as compared to the packing in the absence of the ions. This is the reason, why the solvent is compressed by the introduction of the ions. Thus, the electrostatic field of the ions causes the compression of the medium giving rise to a phenomenon called *'Electrostriction'*. Since the water molecules are compressed, they do not respond to a further application of pressure. So the solutions become harder to compress. This will lead to the decrease in compressibility values. This may further ascribed that such a decrease in adiabatic compressibility (β) is attributed to the influence of the electrostatic field of ions (Na^+, Cl^-, K^+, Br^-, I^-….etc) on the accompanying molecules. It may be inferred that weakening of hydrogen bond strength formed by the solute and solvent molecules may also be the reason for decrease in compressibility.

Table 2. Values of adiabatic compressibility (β) and molal hydration number (n_H) of alkali metal halides in aqueous D-glucose solution at different temperatures.

Molality (mol.kg^{-1})	β / (× 10^{-10}m²N¹)						n_H					
	0.2 m			0.4 m			0.2 m			0.4 m		
	Temperature (K)											
	303.15	308.15	313.15	303.15	308.15	313.15	303.15	308.15	313.15	303.15	308.15	313.15
Sodium chloride + aqueous D-glucose solution												
0.00	4.2630	4.2397	4.2188	4.1744	4.1634	4.1578	-	-	-	-	-	-
0.05	4.2216	4.1987	4.1782	4.1355	4.1266	4.1191	5.2243	5.1885	5.1636	4.8372	4.5958	4.8293
0.10	4.1820	4.1622	4.1399	4.0980	4.0869	4.0814	5.1092	4.9131	5.0263	4.7592	4.7768	4.7731
0.15	4.1423	4.1248	4.1059	4.0602	4.0495	4.0431	5.0742	4.8529	4.7915	4.7361	4.7358	4.7760
0.20	4.1028	4.0876	4.0688	4.0226	4.0119	4.0056	5.0481	4.8187	4.7748	4.7210	4.7243	4.7531
0.25	4.0648	4.0506	4.0365	3.9849	3.9741	3.9700	4.9996	4.7940	4.6453	4.7167	4.7237	4.6934
0.30	4.0264	4.0137	4.0045	3.9477	3.9383	3.9350	4.9707	4.7726	4.5475	4.7003	4.6780	4.6365
Potassium chloride + aqueous D-glucose solution												
0.00	4.2630	4.2397	4.2188	4.1744	4.1634	4.1578	-	-	-	-	-	-
0.05	4.2126	4.1902	4.1741	4.1158	4.1107	4.1087	6.3552	6.2668	5.6816	7.2857	6.5785	6.1290
0.10	4.1647	4.1479	4.1387	4.0736	4.0695	4.0666	6.2008	5.8203	5.1015	6.2750	5.8613	5.6978
0.15	4.1229	4.1104	4.0972	4.0286	4.0261	4.0244	5.8902	5.4646	5.1626	6.0480	5.7119	5.5530
0.20	4.0798	4.0702	4.0614	3.9840	3.9830	3.9826	5.7732	5.3714	5.0099	5.9213	5.6253	5.4710
0.25	4.0378	4.0288	4.0278	3.9431	3.9477	3.9426	5.6792	5.3463	4.8673	5.7577	5.3829	5.3770
0.30	4.0032	4.0010	3.9960	3.9046	3.9078	3.9025	5.4579	5.0404	4.7286	5.5930	5.3122	5.3136
Potassium bromide + aqueous D-glucose solution												
0.00	4.2630	4.2397	4.2188	4.1744	4.1634	4.1578	-	-	-	-	-	-
0.05	4.2068	4.1790	4.1687	4.0986	4.0874	4.0841	7.0838	7.6902	6.3705	9.4280	9.4741	9.1990
0.10	4.1598	4.1366	4.1212	4.0532	4.0418	4.0391	6.5083	6.5388	6.2151	7.5443	7.5870	7.4172
0.15	4.1129	4.0892	4.0753	4.0088	3.9975	3.9952	6.3087	6.3606	6.0937	6.8697	6.9011	6.7700
0.20	4.0664	4.0478	4.0296	3.9643	3.9527	3.9510	6.1956	6.0790	6.0240	6.5343	6.5697	6.4572
0.25	4.0215	4.0091	3.9881	3.9214	3.9103	3.9091	6.0919	5.8460	5.8785	6.2983	6.3161	6.2148
0.30	3.9763	3.9641	3.9523	3.8778	3.8671	3.8670	6.0224	5.8195	5.6539	6.1482	6.1580	6.0506
Potassium iodide + aqueous D-glucose solution												
0.00	4.2630	4.2397	4.2188	4.1744	4.1634	4.1578	-	-	-	-	-	-
0.05	4.1803	4.1548	4.1384	4.0114	4.0023	3.9957	10.4190	10.7469	10.2269	20.2663	20.0887	20.2255
0.10	4.1275	4.1115	4.0969	3.9536	3.9487	3.9403	8.5468	8.1262	7.7628	13.7416	13.4023	13.5875
0.15	4.0749	4.0579	4.0484	3.9049	3.8993	3.8994	7.9049	7.6810	7.2357	11.1792	10.9835	10.7581
0.20	4.0212	4.0059	3.9888	3.8588	3.8533	3.8500	7.6202	7.4060	7.3227	9.8156	9.6699	9.6100
0.25	3.9675	3.9550	3.9484	3.8112	3.8083	3.8050	7.4531	7.2176	6.8898	9.0399	8.8625	8.8158
0.30	3.9162	3.9070	3.8954	3.7638	3.7589	3.7519	7.2839	7.0257	6.8614	8.5110	8.4079	8.4461

The hydration number that usually reflects the electrostriction effect of the alkali metal halides in the vicinity of the water molecules. From Table 2, one can observe that the values of n_H are positive in all the four liquid systems studied and such positive values of n_H indicate an appreciable salvation of solutes [28]. It can be taken as an added support for the structure making nature of solutes as well as the presence of dipolar interactions between the solutes and water molecules. This parameter also suggests that the compressibility of the solution will be less than that of the solvent, resulting in solutes will gain more mobility and have a more probability of contacting solvent molecules. This may enhance the interaction between the solute solvent molecules. Our present study shows that he values of n_H which are decreasing with increasing molal concentration of solutes (alkali metal halides) and content of D-

glucose as well as rise in temperature. The decreasing value of n_H suggest that an enhancement of solute- co-solute interactions. Further the decreasing values of n_H with rise in temperature clearly indicates that the strength of the interactions get weakened among the solute- solvent molecules.

It can be qualitatively ascribed that, when the alkali metal halides are dissolved in water + D-glucose mixtures, the water molecules are attached to the ions strongly to the electrostatic forces, which introduce a greater cohesion in the solutions [29] resulting the increasing of cohesion, whenever an increase of metal halide concentration in the solution. Such an increased association observed in the solution may also be due to the water structure enhancement brought about by the increased electrostriction in the presence of D-glucose. Similar effect was reported by earlier workers [30].

Molal compressibility and volume studies

The following observations from Table 3 noticed by the authors on apparent molal compressibility (φ_k) and apparent molal volume (φ_v) of alkali metal halides namely NaCl, KCl, KBr and KI in aqueous D-glucose solution at 303.15, 308.15 and 313.15 K which are listed as

i.   The values of φ_k and φ_v are all negative over the entire range of molality of solutes as well as solvent.
ii. In the present study, it is observed that the values of φ_k and φ_v which are found to be increased with increase in molal concentration of solute (alkali metal halides) and rise in temperature, and however the same found to be decreased with increase in molal concentration of solvent (aqueous D-glucose solution).
iii. Our present study also observes that the maximum value of φ_k and φ_v recorded for NaCl system which indicates that molecular interaction is more pronounced in that system.

Further, from Table 3, the magnitude of φ_k and φ_v, the molecular interaction is of the order NaCl > KCl > KBr > KI.

All the above observation clearly shows that the solute – solvent interactions taking place in all the four liquid systems. The negative values of φ_k and φ_v indicates hydrophilic interactions occurring in these systems. As more number of water molecules is available at lower concentration of metal halides, the chances for the penetration of solute molecules in the solvent mixtures are highly favored [31]. Our present decreasing trend of φ_k and φ_v values with increasing molal concentration of aqueous D-glucose content reveals that the weakening solute – solvent interactions in the mixtures.

The evaluated parameter limiting apparent molal compressibility (φ_k^0) which provide informations regarding the ion – solvent interactions and its related constant (S_k) of the ion – ion interaction in the solution, which are systematically tabulated in Table 4. The authors noticed that the values of φ_k^0 negative in all the systems and decreases with increasing concentration of the solute as well as the aqueous D-glucose content (except in the first system, where it is found to be increased) and the same increases with change of temperature. The magnitude of negative values of φ_k^0 is higher in NaCl system suggesting that the presence of strong ion – solvent interactions, which are more pronounced in this system comparing the other. This once again supports our earlier conclusion. Generally, the decreasing values of φ_k^0 with elevation of temperature shows that the weakening of ion – solvent interactions in the solution. Its related constant (S_k) whose values are positive in all the four systems studied. These are tabulated in Table 4. From this tabulation, one can notice that the values of S_k increases with increasing molal concentration of solutes (metal halides) and aqueous D-glucose content. The increasing trend in the solution attributing the presence of ion – ion interaction of the solution. However the same found to be decreased with the elevation of temperature suggesting the weakening of ion – ion interactions in the liquid mixtures.

Table 3. Values of apparent molal compressibility (φ_k) and apparent molal volume (φ_v) of alkali metal halides in aqueous D-glucose solution at different temperatures.

Molality (mol.kg^{-1})	$-\varphi_k$ / ($\times 10^{-5}$m^{2}N^{-1})						$-\varphi_v$ / (m^{2}N^{-1})					
	0.2 m			0.4 m			0.2 m			0.4 m		
	Temperature (K)											
	303.15	308.15	313.15	303.15	308.15	313.15	303.15	308.15	313.15	303.15	308.15	313.15
Sodium chloride + aqueous D-glucose solution												
0.05	12.6257	12.0554	11.8409	12.4230	12.1590	11.9181	101.5728	91.0852	88.3379	111.1730	114.9211	100.5243
0.10	12.5050	11.9483	11.7077	12.1147	11.9948	11.8431	103.2633	99.0453	90.5281	107.0241	104.2346	101.1195
0.15	12.4655	11.8959	11.5355	12.0532	11.9295	11.8235	103.5616	99.9740	95.1069	106.3655	104.1686	100.4582
0.20	12.4088	11.8421	11.4793	11.9158	11.8454	11.7623	103.1638	99.9409	94.3603	103.6160	102.5525	99.8299
0.25	12.3238	11.7590	11.2896	11.8884	11.8309	11.7060	103.0445	98.9657	94.7486	103.1913	102.2952	100.8417
0.30	12.2325	11.6963	10.9691	11.8464	11.6986	11.6569	101.8711	98.1830	90.6938	102.7105	100.7714	101.7477
Potassium chloride + aqueous D-glucose solution												
0.05	15.0483	14.1120	13.0069	18.7285	16.9711	15.6745	116.2743	99.42732	96.68361	167.8591	154.0890	140.7809
0.10	14.5915	13.4460	12.2995	15.6961	14.7002	14.1884	111.6005	100.6213	101.7608	134.4701	127.4717	121.9341
0.15	14.0732	12.9842	12.1427	15.0715	14.1420	13.7542	110.9044	102.8767	95.68816	128.1479	119.7207	116.9744
0.20	13.8237	12.9395	12.0914	14.7378	13.6274	13.3629	109.3630	105.2482	100.1179	124.9869	110.6503	110.6757
0.25	13.6081	12.7596	11.5081	14.2322	13.3369	13.2219	107.8813	102.0144	91.66653	119.2574	113.0845	110.9832
0.30	13.0843	12.1705	11.2641	13.7198	13.1807	13.0679	103.7113	99.39415	90.94317	113.1986	111.9367	109.6011
Potassium bromide + aqueous D-glucose solution												
0.05	16.8223	16.5857	14.5496	25.4392	25.3809	24.5266	130.7488	104.7562	107.5893	246.0521	244.4846	235.3675
0.10	15.3020	14.7714	14.2595	19.3956	19.3425	18.8355	116.8268	105.1542	106.7936	174.2362	172.5485	167.5191
0.15	14.8342	14.5142	14.0143	17.2895	17.2058	16.8392	113.1805	105.6185	105.3993	149.6389	147.5144	144.3078
0.20	14.5918	14.0776	13.9047	16.2693	16.2049	15.9136	111.6557	105.7512	105.3496	138.5257	136.1847	134.0412
0.25	14.3507	13.6151	13.5152	15.5824	15.4521	15.1865	109.9453	103.6020	101.6166	130.7910	127.9620	125.9768
0.30	14.2285	13.5840	12.8683	15.1757	15.0243	14.7360	103.7280	103.7280	94.51573	126.6881	123.6347	121.3279
Potassium iodide + aqueous D-glucose solution												
0.05	26.4488	24.9713	22.5983	60.1358	59.6887	59.2430	232.3329	188.6887	154.7269	659.5154	659.4308	645.3870
0.10	20.6525	19.0618	17.6651	38.6173	37.3567	37.2581	166.5016	147.2960	129.9414	396.1573	381.3837	373.1007
0.15	18.7467	17.7628	16.4465	30.3097	29.6400	29.0129	145.5522	133.1005	120.5498	295.5952	288.9652	283.5289
0.20	17.8658	16.9967	16.3874	26.0221	25.5948	25.2539	135.4256	125.2067	115.8545	245.3142	242.3107	237.2551
0.25	17.3405	16.5533	15.7543	23.5661	23.2035	23.1144	129.4292	121.8635	117.0590	216.4890	216.0990	216.5137
0.30	16.9028	16.0486	15.5105	21.8752	21.6328	21.5335	125.2990	116.9481	112.1880	196.1527	195.6891	192.5354

Table 4. Values of limiting apparent molar compressibility (φ_k^0) and limiting apparent molar volume (φ_v^0) their constant S_k and S_v of alkali metal halides in aqueous D-glucose solution at different temperatures

Alkali metal halides	Molality (mol.kg⁻¹)	φ_k^0 (×10⁻⁸ m²N⁻¹)			S_k (×10⁻⁸ N⁻¹ m¹ mol⁻¹)			φ_v^0 (× m³ mol⁻¹)			S_v (×10⁻⁸ N⁻¹ m¹ mol⁻¹)		
		303.15	308.15	313.15	303.15	308.15	313.15	303.15	308.15	313.15	303.15	308.15	313.15
NaCl	0.2	-12.8847	-12.2991	-12.4635	1.1337	1.0729	2.4604	-102.3352	-90.4624	-87.1755	-1.0182	-18.3396	-12.6844
	0.4	-12.7313	-12.4318	-12.1018	1.7121	1.2929	0.7848	-116.1554	-119.8069	-100.0519	25.9497	37.1161	-1.7380
KCl	0.2	-16.3784	-15.2153	-14.0589	5.7976	5.3182	4.9716	-123.4870	-99.7150	-105.0160	33.5198	-4.6622	21.9794
	0.4	-20.9679	-18.7763	-16.9549	13.8813	11.0236	7.6217	-191.9361	-173.2236	-155.5502	150.1594	124.8473	91.8025
KBr	0.2	-18.0556	-18.0726	-15.7285	7.51570	8.7889	4.6485	-139.8142	-106.2481	-117.2331	60.6894	3.6656	33.9109
	0.4	-30.2861	-30.3121	-29.1882	29.9602	30.2476	28.5254	-301.2999	-300.9856	-288.5451	347.5819	352.4196	331.4234
KI	0.2	-30.7931	-28.6676	-25.3167	27.5795	25.0243	19.6271	-280.7197	-222.6654	-173.7690	309.5608	207.6279	120.6796
	0.4	-78.9403	-77.7396	-77.1122	112.7615	111.1944	110.3425	-884.8792	-874.0594	-853.0065	1362.4926	1346.1540	1308.6820

The perusal of Table 4 represents the values of (S_v) which are exhibiting the positive values in all the four liquid systems studied. (Except in NaCl system, in which the values are negative at lower molality and becomes positive at higher molality of the solvent content) and decrease with increase in molal concentration of solutes (alkali meal halides) and content of solvent (aqueous D-glucose solution).However, the same is found to be increased with the rise of temperature. This may enhance/reduce electrostriction of water molecules. The negative values of φ_v^0 for the systems indicate the existence of smaller solute-solute interactions. Further, the decrease in φ_v^0 for alkali metal halides indicate the solute-solute interactions decreasing with increase of aqueous D-glucose content. Further, the increasing trend of limiting apparent molal volume values with the elevation of temperature too suggests the weakening of solute-solute interaction. The values of (φ_v^0) are reported in Table 4 which are all negative in all the four systems studied. The negative values of S_v indicate the presence of solute-solute interaction and less complex ion formation taking place in the systems. For saccharide, the values of S_v increases with increasing concentration of alkali metal halides which indicate the decreased solute-solute interaction present in the mixture.

Partial transfer volume studies

The co-sphere overlap model [32] can be utilized to rationalize the partial transfer volume values ($\Delta\varphi_v^0$) in terms of solute–co – solute interactions. Our present study shows that the value of partial transfer volume of alkali metal halides in aqueous D-glucose solution are all almost negative and (from Fig I) they become non-linear with increase in concentration of the solutes (alkali metal halides) as well as aqueous D-glucose content. The non-linear behavior of $\Delta\varphi_v^0$ values indicates weaking of interactionsbetween the D-glucose and co-solutes (NaCl/ KCl/ KBr/ KI). Based on this model, the transfer volume $\Delta\varphi_v^0$ can be interpreted that ions of co – solute and D-glucose comes into play because of the interactions between

i. ions of co–solutes (NaCl/ KCl/ KBr/KI) and hydrophobic, - OH sites of saccharide molecules and
ii. Ions of co–solutes and hydrophilic parts/groups of the saccharide molecules.

From our present investigation, we realized the feasibility of former type of interaction contributes the non-linear behavior between solutes and co – solutes and there is no feasibility for the existence of second type of interactions. Further the non-linear nature of the $\Delta\varphi_v^0$ values over the rise of temperature clearly supporting our above cause. Hence, it may be presumed from the $\Delta\varphi_v^0$ values studied, the hydrophobic-ionic interactions dominate over hydrophilic-ionic interactions in the present study.
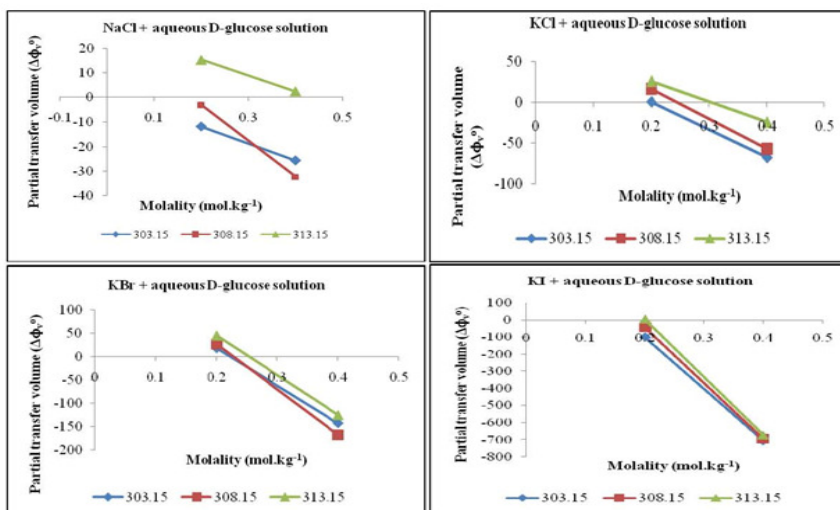

Fig 1. Value of partial transfer volume ($\Delta\varphi_v^0$) with molality of aqueous D-glucose solution different temperatures

Viscometric Studies

Viscosity is another important parameter in understanding the structure as well as molecular interactions occurring in the solutions. From Table 1, the values of viscosity decreases with increasing molal concentration of solutes and aqueous D-glucose content, whereas a reverse trend is observed in NaCl system. But however, the same is found to be decreased with increase of temperature. This increasing or decreasing trend indicates the presence of molecular interactions occurring in these systems. In order to shed more light on this, role of viscosity B-coefficient has also been obtained. From Table 5, it is observed that the values of A are almost positive in all the systems. (Except in NaCl, where the values are negative at lower molality and becomes positive at higher molality of the solvent). Since A is a measure of ionic interactions [33], this behaviour shows the existence of strong ion-ion interactions prevailing in NaCl system comparing the other three systems.

Table 5. Values of partial transfer volume ($\Delta\phi_v{}^o$), A and B co-efficient of Jones – Dole equation of alkali metal halides in aqueous D-glucose solution at different temperatures

Alkali metal halides	Molality (mol.kg^{-1})	Partial transfer volume ($\Delta\phi_v{}^o$)			A (dm$^{3/2}$mol$^{-1/2}$)			B(dm^{3}mol^{-1})		
		303.15	308.15	313.15	303.15	308.15	313.15	303.15	308.15	313.15
NaCl	0.2	-11.8040	-2.9898	15.2459	-0.0020	-0.0022	-0.0071	0.3223	0.3322	0.3566
	0.4	-25.6242	-32.3343	2.3695	0.0130	0.0162	0.0461	0.2884	0.2957	0.2481
KCl	0.2	0.7653	16.5449	26.5368	0.2551	0.3449	0.5333	-0.4487	-0.5763	-0.8437
	0.4	-67.6838	-56.9637	-23.9974	0.2277	0.4302	0.6078	-0.3988	-0.6821	-0.9300
KBr	0.2	18.3010	26.3239	45.7081	0.1563	0.3003	0.4580	-0.2624	-0.4617	-0.6879
	0.4	-143.1847	-168.4086	-125.6039	0.1501	0.2778	0.4382	-0.2501	-0.4289	-0.6494
KI	0.2	-101.3465	-43.2525	5.6565	0.1814	0.1315	0.0803	-0.3503	-0.2964	-0.2432
	0.4	-705.5060	-694.6465	-673.5810	0.2750	0.2727	0.3104	-0.4797	-0.4792	-0.5427

Further, B-coefficient which is also known as a measure of order or disorder which is introduced by solute with the solvent molecules. It is also measure of ion-solvent interactions in the liquid mixtures. In our present study, the B-values are positive in NaCl system and are negative in all the remaining systems. The positive values of B may be ascribed to the increased ion-solvent interactions owing to the structure-making tendency of the D-glucose molecules. The positive values of B-coefficient clearly suggest that the existence of strong ion – solvent interaction. Hence, a strong molecular interaction is found to exist in NaCl system comparing the other three liquid systems. The decreasing behaviour of viscosity values with rise of temperature clearly establishes the weakening of ion – solvent interaction in the solvent mixture.

Hence, it is very obvious that our present investigation clearly establishes the molecular interactions are more pronounced in NaCl system comparatively with other three systems and such interactions are of the order: NaCl > KCl > KBr > KI.

CONCLUSION

In the present investigation, density, viscosity and ultrasonic velocity data have been measured for alkali metal halides in aqueous D-glucose solution at 303.15, 308.15 and 313.15 K and their acoustical parameters have been applied to explore the possible molecular interaction existing in the present system of mixtures. From the trends and behaviour of acoustical parameters, the authors have summarized their investigations as follows,

- A very weak molecular interionic interactions such as solute-solvent, ion-ion, ion-solvent, solute-solute, solute-solvent etc., are generally observed in the present systems of liquid mixtures.
- Our viscometric study also diagnoses that a weak ion-ion and ion-solvent interactions are existing in the present study.

- The trends of our partial transfer volume values which predicts about the interactions between the solute and the co-solute suggesting that the hydrophobic-ionic interactions dominate over hydrophilic-ionic interactions.
- The elevation of temperature in the present study may play a vital tool for weakening of the molecular association between the solutes (alkali metal halides) and solvent (D-glucose solution).
- Of all the liquid systems taken for study, the molecular associations are more pronounced in NaCl System comparing the other systems.
- The molecular interaction among the present liquid systems studied are of the order: NaCl > KCl > KBr > KI.

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