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Physico-Chemical Study of Solute- Solute and Solute-Solvent Interactions of Metal Chlorides in Aqueous Sucrose Solution AT 301.15 K

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Abstract: The present study aims for the behavior of some metal chlorides, namely magnesium chloride, calcium chloride and cadmium chloride in aqueous sucrose solution at 301.15K under normal atmospheric pressure. Experimental values of density, viscosity and ultrasonic velocities were carried out on the ternary mixtures of water + sucrose + metal chlorides (namely, magnesium chloride, calcium chloride and cadmium chloride) at 301.15K. For this, binary solvent mixture (water + sucrose) was prepared at different molarities. (Say, from 0.1 to 0.4 molarities(M). The volumetric, compressibility, partial transfer volume and viscometric studies have been rigorously employed to explore the possible interionic interactions existing in the solution. These studies predict a moderate solute-solvent interactions and a weak solute-solute interactions in the present study. Dominance of ionic-hydrophilic group of interactions over the ion-ion-hydrophobic group of interactions is observed. Eventually viscometric study advocates the presence of weak ion-ion interactions in the solution.

Key words: Solute-Solvent · Solute-Solute · Viscosity-B · co-efficient · Ion-hydrophilic · Partial Transfer volume

INTRODUCTION

The behavior of metal chlorides such as, Magnesium chloride ($MgCl_2$), Calcium chloride ($CaCl_2$), Cadmium chloride ($CdCl_2$), Strontium chloride ($SrCl_2$), Barium chloride ($BaCl_2$), Zinc chloride ($ZnCl_2$), Copper chloride ($CuCl_2$), sodium chloride (NaCl) and potassium chloride (KCl) in different solvents were extensively studied by several workers [1-5]. They have studied about their compressibility, ultrasonic and transport behavior in aqueous solvent mixtures under different molar concentrations and temperatures. They established their investigations to explore more about the interionic interactions existing in the solution. They have further attempted to study about the structure-making and structure breaking of metal chlorides in the solution. The present work is aimed in such a way to explore more possible molecular interactions such as solute-solvent and solute-solute interactions which are taking place in the solution. The present study further observes their structure Making/breaking behavior of metal chlorides in aqueous saccharide (sucrose) solution.

Owing to many works extended to study the behavior of metal chlorides in aqueous solvents, an attempt has been made by the authors to study the behavior of some metal chlorides, namely, magnesium chloride, calcium chloride and cadmium chloride in aqueous sucrose solution. Since, a few and scarce literature survey is available for the behavior of metal chlorides in aqueous sucrose solution, the present study has been initiated. The density(ρ), viscosity(η), speed of sound(U) values have been measured for metal chlorides such as magnesium chloride, calcium chloride, cadmium chloride in aqueous solvent(sucrose) mixture at 303.15K under normal atmosphere pressure. Using these measured values, the following related parameters adiabatic compressibility (β), molar hydration number (n_H), apparent molar compressibility (φ_k), apparent molar volume (φ_v), limiting apparent molar compressibility (φ_k^0), limiting apparent molar volume (φ_v^0), partial transfer volume ($\Delta\varphi_v^0$) have been evaluated. To shed more light on viscometry study, Jones-Dole equation of viscosity B-coefficient has also been determined.

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MATERIALS AND METHOS

All the chemicals used in this present research work are spectroscopic reagent (SR) and analytical reagent (AR) grades of minimum assay of 99.9%. Water used in these experiments was deionized, distilled and degassed prior to prepare solutions. Required amount of water and sucrose were taken to prepare the composition of binary mixtures (0.1, 0.2, 0.3 and 0.4 (molarity) mol dm^{-3}) in a dry clean conical flask with a ground stopper. The required quantity of metal chlorides for given molarity was dissolved in binary mixture of aqueous sucrose and similar procedure has been adopted for different molarities of metal chlorides. For each concentration, the mass of the metal chloride can be measured using electronic digital balance having an accuracy of ± 0.1 mg (Model: Shimadzu AX-200). The density was using a specific gravity bottle by relative measurement method with an accuracy of ±0.1 Kg m^{-3}. Am Ostwald's viscometer (10ml capacity) was used for the viscosity measurement and efflux time was determined using a digital chronometer within ± 0.01 s. An ultrasonic interferometer having the frequency 2 MHz (Mittal enterprises, New Delhi, Model: F81) with an overall accuracy of ±0.1% has been used for velocity measurement. An electronically digital operated constant temperature bath (RAAGA industries) has been used to circulate water through the double walled measuring cell made up of steel containing the experimental solution at the desired temperature. The accuracy in the temperature measurement is ±0.1 K.

RESULTS AND DISSCUSSION

In the all three metal chloride liquid systems studied, (from Table 1a and 1b) our present study notices the values of density increase with increase in molar concentration of metal chlorides (solutes) as well as of aqueous sucrose content (solvent). The other measured parameter ultrasonic velocity (U) which is also found (from Table-1a and1b) to be increased with increase in same molar concentration of solutes as well as aqueous sucrose content. The observed increase in the ultrasonic velocity in these solutions may be attributed to the cohesion brought about by the ionic hydration, which may also be due to the overall increase of cohesion brought about by solute-solute and solute-solvent interaction in solution.

Incidentally, the density (ρ) which is a measure of solute-solvent interactions can be attributed as increase of density with concentration indicates the increase in solute-solvent interactions, whereas the decreasing trend indicates the lesser magnitude of solute-solvent interactions. Further, increase in density with concentration is due to the shrinkage in the volume which in turn is due to the presence of solute molecules. From the scrutiny of the Table-1a and 1b, an increasing trend of density is observed in all the metal chloride systems, may be attributed due to the structure-making behavior of the solvent added to the solute [6]

Adiabatic compressibility (β) is given by:

$$\beta = \frac{1}{U^2 \rho} \quad (1)$$

Where U- Ultrasonic velocity and ρ- Density.

The adiabatic compressibility (β) of the solute can be expressed as the extent to which hydration around the solute molecule can be compressed. The perusal of Table-2 exhibits the values of adiabaticcompressibility (β), which are found to be decreased with increase in molar concentration of solute (metal chlorides) as well as solvent (aqueous sucrose). The decrease in adiabatic compressibilities values may be attributed to weakening of hydrogen bond between the metal ions in the solution. When a solute dissolves in a solvent, some of the solvent molecules are attached to the ions (produced from the solutes), because of solute-solvent interaction. Since, the solvent molecules are oriented in the ionic field, these molecules are more compactly packed in the primary salvation shells. It is obvious that the solvent is compressed by the introduction of the ions resulting the electrostatic field of the ions causes the compression of the medium giving rise to a phenomenon called *'Electrostriction'*. As the water molecules are being compressed, they do not respond to a further application of pressure and hence the solutions become harder to compress, which will lead to a decrease in compressibility values. The present investigation finds that β values are larger in Cadmium chloride system comparing other metal chlorides, advocating the strong molecular association in this system.

Molar hydration number (n_H) is given by:

Table 1a: values of density (ρ), viscosity (η) and ultrasonic velocity (U) of metal chlorides in aqueous sucrose mixtures at 301.15K

	Density (kg m^{-3})					Viscosity (x10^{-3} Nsm^{-2})					Ultrasonic velocity U(ms^{-1})				
	Water + sucrose					Water + sucrose					Water + sucrose				
Molarity M (mol dm^{-3})	0.00M	0.1M	0.2M	0.3M	0.4M	0.00M	0.1M	0.2M	0.3M	0.4M	0.00M	0.1M	0.2M	0.3M	0.4M
System-I: water + sucrose + magnesium chloride															
0.00	996.32	1007.59	1022.76	1035.52	1046.81	0.8330	0.8937	0.9591	1.0207	1.0831	1508.08	1518.19	1527.80	1537.12	1549.04
1.0	1061.04	1071.38	1081.99	1095.69	1106.78	1.1575	1.2233	1.2915	1.3503	1.4080	1603.00	1610.00	1615.21	1626.20	1635.20
2.0	1111.54	1119.87	1124.84	1134.49	1147.54	1.4774	1.5547	1.6256	1.6817	1.7292	1673.20	1677.00	1691.48	1708.91	1721.41
3.0	1148.21	1158.01	1179.91	1180.44	1185.28	1.8048	1.8833	1.9550	2.0103	2.0567	1718.56	1728.40	1743.80	1748.16	1759.60
4.0	1179.50	1190.38	1208.38	1219.80	1227.59	2.1349	2.2175	2.2889	2.3449	2.3868	1756.00	1772.60	1783.61	1798.18	1811.37
5.0	1204.49	1229.56	1241.72	1253.62	1259.96	2.4636	2.5481	2.6206	2.6758	2.7115	1796.16	1813.46	1836.88	1848.80	1865.34
6.0	1228.53	1259.10	1272.85	1282.38	1297.83	2.7932	2.8775	2.9518	3.0054	3.0404	1822.16	1836.16	1853.71	1867.74	1891.44
System-II: water + sucrose + calcium chloride															
0.00	996.32	1007.59	1022.76	1035.52	1046.81	0.8330	0.8937	0.9591	1.0207	1.0831	1508.08	1518.19	1527.80	1537.12	1549.04
1.0	1077.16	1086.16	1093.81	1104.68	1118.50	1.2342	1.3152	1.3853	1.4532	1.5287	1604.20	1615.27	1622.28	1634.49	1646.68
2.0	1145.93	1149.96	1160.70	1174.94	1190.52	1.6465	1.7353	1.8110	1.8901	1.9762	1651.73	1658.60	1671.47	1685.59	1699.36
3.0	1205.43	1214.02	1226.38	1232.42	1242.63	2.0617	2.1571	2.2408	2.3275	2.4251	1701.80	1717.40	1729.12	1744.64	1754.87
4.0	1257.67	1262.37	1264.92	1268.28	1275.67	2.4806	2.5805	2.6708	2.7676	2.8752	1748.80	1754.04	1763.91	1776.69	1788.78
5.0	1297.02	1302.26	1318.92	1322.14	1327.78	2.9007	3.0106	3.1010	3.1975	3.3250	1777.60	1788.56	1799.19	1814.39	1828.56
6.0	1334.90	1337.05	1355.85	1379.76	1385.74	3.3209	3.4397	3.5309	3.6381	3.7689	1801.76	1814.20	1827.41	1841.56	1856.13

Table 1b: values of density (ρ), viscosity (η) and ultrasonic velocity (U) of metal chlorides in aqueous sucrose mixtures at 301.15K

	Density (kg m^{-3})					Viscosity (x10^{-3} Nsm^{-2})					Ultrasonic velocity U(ms^{-1})				
	Water + sucrose					Water + sucrose					Water + sucrose				
Molarity M (mol dm^{-3})	0.00M	0.1M	0.2M	0.3M	0.4M	0.00M	0.1M	0.2M	0.3M	0.4M	0.00M	0.1M	0.2M	0.3M	0.4M
System-III: water + sucrose + cadmium chloride															
0.00	996.32	1007.59	1022.76	1035.52	1046.81	0.8330	0.8937	0.9591	1.0207	1.0831	1508.08	1518.19	1527.80	1537.12	1549.04
0.2	1028.94	1040.36	1054.73	1056.09	1065.08	0.8786	0.9406	1.0071	1.0696	1.1332	1516.40	1531.68	1547.53	1561.17	1576.31
0.4	1057.67	1067.03	1075.98	1086.81	1099.65	0.9261	0.9872	1.0556	1.1191	1.1842	1521.19	1534.14	1556.33	1567.53	1581.55
0.6	1087.37	1097.84	1108.99	1120.00	1130.57	0.9701	1.0339	1.1036	1.1684	1.2352	1526.14	1539.63	1560.91	1574.31	1589.74
0.8	1115.17	1122.29	1134.23	1145.40	1156.40	1.0166	1.0810	1.1524	1.2180	1.2857	1532.11	1547.12	1566.36	1581.59	1598.11
1.0	1141.49	1147.54	1159.85	1171.37	1184.37	1.0627	1.1281	1.2013	1.2671	1.3367	1537.59	1554.03	1573.25	1588.67	1609.13

Table 2: values of adiabatic compressibility (β) and molar hydration number (n_H) of metal chlorides in aqueous sucrose mixtures at 301.15K

	β (x10^{-1}0 m^2N^{-1})					n_H				
	Water+ sucrose					Water+ sucrose				
Molarity M (mol dm^{-3})	0.00M	0.1M	0.2M	0.3M	0.4M	0.00M	0.1M	0.2M	0.3M	0.4M
System-I: water + sucrose + magnesium chloride										
0.00	4.4132	4.3058	4.1880	4.0872	3.9811	-----	-----	-----	-----	-----
1.0	3.6677	3.6008	3.5425	3.4511	3.3760	9.3835	8.8001	8.0063	7.8039	7.3476
2.0	3.2142	3.1751	3.1072	3.0182	2.9407	7.5421	7.0496	6.6994	6.5541	6.3135
3.0	2.9488	2.8906	2.7871	2.7720	2.7249	6.1400	5.8844	5.7880	5.3748	5.0812
4.0	2.7494	2.6735	2.6013	2.5353	2.4827	5.2320	5.0903	4.6931	4.7566	4.5456
5.0	2.5733	2.4670	2.3867	2.3340	2.2810	4.6265	4.5853	4.4633	4.2969	4.1241
6.0	2.4515	2.3500	2.2863	2.2353	2.1537	4.1109	3.8214	3.9270	3.7826	3.6943
System-II: water + sucrose + calcium chloride										
0.00	4.4132	4.3058	4.1880	4.0872	3.9811	-----	-----	-----	-----	-----
1.0	3.6074	3.5287	3.4738	3.3670	3.2825	10.132	9.6904	8.8466	8.8268	8.4744
2.0	3.1992	3.1611	3.0837	2.9955	2.9086	7.6326	7.1371	6.8416	6.6900	6.5051
3.0	2.8644	2.8126	2.7272	2.6658	2.6132	7.2478	6.2136	6.0349	5.8134	5.5373
4.0	2.5998	2.5630	2.5408	2.4978	2.4498	5.7006	5.4331	5.1025	4.8531	4.6439
5.0	2.4399	2.4005	2.3422	2.2975	2.2544	4.9632	4.7524	4.5748	4.3751	4.1897
6.0	2.3076	2.2723	2.2085	2.1371	2.0795	5.2012	4.9818	4.8200	3.9838	3.8450
System-III: water + sucrose + cadmium chloride										
0.00	4.4132	4.3058	4.1880	4.0872	3.9811	-----	-----	-----	-----	-----
0.2	4.2265	4.1129	3.9968	3.8486	3.7744	11.937	12.231	12.046	11.869	10.749
0.4	4.0858	3.9931	3.8370	3.7446	3.6356	10.378	11.503	10.964	10.585	10.565
0.6	3.9485	3.8426	3.7009	3.6024	3.4998	9.7932	10.680	10.115	9.8555	9.7851
0.8	3.8201	3.7226	3.5934	3.4902	3.3893	9.3613	9.4286	9.2481	9.1844	9.0111
1.0	3.7054	3.6083	3.4833	3.3825	3.2718	8.9299	8.9269	8.7611	8.6657	8.6330

$$n_H = \left(\frac{n_1}{n_2}\right)\left(1 - \frac{\beta}{\beta_0}\right) \quad (2)$$

Where β and β_0 are adiabatic compressibilities of solute and solvent respectively, n_1 and n_2 are number of moles of solvent and solute respectively.

The scrutiny of Table 2 represents the molar hydration values for metal chlorides in aqueous sucrose solvent, which are seemed less than those in water and decrease with increase in concentration of sucrose. The hydration number (n_H) mainly dealing about solute-cosolute interactions and for this present study come from the electrostriction effect of the ions of metal chlorides (Ca^{2+}, Cd^{2+}, mg^{2+}, cl^-) with water. From Table 2, one can notice that the n_H are positive in all the three liquid systems and such positive values of n_H indicate an appreciable salvation of solutes [7]. This may be considered 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. The present parameter is a sensitive parameter which suggests that the compressibility of the solution will be less than that of the solvent, resulting in solutes will gain more mobility as well as more probability of contacting solvent molecules, which in turn may enhance the interaction between the solute-solvent molecules. The present study finds that the values of n_H which are decreasing with further addition of solute (metal chlorides) as well as with aqueous sucrose (solvent). The decreasing values of n_H may be presumed as that the strength of the interactions may be weakened among the solute-co solute molecules. The decreasing values may further be attributed as the reduction in electrostriction with increase of solvent concentration.

The apparent molar compressibility (φ_k) and apparent molar volume (φ_v), of these solutions were calculated by using the relations

$$\phi_K = \frac{1000}{m\rho_0}\left(\rho_0\beta - \rho\beta_0\right) + \left(\frac{\beta_0 M}{\rho_0}\right) \quad (3)$$

$$\phi_V = \frac{1000}{m\rho_0}\left(\rho_0 - \rho\right) + \left(\frac{M}{\rho_0}\right) \quad (4)$$

Where m is the molar concentration of the solute (metal chlorides), ρ and ρ_o are the densities of the solution and the solvent (aqueous sucrose) respectively; M is the molar mass of the solute (metal chlorides) and β, β_0 are the adiabatic compressibilities of the solution and the solvent (aqueous sucrose), respectively.

The following observations are noticed from Table 3 on apparent molar compressibility (φ_k) and apparent molar volume (φ_v) of metal chlorides namely, magnesium chloride, calcium chloride and cadmium chloride in aqueous sucrose solution at 301.15K.

- The values of the apparent molar compressibility (φ_k) and apparent molar volume (φ_V) are all negative over the entire molarity range of solutes (metal chlorides).
- The negative values of both parameters, φ_k and φ_v are found to be increased with increasing molarities (M) of solute and solvent content.

The above observations clearly suggesting the existence of solute-solvent interaction in the solution. The negative values of apparent molar compressibility (φ_k) and volume (φ_v) indicate the presence of hydrophilic-ionic interactions occurring in these liquid systems. Since, more number of water molecules are available at lower concentration of aqueous sucrose, the chances for the penetration of solute molecules in the solvent molecules are highly [8] favored. The increasing values of apparent molar compressibility (φ_k) and apparent molar volume (φ_v) with addition of solute and solvent contents revealing the strengthening of the solute-solvent interaction in the solution. The values of limiting apparent molar compressibility (φ_k^0) and the slope (S_k), limiting apparent molar volume (φ_v^0) and the slope (S_v), have been obtained using method of linear regression of (φ_k^0) and (φ_v^0) vs. molarity of metal chlorides in aqueous sucrose solvent from the following relations [9]

$$\phi_K = \phi_K^0 + S_K m^{1/2} \quad (5)$$

$$\phi_V = \phi_V^0 + S_V m^{1/2} \quad (6)$$

Where the intercepts, φ_k^0 or, φ_v^0 by definition are free from solute-solute interactions and therefore provide a measure of solute-solvent interactions, whereas the experimental slope, S_k or S_v provides information regarding solute-solute interaction.

The perusal of Table 4 reports that limiting apparent molar compressibility (φ_k^0) and limiting apparent molar volume (φ_v^0) values are negative in the present study and increase with the further addition of aqueous sucrose (solvent), suggesting the presence of strong solute-solvent interactions. The reported S_k and S_v values are positive and exhibit a decreasing trend, when the concentration of solvent increases [10, 11].

Table 3: values of apparent molar compressibility (ϕ_k) and apparent molar volume (ϕ_v) of metal chlorides in aqueous sucrose mixtures at 301.15K

	$-\phi_k$(x 10^{-8} m^2 N^{-1})					$-\phi_v$ (x 10^{-3} m^3 mol^{-1})				
	Water+ sucrose					Water+ sucrose				
Molarity										
M ($moldm^{-3}$)	0.00M	0.1M	0.2M	0.3M	0.4M	0.00M	0.1M	0.2M	0.3M	0.4M
System-I: water + sucrose + magnesium chloride										
0.00	------	-----	-----	-----	------	-----	-----	-----	-----	-----
1.0	10.3110	9.7672	8.8721	8.7257	8.3620	64.754	63.107	57.710	57.609	57.094
2.0	8.5372	8.0438	7.6083	7.5206	7.1096	57.618	55.514	51.017	47.590	47.418
3.0	7.1145	6.8512	6.0546	6.1824	5.9349	50.612	49.560	49.705	46.451	43.897
4.0	6.1786	6.0247	5.8553	5.6901	5.4570	45.759	45.151	45.037	44.292	42.979
5.0	5.5144	5.2916	5.3874	5.2197	5.0137	41.581	43.460	42.616	41.925	40.528
6.0	4.9745	4.9036	4.8677	4.7023	4.6289	38.640	41.400	40.555	39.535	39.477
System-II: water + sucrose + calcium chloride										
0.00	--------	-----	-----	-----	-----	-----	-----	-----	-----	-----
1.0	11.6322	11.1232	10.0538	10.2020	9.8969	80.990	77.831	69.321	70.507	68.343
2.0	9.3769	8.7592	8.3441	8.2041	8.0895	74.933	70.502	67.290	67.175	68.501
3.0	8.2435	7.9115	7.6456	7.3225	7.0363	69.813	68.145	66.361	63.238	62.212
4.0	7.4211	7.0724	6.5934	6.2644	5.9985	65.430	63.069	59.247	56.050	54.515
5.0	6.6039	6.3226	6.1127	5.8358	5.5888	60.211	58.344	57.767	55.212	53.538
6.0	6.0023	5.7293	5.5680	5.5088	5.3754	56.490	54.350	54.133	53.263	52.458
System-III: water + sucrose + cadmium chloride										
0.00	--------	-----	-----	-----	-----	-----	-----	-----	-----	-----
0.2	16.5462	15.7843	14.0914	14.016	13.947	163.51	162.43	156.11	152.25	144.58
0.4	14.9748	14.6417	14.2366	13.6214	13.4155	153.75	149.77	139.68	139.68	137.95
0.6	14.4568	14.1400	14.0101	13.6326	13.3237	152.31	149.10	139.27	137.12	133.18
0.8	13.9848	13.4090	13.1416	12.8788	12.6427	148.92	142.11	136.81	132.48	130.68
1.0	13.4978	12.9477	12.6621	12.4040	12.1654	145.52	138.89	133.86	131.03	131.23

Table 4: Values of limiting apparent molar compressibility (ϕ^0_k), limiting apparent molar volume (ϕ^0), constants (S_k,S_v), transfer volume($\Delta\phi^0_v$), viscosity A and B-coefficient of Jones Dole equation of metal chlorides in aqueous sucrose mixtures at 301.15K

Metal chlorides	Molarity M (mol dm^{-3})	$-\phi^0_k$ (x $10^{-7}m^2$ N^{-1})	$-\phi^0_v$ (x 10^{-3} m^3 mol^{-1})	S_k (x $10^{-7}m^{-1}$ $N^{-1}mol^{-1}$)	S_v (x 10^{-3} m^3 $mol^{-3/2}$)	-A (x 10^{-2} $dm^{3/2}mol^{-1}$)	B (x 10^{-2} dm^3 mol^{-1})	$\Delta\phi^0_v$ (x 10^{-3} m^3 mol^{-1})
Magnesium Chloride	0.00	48.82	338.68	26.64	19.03	8.26	0.394	----
	0.1	46.81	336.04	25.55	18.64	2.64	0.371	2.64
	0.2	44.25	323.02	24.15	17.91	2.43	0.346	15.66
	0.3	43.56	312.62	23.78	17.34	2.19	0.325	26.06
	0.4	41.80	305.84	22.82	16.96	0.021	0.311	32.84
Calcium Chloride	0.00	56.43	528.30	30.80	25.49	0.302	0.650	----
	0.1	53.73	449.23	29.33	24.52	8.28	0.477	79.07
	0.2	50.75	428.45	27.70	23.38	5.61	0.448	99.85
	0.3	49.64	418.52	27.09	22.84	5.17	0.429	109.78
	0.4	48.08	411.79	26.24	22.47	3.59	0.415	116.51
Cadmium chloride	0.00	9.904	119.23	13.01	13.86	+1.14	0.274	----
	0.1	9.565	115.82	12.65	13.46	+0.60	0.261	3.41
	0.2	9.187	110.10	12.07	12.80	1.01	0.253	9.13
	0.3	8.706	108.08	11.79	12.56	1.06	0.242	11.15
	0.4	8.568	105.72	11.60	12.29	1.65	0.235	13.51

The decreasing positive values of S_k and S_v advocating the existence of weak solute-solute interaction in the ternary liquid mixtures.

From Fig- 3 and 4 one can notice, an increase of φ_k^0 and φ_v^0 values with increase of concentration of solvent (aqueous sucrose) that reduces the electrostriction leading to increasing of φ_k^0 and φ_v^0. The electrostriction due to ionic-hydrophilic interactions between the ions of the metal chlorides (ca^{2+}, cd^{2+}, mg^{2+}, cl) and the -OH group of sucrose molecules increases, which in turn, causing the larger values of φ_v^0 of Cadmium chloride in aqueous solution. The presence of large values of φ_v^0 and φ_k^0 in cadmium chloride system in aqueous sucrose solution is due to the strong hydrophilic-ionic interactions in the solution, as well as cpresence of larger number of -OH groups in sucrose. This clearly suggesting that cadmium chloride serves as an effective structure-maker in the solution.

The transfer volumes $\Delta\varphi_v^0$ of metal chlorides from water to aqueous sucrose solutions were calculated by using the relation

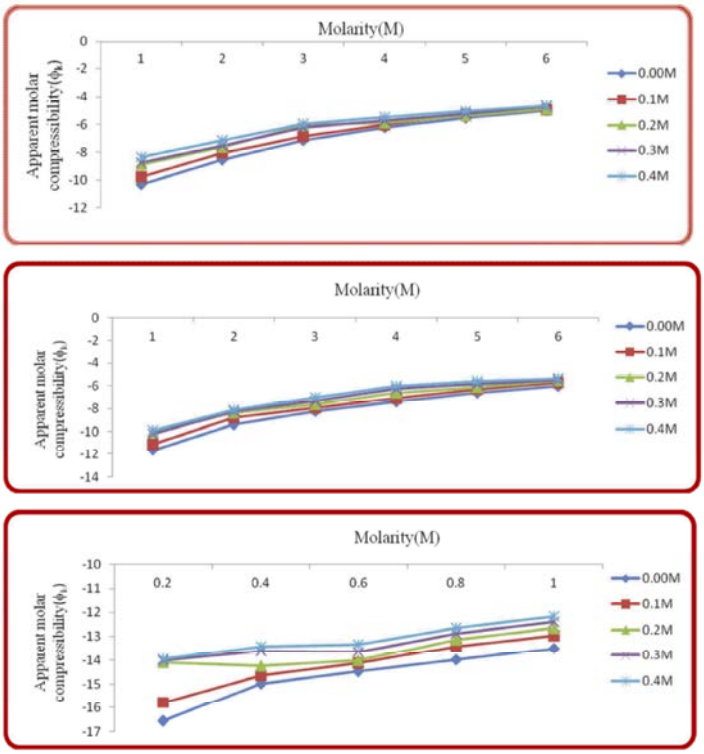

Fig. 1: Variation of Apparent Molar Compressibility (ϕ_k) with Molarity (M) of Aqueous Sucrose at 301.15K for Three Metal Chlorides

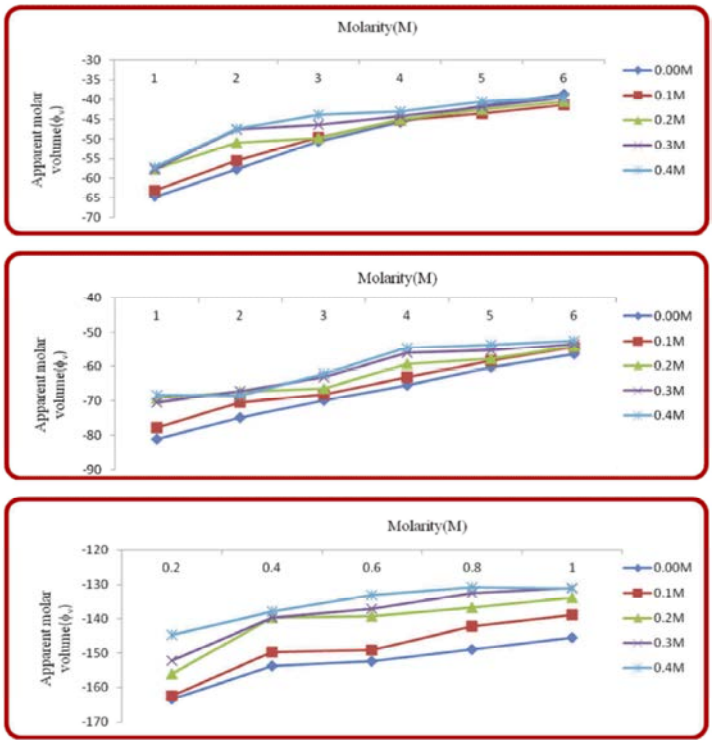

Fig. 2: Variation of Apparent Molar Volume (ϕ_k) with Molarity (M) of Aqueous Sucrose at 301.15K for Three Metal Chlorides

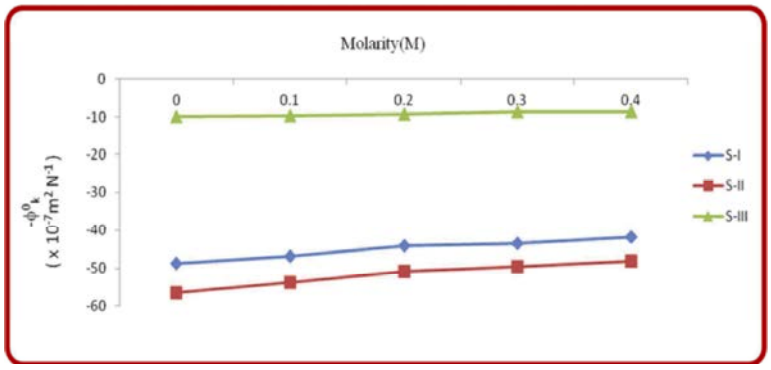

Fig. 3: Variation of Limiting Apparent Molar Compressibility(ϕ^{o}_{k}) with Molarity (M) of Aqueous Sucrose at 301.15K for Three Metal Chlorides

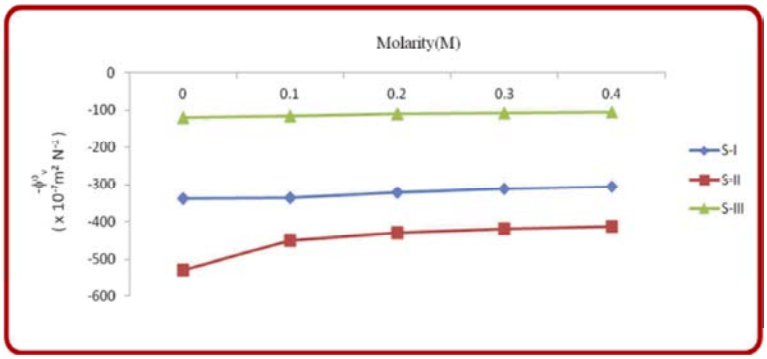

Fig. 4: Variation of Limiting Apparent Molar Volume (Φ^{o}_{v}) with Molarity (M) of Aqueous Sucrose at 301.15K

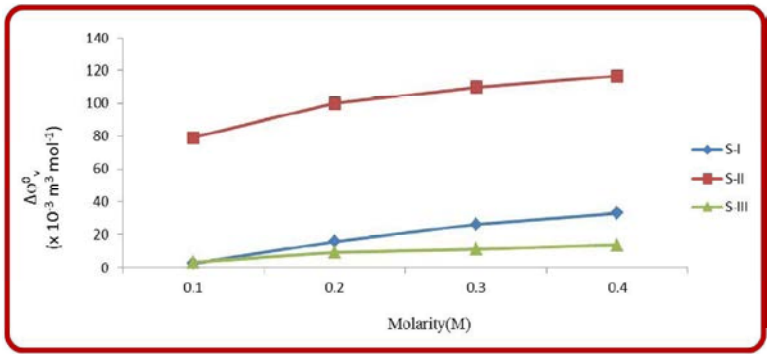

Fig. 5: Variation of Partial Transfer Volume $\Delta\phi^{o}_{v}$ with Molarity (M) of Aqueous Sucrose at 301.15K

$$\Delta\varphi_v^{0} = \varphi_v^{0}\,(\text{aqueous sucrose}) - \varphi_v^{0}\,(\text{aqueous}) \qquad (7)$$

Our present investigation from Table 4 monitoring the partial transfer volume ($\Delta\varphi_v^{0}$) studies from water to aqueous sucrose solution exhibit positive deviations in all the three metal chlorides liquid systems and increase with addition of solvent (sucrose). The increasing behavior suggesting a stronger and more extensive interactions between metal chlorides (co-solute) and sucrose (solute) and vice versa. The enhancement of ionic-hydrophilic interactions between the ions of the metal chlorides (ca^{2+}, cd^{2+}, mg^{2+}, cl^{-}) and the -OH group of sucrose molecules, resulting in positive deviation in the present liquid systems.

The sign of partial transfer volume ($\Delta\varphi_v^{0}$) is often interpreted in terms of strength of solute-co solute interactions on the basis of Co-Sphere Overlap Model [12]. The overlap of ions of co-solute (metal chlorides) and solute (sucrose) comes into play because of the interaction between (i) ionic-hydrophilic interaction

between the ions of metal chlorides (ca^{2+}, cd^{2+}, mg^{2+} and cl^{-}) and the polar group of saccharide (-OH sites) and (ii) ionic-hydrophobic interaction between the ions of metal chlorides and the non-polar side group of saccharide. Out of which, the former type of interaction contributes positively and later type of interaction to negatively to $\Delta\varphi_v^0$ values. Since our present study providing the positive values of $\Delta\varphi_v^0$, from Fig 5 suggesting the dominance of hydrophilic-ionic interactions. The overlap of hydration co-spheres of two ionic species results in an enhanced volume as some electrostricted water molecules return to a higher volume contribution with electrostricted water molecules, whereas, overlap of hydration co-spheres of hydrophobic- hydrophobic groups and ion- hydrophobic/hydrophilic- hydrophobic groups and results in a net volume decrease. This may due to greater hydrophilic- ionic groups and hydrophilic- hydrophilic groups interactions, with the presence of more hydroxyl groups in sucrose molecules. Similar trend is noticed in earlier studies, supporting the present study [13, 14].

The present study also incorporated viscosity data in the light of Jones-Dole semi empirical equation (Jones and Dole, 1929) [15].

$$\frac{\left(\eta/\eta_0\right)-1}{m^{1/2}} = A + Bm^{1/2} \quad (8)$$

Where η and η_0 are the viscosities of the solution and solvent respectively and 'm' is the molar concentration of the solute-solvent system. A is known as Falkenhagen coefficient which characterizes the ionic interaction and B is the Jones-Dole or viscosity B-coefficient which depends on the size of the solute and nature of solute-solvent interactions.

Viscosity is one of the key transport properties providing accurate viscosity data give useful information regarding solute-solvent and ion-ion interactions which are the controlling force in dilute solutions. The Jones-Dole equation of [15, 16] values A and B are evaluated and listed in Table 4. The values of A are negative and B are positive, also, the A-coefficients are much smaller in magnitude as compared to B co-efficients, suggesting a weak ion-ion interactions in these solutions. The close scrutiny of the Table 4 shows the B co-efficients decrease with increasing concentration of sucrose attributing a structure to allow the co-solute to act on solvent [17]. The decrease of B coefficients, when the water is replaced by sucrose, i.e. sucrose acts as water structure-maker by H-bonding. The present trend of B co-efficients suggesting a moderate solute-solvent interaction in these systems, which may be, as interpreted earlier due to greater hydrophilic-ionic group interactions with the preface of more hydroxyl group in sucrose molecules which enhances a moderate solute-solvent interaction in the mixture.

CONCLUSION

The physico-chemical studies of solute-solute and solute-solvent interactions of metal chlorides namely, magnesium chloride, calcium chloride and cadmium chloride in aqueous sucrose at 301.15K have been investigated and are consolidated as,

- Moderate solute-solvent interactions and weak solute-solute interactions are noticed in the present study.
- Our partial transfer volume study predicts the dominance of ionic- hydrophilic group of interactions over ion-ion-hydrophobic group of interactions.
- Among the metal chlorides taken for study, the cadmium chloride possessing the more prominent solute-solvent interactions in the present systems of liquid mixture.
- The present study of viscometric analysis advocating a weak ion-ion and a moderate solute-solvent interaction in the solution.

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