

## Partial molar compressibilities and partial molar volumes in some aqueous salt solutions

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Received 26 July 1994, accepted 28 October 1994

**Abstract** : Ultra-sound velocity, density and viscosity of magnesium, calcium and barium chloride in 10, 20 and 30% of 1,4-dioxane in 1,4-dioxane-water mixtures have been measured at various concentrations of salt and temperatures. The derived parameters namely adiabatic compressibility ( $\beta_{ad}$ ), apparent molar compressibility ( $\Phi_k$ ) and apparent molar volume ( $\Phi_v$ ) have been calculated from the experimental data. The limiting molar compressibility ( $\Phi_k^0$ ), limiting molar volume ( $\Phi_v^0$ ) and the experimental slope  $S_k$  and  $S_v$  have also been obtained from the plots of  $\Phi_k$  and  $\Phi_v$  versus concentration. The results have been interpreted in terms of structure making characteristics of the salts.

**Keywords** : Aqueous solution, limiting compressibility, limiting volume, structure making

**PACS Nos.** : 43.35. Bf, 62.60. +v

### 1. Introduction

Acoustical measurements in mixed electrolytic solutions provide valuable information about the arrangement of matter in aqueous solutions. The study of adiabatic compressibility and other related properties of aqueous solutions of electrolytes has proved to be very useful in obtaining information regarding the state of affairs in a solution. These determinations involve accurate measurement of ultrasonic velocity and density. Such measurements in binary electrolytes have been extensively made by several workers [1,2]. However, little work has been done on ternary electrolytes [3–5]. Moreover, physico-chemical studies on ternary electrolytes are gaining importance, since it is some times difficult to arrive at a definite conclusion regarding structure and properties of solutions from the study of binary system

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alone. Such an investigation would lead to the possible deduction of general laws with regard to the acoustic and molecular properties in aqueous solutions.

These considerations lead us to undertake the present work of determining the acoustical parameters for magnesium, calcium and barium chloride in 10, 20 and 30% of 1,4-dioxane in 1,4-dioxane-water mixtures from ultrasonic velocity measurements at various salt concentrations and temperatures. From the knowledge of these parameters structural changes around the ion and effect of the solvent have been discussed. The 1,4-dioxane-water mixture is of particular interest, since 1,4-dioxane is miscible freely with water at all proportions and has identical density. The physical properties and the nature of interaction between the two liquids are readily available [6–8].

## 2. Experimental

The ultrasonic velocities of magnesium, calcium and barium chloride in 10, 20 and 30% of 1,4-dioxane in 1,4-dioxane-water mixtures are measured for various salt concentrations at the temperatures 303.15, 308.15, 313.15, 318.15 and 323.15 K using pulse-echo overlap [9] intervalometer (UTI 101, India) operating at a frequency of 3 MHz. The accuracy of velocity measurements is 2 parts in  $10^4$ . The density of the solutions at these temperatures are measured using a specific gravity bottle and the accuracy of the measurements is  $\pm 0.1 \text{ Kgm}^{-3}$ . The electrolytes used in the present investigation are of extra pure quality (E. Merk). Fresh double distilled water was used for preparing the binary solutions. The binary mixtures of varying composition as well as the solutions of electrolytes are made by weight and the molalities are converted into molarities using the standard expressions [10].

## 3. Theory and calculation

The adiabatic and apparent molar compressibilities of the systems have been calculated using the relations

$$\beta_{\text{ad}} = U^{-2} \rho^{-1}, \quad (1)$$

$$\Phi_k = \frac{1000}{C\rho^0} [\beta_{\text{ad}}\rho^0 - \beta_{\text{ad}}^0\rho] + \frac{\beta_{\text{ad}}^0 m}{\rho^0} \quad (2)$$

where  $\beta_{\text{ad}}$ ,  $\rho$  and  $\beta_{\text{ad}}^0$ ,  $\rho^0$  are the adiabatic compressibility and density of the solution and solvent respectively.  $C$  is the molar concentration and  $M$  the molecular weight of the solute.  $\Phi_k$  is a function of  $C$  obtained by Gucker [11] from Debye-Hückel theory [12] and is given by

$$\Phi_k = \Phi_k^0 + S_k C^{1/2} \quad (3)$$

where  $\Phi_k^0$  is the limiting apparent molar compressibility at infinite dilution and  $S_k$  is a constant.

The apparent molar volume [13] of a solute have been obtained as,

$$\Phi_v = \frac{1000}{C\rho^0} (\rho^0 - \rho) + \frac{M}{\rho^0}. \quad (4)$$

The apparent molar volume has been found to vary with concentration in conformity with the Masson's empirical relation [14] as,

$$\Phi_v = \Phi_v^0 + S_v C^{1/2}, \quad (5)$$

where  $\Phi_v^0$  is the limiting apparent molar volume at infinite dilution and  $S_v$  is a constant.

#### 4. Results and discussion

The experimental values of sound velocity, density and viscosity for magnesium, calcium and barium chloride in 10, 20 and 30% of 1,4-dioxane in 1,4-dioxane-water mixtures at various

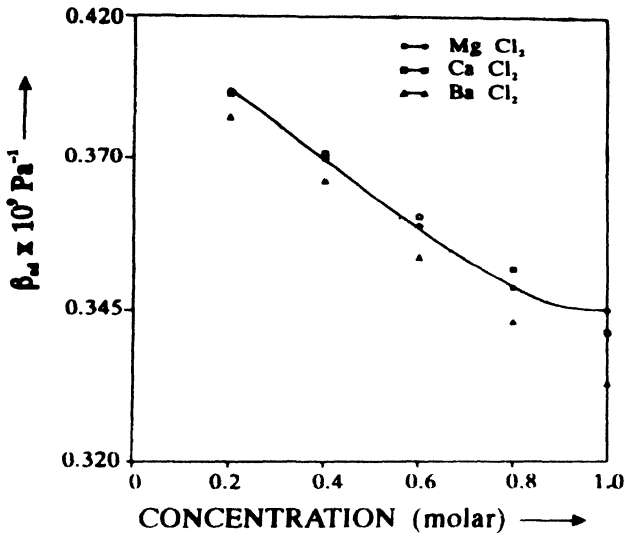


Figure 1(a). Adiabatic compressibility as a function of concentration of salt in 10% of 1,4-dioxane in 1,4-dioxane-water mixture.

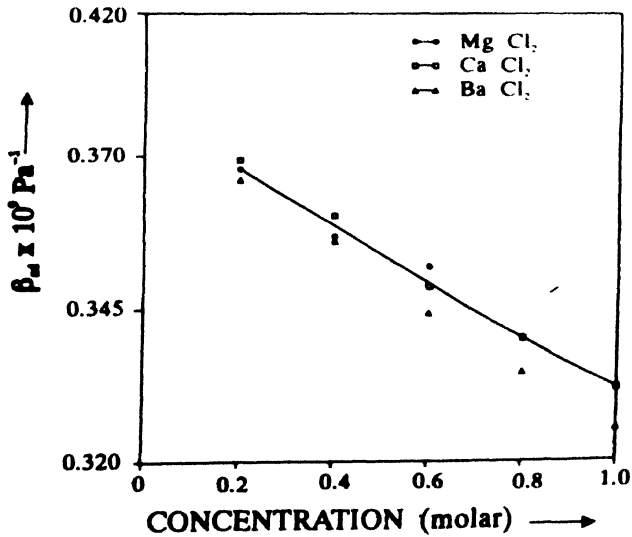


Figure 1(b). Adiabatic compressibility as a function of concentration of salt in 20% of 1,4-dioxane in 1,4-dioxane-water mixture.

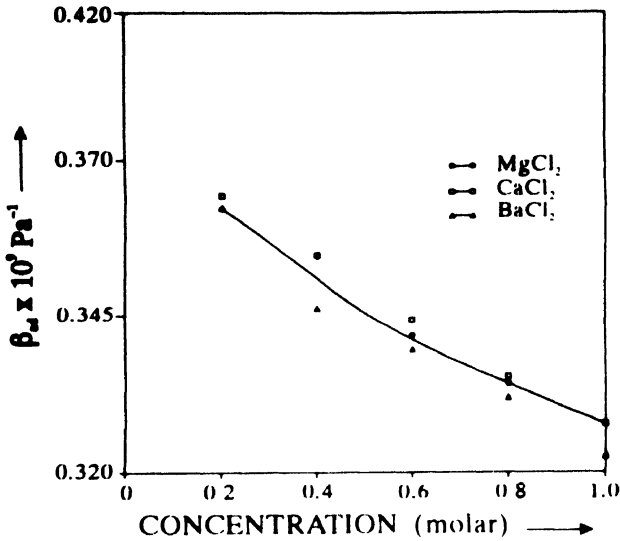


Figure 1(c). Adiabatic compressibility as a function of concentration of salt in 30% of 1,4-dioxane in 1,4-dioxane-water mixture.

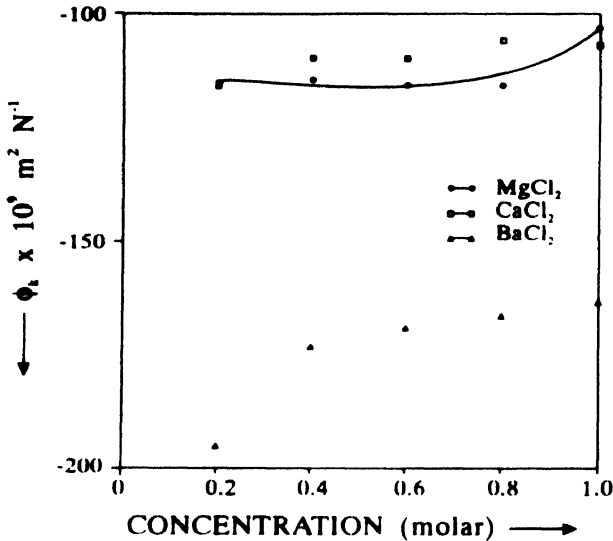


Figure 2(a). Apparent molar compressibility as a function of concentration of salt in 10% of 1,4-dioxane in 1,4-dioxane-water mixture.

salt concentrations and temperatures are presented in Tables 1–3. The variation of derived parameters namely adiabatic compressibility, apparent molar compressibility and apparent molar volume with concentration of salt in various 1,4-dioxane content at 303.15 K for all the salts are depicted in Figures 1, 2 and 3 respectively. While the limiting apparent molar compressibility and apparent molar volume are presented in Figures 4 and 6, and the same for the constants  $S_k$  and  $S_v$  for all the salts at different temperatures in Figures 5 and 7.

From Figure 1, it is inferred that for all the salts in 10% of 1,4-dioxane in 1,4-dioxane-water mixtures, the adiabatic compressibility decreases and ultrasonic velocity increase (Tables 1-3) with increase in salt concentration. In the aqueous solutions of these salts the ions of opposite charges are dissociated due to the interaction between the ions and solvent and there will be a cloud of ions of positive and negative charges around a solvated finite charged ion in the solution [14]. The cations  $Mg^{2+}$ ,  $Ca^{2+}$  and  $Ba^{2+}$  solvate themselves

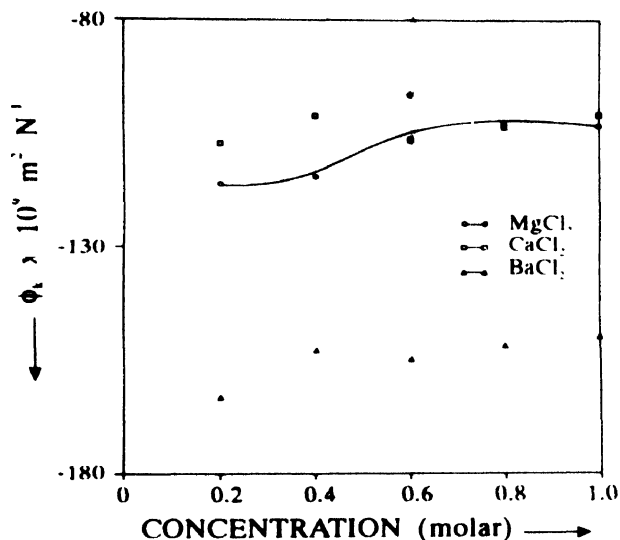


Figure 2(b). Apparent molar compressibility as a function of concentration of salt in 20% of 1,4-dioxane in 1,4-dioxane-water mixture

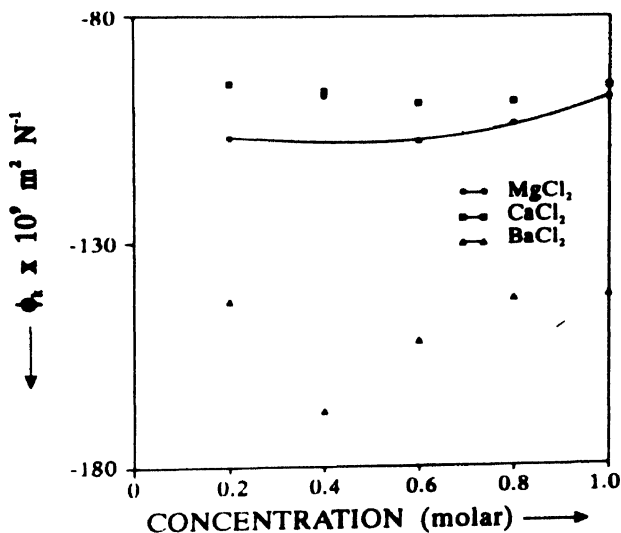


Figure 2(c). Apparent molar compressibility as a function of concentration of salt in 30% of 1,4-dioxane in 1,4-dioxane-water mixture.

Table 1. Values of density ( $\rho$ ), viscosity ( $\eta$ ) and velocity ( $U$ ) of magnesium chloride in 1,4-dioxane-water mixtures.

Molality of Salt	$\rho$ Kg.m <sup>-3</sup>			$\eta \times 10^3$ Nsm <sup>-2</sup>			$U$ ms <sup>-1</sup>		
	303.15	313.15	323.15	303.15	313.15	323.15	303.15	313.15	323.15
(m)	303.15	313.15	323.15	303.15	313.15	323.15	303.15	313.15	323.15
0.197	1015.6	1014.3	1012.3	1010.7	1009.0				
0.399	1031.1	1029.1	1026.8	1025.9	1024.2				
0.599	1045.3	1043.7	1042.1	1041.5	1040.1				
0.800	1059.9	1058.1	1056.2	1055.3	1053.9				
1.001	1066.1	1064.8	1063.3	1062.2	1061.2				
						1,4-dioxane-water (10:90%)			
0.197	1.1387	1.0349	0.9333	0.8500	0.7790				
0.399	1.2765	1.2343	1.0548	0.9282	0.8222				
0.599	1.3746	1.3291	1.1414	0.9984	0.8892				
0.800	1.4751	1.4253	1.2238	1.0761	0.9639				
1.001	1.5986	1.5285	1.3177	1.1586	1.0509				
						1,4-dioxane-water (20:80%)			
0.201	1.3512	1.2240	1.0875	0.9811	0.8768				
0.402	1.4912	1.3691	1.1873	1.0648	0.9480				
0.599	1.6038	1.4850	1.2865	1.1540	1.0282				
0.802	1.7268	1.5973	1.3826	1.2375	1.1130				
0.999	1.9118	1.7937	1.5382	1.3990	1.2749				
						1,4-dioxane-water (30:70%)			
0.210	1.5366	1.3631	1.2014	1.0764	0.9971				
0.400	1.6982	1.5489	1.3953	1.2560	1.1208				
0.599	1.8359	1.6766	1.5130	1.3543	1.2082				
0.802	1.9861	1.7871	1.6213	1.4439	1.2926				
1.004	2.2048	2.0469	1.8717	1.6676	1.4943				

Table 2. Values of density ( $\rho$ ), viscosity ( $\eta$ ) and velocity ( $U$ ) of calcium chloride in 1,4-dioxane-water mixtures.

Molality of Salt	$\rho$ Kg.m <sup>-3</sup>		$\eta \times 10^3$ Nsm <sup>-2</sup>		$U$ ms <sup>-1</sup>										
	Temperature (K)		Temperature (K)		Temperature (K)										
(m)	303.15	308.15	313.15	318.15	323.15	303.15	308.15	313.15	318.15	323.15					
0.199	1016.7	1015.4	1013.3	1011.2	1008.3	1.0081	0.9093	0.8182	0.7349	0.6712	1563.4	1569.1	1572.6	1573.4	1574.5
0.401	1033.2	1031.3	1029.3	1027.1	1022.8	1.0533	0.9604	0.8603	0.7601	0.7044	1577.0	1580.8	1584.2	1586.9	1589.8
0.598	1050.7	1048.5	1046.7	1045.0	1042.5	1.1427	1.0395	0.9295	0.8417	0.7614	1593.3	1595.5	1599.9	1602.7	1604.6
0.802	1066.6	1064.7	1062.3	1060.7	1057.9	1.2156	1.0986	0.9770	0.8861	0.8040	1606.5	1609.4	1612.5	1614.7	1617.4
0.999	1082.6	1080.5	1077.6	1076.2	1073.4	1.2865	1.1648	1.0266	0.9373	0.8534	1627.2	1632.3	1634.4	1635.2	1638.7
						1,4-dioxane-water (10:90%)									
0.201	1029.5	1027.2	1025.5	1022.9	1020.0	1.2091	1.0872	0.9687	0.8613	0.7863	1584.0	1586.6	1587.8	1583.6	1581.1
0.400	1044.9	1042.8	1040.3	1038.4	1035.1	1.2888	1.1627	1.0299	0.9124	0.8310	1598.4	1600.2	1601.3	1597.7	1596.1
0.599	1063.2	1060.9	1059.2	1056.3	1054.5	1.4208	1.2711	1.1231	0.9832	0.9078	1619.3	1621.4	1623.1	1616.8	1612.8
0.804	1079.6	1077.1	1074.1	1072.5	1070.0	1.5040	1.3466	1.2035	1.0626	0.9681	1633.9	1636.4	1639.4	1634.2	1631.8
1.002	1094.6	1092.3	1089.8	1087.0	1084.8	1.6149	1.4514	1.2989	1.1360	1.0398	1649.2	1651.2	1651.9	1647.4	1644.7
						1,4-dioxane-water (20:80%)									
0.199	1034.3	1032.0	1029.3	1026.6	1023.5	1.4217	1.2687	1.1265	0.9852	0.8935	1594.0	1592.0	1588.6	1582.9	1579.8
0.403	1050.2	1047.5	1044.9	1042.1	1039.5	1.5529	1.3762	1.2098	1.0810	0.9758	1610.4	1607.3	1602.4	1594.9	1591.0
0.600	1066.4	1064.1	1061.8	1059.1	1056.0	1.6731	1.5061	1.3028	1.1751	1.0481	1630.1	1621.6	1616.2	1610.4	1603.3
0.801	1084.0	1081.3	1078.8	1076.5	1073.4	1.8713	1.6792	1.4718	1.3162	1.1678	1646.2	1643.5	1636.1	1632.0	1627.3
1.011	1099.0	1096.7	1094.0	1091.9	1088.9	2.0486	1.8221	1.6129	1.4100	1.2634	1659.6	1654.7	1648.6	1643.4	1638.9

Table 3. Values of density ( $\rho$ ), viscosity ( $\eta$ ) and velocity ( $U$ ) of barium chloride in 1,4-dioxane-water mixtures.

Molarity of Salt	$\rho$ Kg.m <sup>-3</sup> Temperature (K)			$\eta \times 10^3$ Nsm <sup>-2</sup> Temperature (K)			$U$ ms <sup>-1</sup> Temperature (K)			
	303.15	308.15	313.15	318.15	323.15	303.15	308.15	313.15	318.15	323.15
(m)	303.15	308.15	313.15	318.15	323.15	303.15	308.15	313.15	318.15	323.15
0.198	1041.0	1039.5	1037.3	1036.2	1034.2	0.9825	0.8929	0.8098	0.7265	0.6591
0.400	1076.4	1074.5	1072.1	1071.0	1068.8	1.0399	0.9473	0.8564	0.7685	0.7068
0.598	1108.7	1106.6	1104.2	1103.2	1101.4	1.1071	1.0053	0.9101	0.8191	0.7489
0.802	1143.6	1141.0	1138.0	1137.0	1134.9	1.1710	1.0653	0.9615	0.8641	0.7928
1.002	1174.8	1172.4	1170.3	1170.0	1168.7	1.2430	1.1298	1.0193	0.9199	0.8475
	1,4-dioxane-water (10:90%)									
0.200	1046.3	1044.5	1041.6	1040.4	1038.0	1.1901	1.0669	0.9521	0.8541	0.7741
0.399	1080.7	1078.7	1076.4	1075.0	1072.5	1.2629	1.1317	1.0181	0.9160	0.8234
0.602	1116.8	1113.7	1111.6	1109.8	1106.8	1.3413	1.2084	1.0753	0.9715	0.8800
0.798	1148.2	1146.0	1143.8	1141.3	1138.1	1.4349	1.2937	1.1480	1.0281	0.9348
1.010	1181.6	1178.5	1176.1	1174.4	1170.8	1.5243	1.3862	1.2364	1.1075	0.9958
	1,4-dioxane-water (20:80%)									
0.210	1051.3	1049.4	1047.1	1045.0	1041.5	1.3928	1.2561	1.1079	0.9773	0.8841
0.398	1092.9	1091.4	1088.3	1086.0	1082.5	1.5099	1.3532	1.2058	1.0735	0.9639
0.601	1126.6	1124.6	1122.0	1119.7	1117.2	1.6294	1.4748	1.3030	1.1578	1.0426
0.800	1152.5	1150.7	1147.5	1145.5	1142.0	1.7482	1.5770	1.3864	1.2314	1.1121
0.998	1186.0	1183.0	1180.3	1177.8	1175.2	1.8689	1.6991	1.4964	1.3433	1.1895
	1,4-dioxane-water (30:70%)									
0.210	1051.3	1049.4	1047.1	1045.0	1041.5	1.3928	1.2561	1.1079	0.9773	0.8841
0.398	1092.9	1091.4	1088.3	1086.0	1082.5	1.5099	1.3532	1.2058	1.0735	0.9639
0.601	1126.6	1124.6	1122.0	1119.7	1117.2	1.6294	1.4748	1.3030	1.1578	1.0426
0.800	1152.5	1150.7	1147.5	1145.5	1142.0	1.7482	1.5770	1.3864	1.2314	1.1121
0.998	1186.0	1183.0	1180.3	1177.8	1175.2	1.8689	1.6991	1.4964	1.3433	1.1895



with water molecules and also with the complex of 1,4-dioxane-water molecules [15], resulting in increase in ultrasonic velocity and hence decrease in compressibility. The trend is same in 20 and 30% 1,4-dioxane mixtures for all the salts. Further, in all the cases, there is no pronounced variation in ultrasound velocity and compressibility with temperatures.

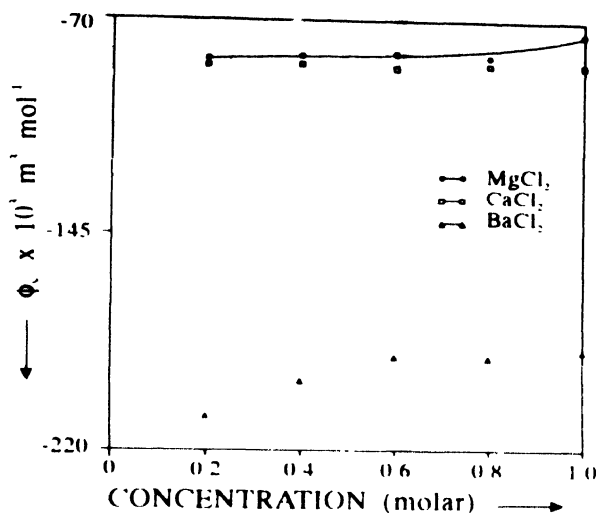


Figure 3(a). Apparent molar volume as a function of concentration of salt in 10% of 1,4-dioxane in 1,4-dioxane-water mixture.

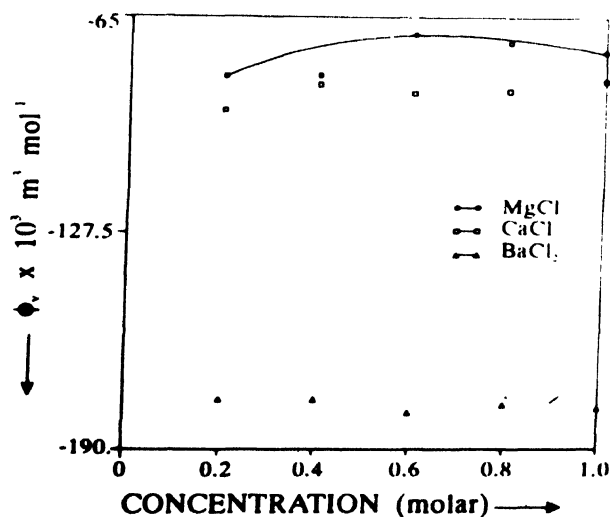


Figure 3(b). Apparent molar volume as a function of concentration of salt in 20% of 1,4-dioxane in 1,4-dioxane-water mixture.

A gradual increase in ultrasonic velocity with increase in 1,4-dioxane content in the solvent mixtures for all the salt solutions is observed. This is may be due to the bond

formation between water and 1,4-dioxane molecules. As 1,4-dioxane content is increased more and more hydrogen bonded 1,4-dioxane-water molecules are formed, resulting in an

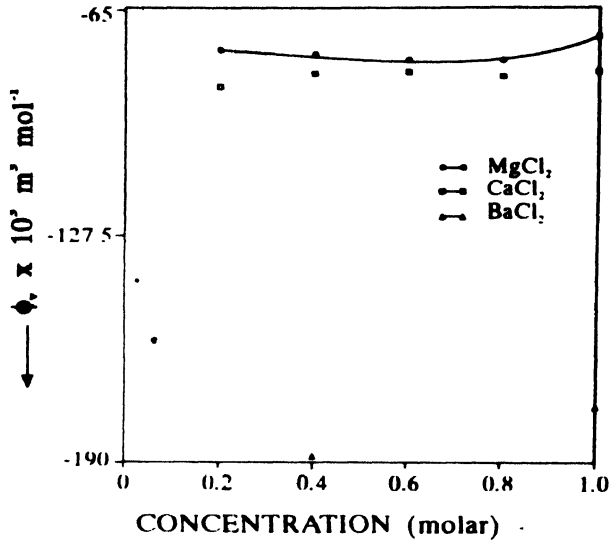


Figure 3(c). Apparent molar volume as a function of concentration of salt in 30% of 1,4-dioxane in 1,4-dioxane-water mixtures.

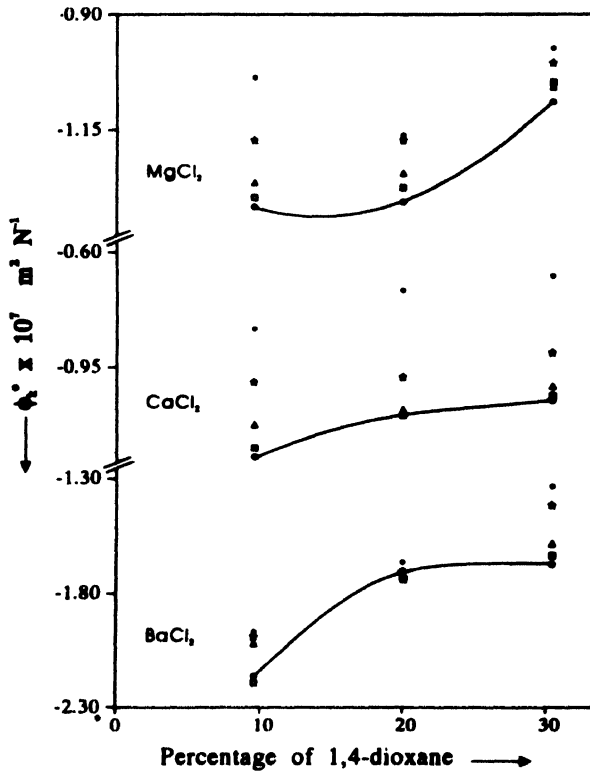


Figure 4. Variation of limiting molar compressibility of salt vs percentage of 1,4-dioxane (●—● 303.15 K, ■—■ 308.15 K, ▲—▲ 313.15 K, ★—★ 318.15 K and \*—\* 323.15 K).

increase in velocity and hence decrease in compressibility. The increase in ultrasonic velocity and decrease in compressibility with increase in 1,4-dioxane content clearly indicate the increasing trend of intermolecular association between 1,4-dioxane and water [15]. The further increase in velocity with increase in concentration of salt at a particular 1,4-dioxane content in all three salt solutions, may be attributed due to the formation of intermolecular ion-dipole bonds between the cations and solvent molecules. As a result the solutions becomes harder to compress, resulting in increase in velocity and hence a further reduction in compressibility.

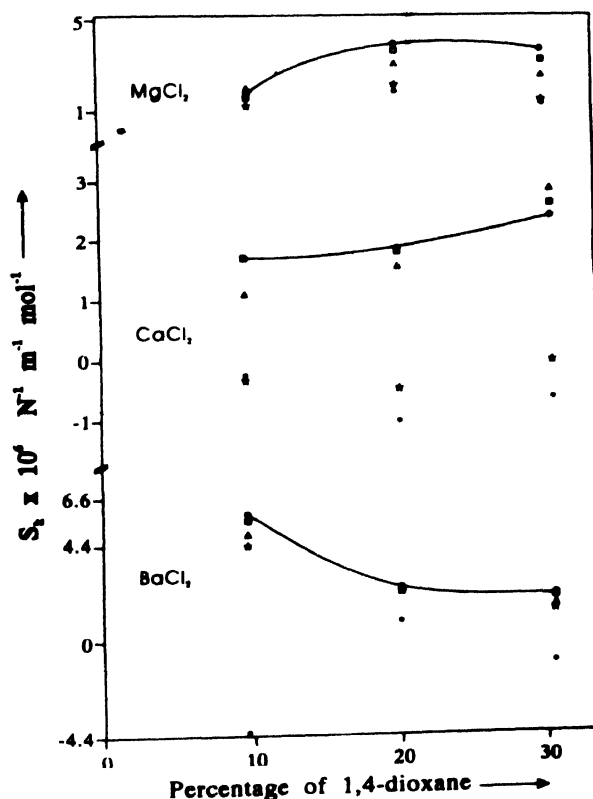


Figure 5. Plot of  $S_k$  of salt vs percentage of 1,4-dioxane (●—● 303.15 K, ■—■ 308.15 K, ▲—▲ 313.15 K, ★—★ 318.15 K and \*—\* 323.15 K).

The ultrasonic velocity decreases (increase in compressibility) as the cationic ( $\text{Mg}^{2+} < \text{Ca}^{2+} < \text{Ba}^{2+}$ ) radius increases in all the aqueous solutions of magnesium, calcium and barium chloride salts. The smaller rate of variations in ultrasound velocity with concentrations of salt in all the solutions may be due to the slight tendency of forming hydrogen-bond with water molecules.

From Figure 2, it is evident that the apparent molar compressibilities are negative for all the three electrolytic solutions over the entire range of salt concentration at all the temperatures studied (a sample plot is given at 303.15 K). The values of  $\Phi_k$  increase with the increasing concentration of salt in all the electrolytic solutions studied; however at higher

concentration, the same are found to decrease. This behaviour of the solution at higher concentration of the salt is due to pair formation and the presence of undissociated solute particles [16].

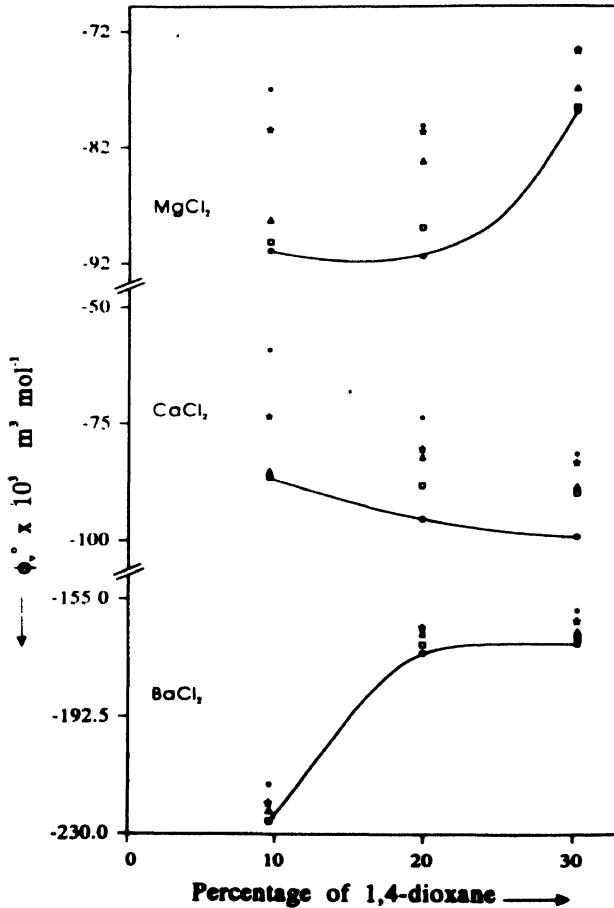


Figure 6. Variation of limiting molar volume of salt vs percentage of 1,4-dioxane (●—● 303.15 K, ■—■ 308.15 K, ▲—▲ 313.15 K, ★—★ 318.15 K and \*—\* 323.15 K).

The limiting apparent molar compressibility  $\Phi_k^0$  and  $S_k$  for each of the electrolytic solutions have been evaluated by least square method using the relation due to Masson [14]. It is evident from Figure 4 that  $\phi_k^0$ , which is a measure of the protection against compression on water exerted by solute molecules is negative and its magnitude decreases in all the cases with the increase in 1,4-dioxane content and temperature. The slope  $S_k$  (Figure 5) is a measure of solute-solvent interaction [17–19], which is positive and decreases with increase in temperature and 1,4-dioxane content.

The apparent molar volume behaves in a similar fashion (Figure 3) as that of apparent molar compressibility in all the solutions. From Figure 6, it is inferred that at all temperatures  $\Phi_v^0$  is negative for all the three electrolytic solutions indicating thereby the

presence of interactions between the ions and solvent [4]. It is also found that  $\phi^0$  increases with increase in cationic radii. The values of  $S_v$  (Figure 7), the measure of ion-ion interaction [4,20], are positive in all the electrolytes and show similar variation with increase in temperature and 1,4-dioxane content, as that of  $S_k$ . However, in the case of barium chloride alone in 20% 1,4-dioxane content, the  $S_v$  values are negative over the entire range of temperature. The negative values at 20% dioxane content indicate that the structure making

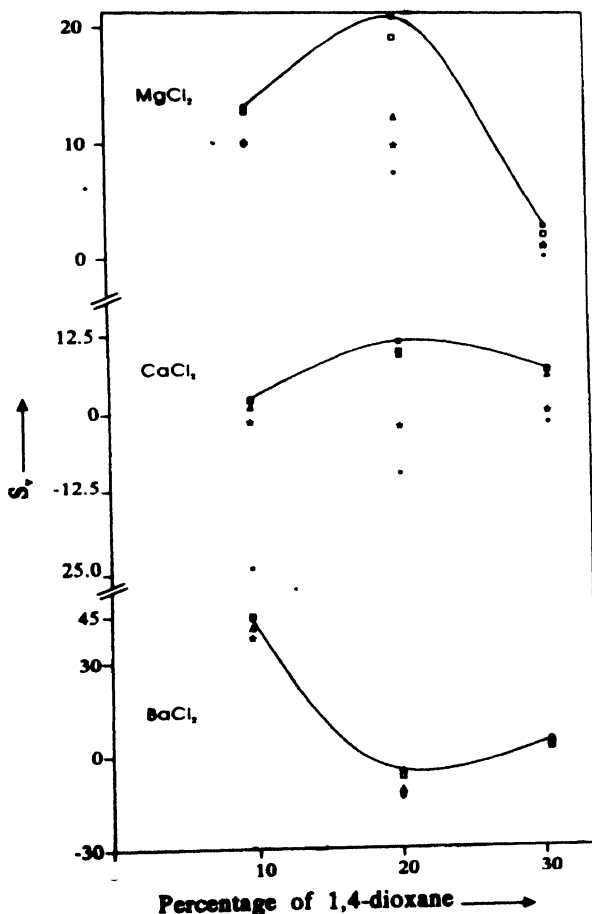


Figure 7. Plot of  $S_v$  of salt vs percentage of 1,4-dioxane (●—● 303.15 K, ■—■ 308.15 K, ▲—▲ 313.15 K, ★—★ 318.15 K and \*—\* 323.15 K).

effect is less predominant in  $Ba^{2+}$  ion than with ions carrying greater charge density ( $Mg^{2+}$ ,  $Ca^{2+}$ ). Since the larger radius (smaller charge density) carries smaller electrolytic force between the ions of salts of  $Ba^{2+}$ , it results in the smaller structure making effect when compared to  $Mg^{2+}$  and  $Ca^{2+}$  ions. A similar behaviour in the viscosity  $B$ -coefficient for the above three salts at 20% 1,4-dioxane content has also been reported [22]. The structure making effect is, therefore, more predominant in ions with greater charge than with ions carrying lower charge and hence the order of structure forming should be  $Mg^{2+} > Ca^{2+} > Ba^{2+}$ .

## 5. Conclusion

In the present investigation, it is evident that the presence of solute-solute and solute-solvent interactions resulting in attractive forces, promote the structure making characteristics of the salts. This interaction becomes weaker with increase in temperature. These conclusions are in good agreement with those drawn from other studies [21,22] like free volume, internal pressure, viscosity  $B$ -coefficient and PMR spin-lattice relaxation time.

## Acknowledgment

One of the author (VR) is highly thankful to Prof. G Shanmugam, Principal and The Management, M S Engg. College for their interest in this publication.

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