Thermodynamic study of calcium chloride and magnesium chloride in binary aqueous mixtures of sucrose at different temperatures

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ABSTRACT

Thermodynamic property (partial molar volumes) of some alkaline earth metal chlorides viz; calcium chloride and magnesium chloride have been determined in binary aqueous mixtures of sucrose (3, 6, 9 and 12% by weight of sucrose) with the help of density measurements at one temperature 303.15K. Effect of temperature was also studied for these electrolytes in 3% (w/w) sucrose + water and five different temperatures (298.15, 303.15, 308.15, 313.15 and 318.15K) were taken for the study. The density measurements were made by using Ward and Millero method and results have been analysed by Masson's equation. The experimental values of slopes and partial molar volumes of these alkaline earth metal chlorides have been interpreted in terms of ion-ion or ion –solvent interactions. The ϕ_E^0 value have also been determined which is interpreted in terms of structure making or breaking capacities of these salts. In the present study the alkaline earth metal chlorides have been found as structure breakers in binary aqueous mixture of sucrose.

Key words: partial molar volumes, structure breaker, alkaline earth metal chlorides.
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INTRODUCTION

Partial molar volume is one of the most important thermodynamic properties that can be used as a tool for determining the various types of interactions like ion-ion, ion - solvent and solvent – solvent interactions occurring in aqueous and non-aqueous solutions   [1-10]. Recently much interest has been shown for the study of saccharides because of their physical, biochemical and industrially useful properties [11–17]. In addition to their importance in the food, pharmaceutical and chemical industries, these saccharides have received considerable attention for their ability to protect biological macromolecules [18,19].The structural and physical properties of the solutions can be determined by ion-ion, ion - solvent and solvent – solvent interactions and a lot of work has been done for various electrolytes in different binary aqueous mixtures but less attention is paid for alkaline earth metal chlorides viz., magnesium chloride and calcium chloride in binary aqueous mixtures of sucrose. The present study is to understand the interactions of magnesium chloride and calcium chloride in sucrose + water system.

Biologically magnesium is vital to health and Mg^{2+} ion is a component of every cell type. It is also available in significant amount in nuts and certain vegetables. Chlorophyll, the pigment that absorbs light in plants, interacts heavily with magnesium and is necessary for photosynthesis. Calcium is an important component in cement and mortars, and thus is necessary for construction. It is also used to aid cheese production. So it is interesting and important to see the interactions of these salts of calcium and magnesium with the aqueous sucrose solutions.

EXPERIMENTAL SECTION

The reagents magnesium chloride [$MgCl_2.6H_2O$, M. W. 203.30 g], calcium chloride [$CaCl_2. 2H_2O$, M.W. 147.02 g] and sucrose [$C_{12}H_{22}O_{11,}$ M. W. 342.30 g] were taken of AR grade in the present study. All these reagents were used after drying over anhydrous calcium oxide in desiccators. Fresh triple distilled water was used as standard solvent

for preparing binary aqueous mixtures of sucrose and other solutions. The binary aqueous mixtures of sucrose and five different concentrations of above mentioned alkaline earth metal chlorides were prepared by weight and the conversion of molality (m) into molar concentration (C) was done by using the standard expression:

$$C = \frac{md1000}{1000+mM_2} \tag{1}$$

Where, d is the density of solution and M_2 is the molecular weight of alkaline earth metal chlorides.

The density was measured with the help of an apparatus similar to the one reported by Ward and Millero [20]. This apparatus consist of a glass float which is suspended with nylon thread from a balance pan into a cylindrical sample container. The sample container has a bakelite top and placed in a water bath. The whole assembly of sample container and water-bath was placed in thermostat whose temperature was controlled with the help of an electronic relay. The fluctuation in temperature was within $\pm$ 0.01K. The densities of different aqueous solution of alkaline earth metal chlorides were calculated with the help of the equation:

$$d - d_0 = \frac{(W_0 - W)}{v_f} \tag{2}$$

Here, d and d_0 are the densities of sample solution and water respectively; w and w_0 are the weights of float in sample solution and water respectively. The calibration of float was checked by measuring density of pure methanol at 308.15K (our value d = 0.7773 gcm^{-3} is in good agreement with literature valued = 0.7770 gcm^{-3}) [21]. The accuracy in the density measurements was 1 x 10^{-4} gcm^{-3}.

The apparent molar volumes (ϕ_v) were calculated from the density data using the following expression [22]

$$\phi_v = \frac{1000(d_0-d)}{cd_0} + \frac{M_2}{d_0} \tag{3}$$

where d_0 is the density of sucrose + water as solvent and d is the density of solution; c is the molar concentration of the salts and M_2 is the molecular weight of alkaline earth metal chlorides. The density measurements were carried out in a well stirred water bath with a temperature control of $\pm$ 0.01 K.

RESULTS AND DISCUSSION

The densities of solutions of magnesium chloride and calcium chloride in different compositions of sucrose + water (3,6,9 and 12 wt %) at 303.15 K have been measured and were used to calculate the apparent molar volumes ϕ_v. The plots of ϕ_v verses $\sqrt{C}$ were found to be linear in different compositions of sucrose + water. A sample plot for calcium chloride in different compositions of sucrose + water at 303.15K is shown in fig.1. The partial molar volumes ϕ_v^0 were calculated by using least square fit to the linear plots of experimental values of ϕ_v versus square root of molar concentration c and using Masson equation

$$\phi_v = \phi_v^0 + S_v^* C^{1/2} \tag{4}$$

where ϕ_v^0 is the partial molar volume and S_v^* is the experimental slope.

Table - 1 Partial molar volumes (ϕ_v^0) and experimental slopes (S_v^*) for magnesium chloride and calcium chloride in sucrose + water mixtures at 303.15K

Sucrose + Water (% w/w)	Magnesium chloride		Calcium chloride	
	ϕ_v^0 (cm^3 mol^{-1})	S_v^* (cm^{3}dm$^{3/2}$mol$^{-3/2}$)	ϕ_v^0 (cm^3 mol^{-1})	S_v^* (cm^{3}dm$^{3/2}$mol$^{-3/2}$)
3	55.14	2.23	77.62	-0.76
6	39.20	2.70	72.66	-0.66
9	24.49	3.10	71.11	-0.65
12	11.66	3.17	63.30	-0.62

Table 1 shows the values of ϕ_v^0 and S_v^*, calculated in different compositions of binary aqueous mixture of sucrose at 303.15 K. It is clear, from table 1, that the values of slopes (S_v^*) are positive for magnesium chloride and negative for calcium chloride in sucrose + water mixture at 303.15K in all the compositions. The positive slope values for magnesium chlorides indicate the presence of strong ion- ion interactions and negative slopes in case of calcium chloride indicate the presence of weak ion- ion interactions. Also, from Table 1, it is clear that the magnitude of S_v^* values of alkaline earth metal chlorides increases with the increase in the amount of sucrose in water, which shows that ion-ion interactions are further, strengthened which may be attributed to the less solvation of ions on the

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addition of sucrose to water for both the alkaline earth metal chlorides studied here. Also from Table 1, it is clear that the ϕ_v^0 values are positive and decrease in magnitude, in all the compositions of sucrose + water at 303.15K for both the alkaline earth metals chlorides. The trend of ϕ_v^0 values, for both the alkaline earth metals chlorides, with the increase of sucrose amount in water, shows that ion- solvent interactions decrease on the addition of sucrose in water Also, on comparing the magnitudes of ϕ_v^0 values with the values of S_v^* , ϕ_v^0 values are more in magnitudes than that of S_v^* of the same alkaline earth metal chlorides indicate that ion-solvent interactions dominate over the ion-ion interactions in water + sucrose mixture at 303.15 K.
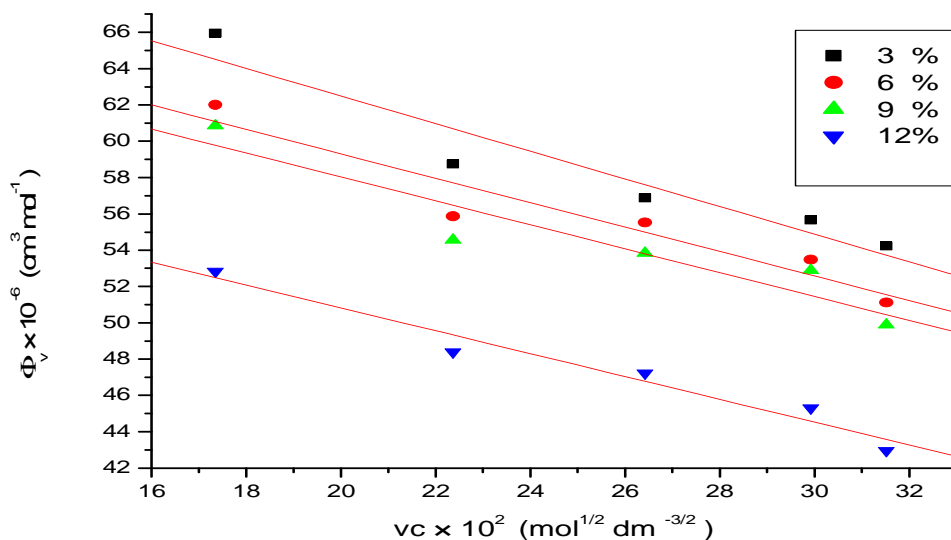

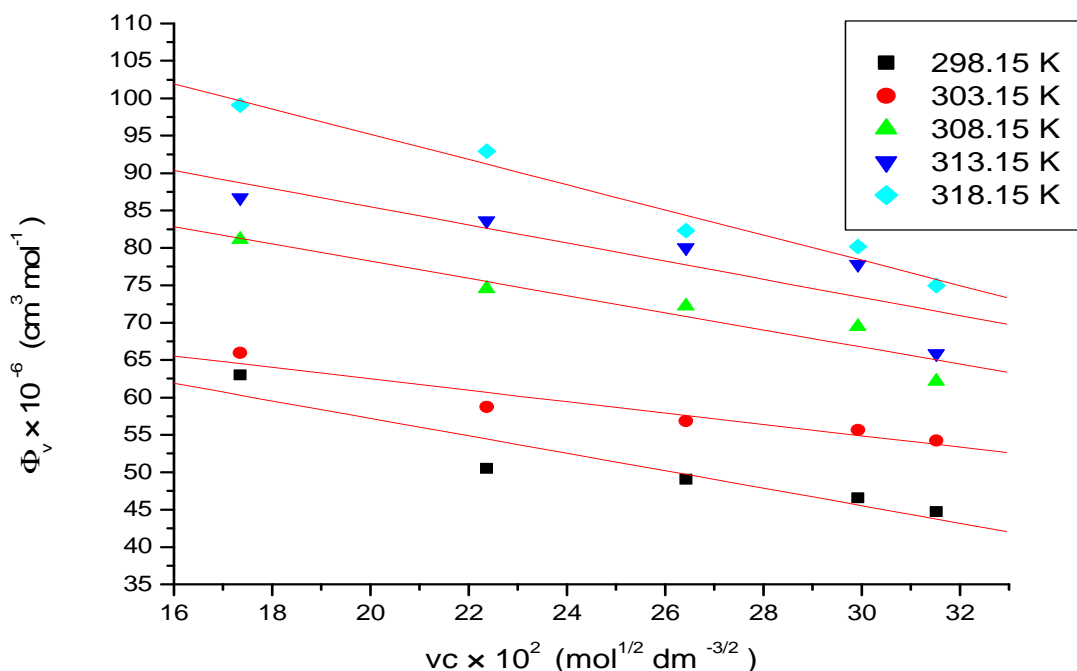**Fig1: Plot of ϕ_v Vs $C^{1/2}$ for calcium chloride in different compositions of sucrose + water at 303.15K**

Fig 2: Plot of ϕ_v Vs $C^{1/2}$ for calcium chloride in 3% binary mixture of sucrose + water at different temperatures

Effect of temperature: Since the behaviour of both the electrolytes was found to be linear and same in different composition of sucrose + water at 303.15 K, so only one composition system (3% w/w) has been selected for analysing the effect of temperature. The experimentally determined values for the five different concentrations of both the alkaline earth metal chlorides at five different temperatures (298.15 – 318.15K) have been used to calculate

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the partial molar volume ϕ_v^0 of the salts.The plot of apparent molar volume ϕ_v against the $\sqrt{C}$ were found to be linear as shown in fig. 2 for calcium chloride as sample plot.

Table - 2 Partial molar volumes (ϕ_v^0) and experimental slopes (S_v^*) for magnesium chloride and calcium chloride in 3% (w/w) sucrose + water mixture at different temperatures

Temperature (K)	Magnesium Chloride		Calcium Chloride	
	ϕ_v^0 (cm^3 mol^{-1})	S_v^* (cm^{3}dm$^{3/2}$mol$^{-3/2}$)	ϕ_v^0 (cm^3 mol^{-1})	S_v^* (cm^{3}dm$^{3/2}$mol$^{-3/2}$)
298.15	52.02	1.99	80.43	-1.16
303.15	55.14	2.23	77.62	-0.76
308.15	104.33	1.07	101.07	-1.14
313.15	114.07	0.75	109.64	-1.21
318.15	153.81	0.60	128.73	-1.68

It is evident from table 2 that the values of S_v^* are negative for calcium chlorides in 3% aqueous mixture of sucrose at all temperatures. The negative S_v^* values indicate the presence of weak ion-ion interactions for calcium chloride and positive S_v^* values indicate the presence of strong ion-ion interactions for magnesium chloride and these values further decrease with the increase in temperature trait to decrease in ion-ion interactions and attribute the increase in the solvation of alkaline earth metal ions with rise in temperature. Also it is clear from table 2 , that the values of ϕ_v^0 increase with increase in temperature , for these alkaline earth metal chlorides in sucrose + water (3 % w/w) , thereby showing that ion – solvent interactions are strengthened with increase in temperature. The increase in ϕ_v^0 values may be trait to increase in solvation of alkaline earth metal ions with rise in temperature.

It has been found that only S_v^* is not only one parameter for determining the structure making or structure breaking nature of any solute. Limiting molar expansibilities ϕ_E^0 is another parameter, which determines the structure making or breaking capacity of any solute in any of the solvent developed by Hepler [23].

The temperature dependence of ϕ_v^0 in 3% Sucrose + water [relations (5) and (6)] for magnesium chloride and calcium chloride can be expressed by the following relations:

ϕ_v^0 = - 11339.83 + 64.76T - 0.094T2 for magnesium chloride   (5)

ϕ_v^0 = -5368.75 + 30.96T - 0.043T2 for calcium chloride   (6)

Limiting molar expansibilities $\phi_E^0 = \left[\frac{\partial \phi_v^0}{\partial T}\right]_P$,which is temperature dependence function of ϕ_v^0 ,is calculated for both the alkaline earth metal chlorides by using relations (5) and (6) and are given in table 3.

Table - 3 Variation of limiting apparent molar volume expansibilities (ϕ_E^0) for magnesium chloride calcium and chloride in 3% (w/w) sucrose + water mixture at different temperatures

Temperature (K)	Magnesium Chloride in 3% (w/w) Sucrose + water ϕ_E^0 (cm^3 mol^{-1} K^{-1})	Calcium Chloride 3% (w/w) Sucrose + water ϕ_E^0 (cm^3 mol^{-1} K^{-1})
298.15	8.708	5.319
303.15	7.768	4.889
308.15	6.828	4.459
313.15	5.888	4.029
318.15	4.948	3.599

It is clear from this table that the values of ϕ_E^0 decrease in magnitude with the rise in temperature for both the alkaline earth metal chlorides. The decrease in magnitude per degree temperature suggesting that the behavior of both the alkaline earth metal chlorides is not similar to that of symmetrical tetra alkyl salts [24] but like those of common electrolytes [25,26].The variation ϕ_E^0 with temperature, for both the alkaline earth metal chlorides, is linear as shown in figure 3. This positive decrease with temperature may be ascribed to the absence of "caging/packing effect''.
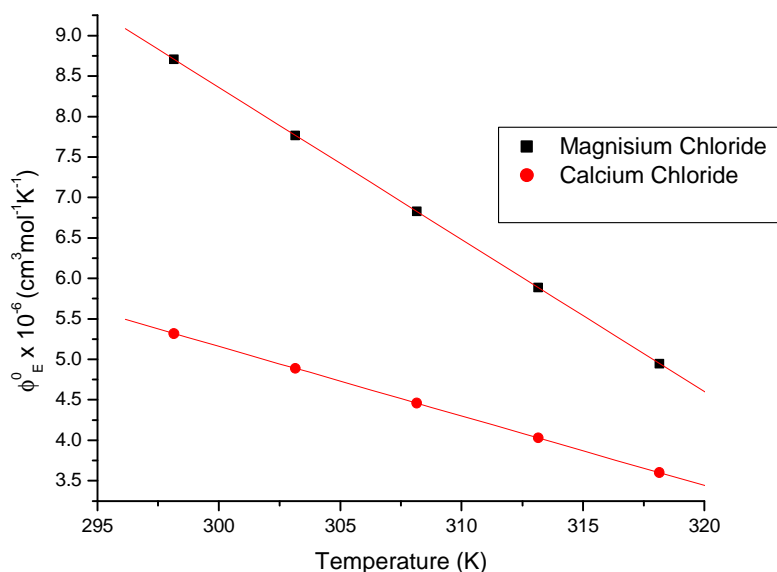
Fig.3 Plot of ϕ_E^0 verse temperature for magnesium chloride and calcium chloride in 3% sucrose + water

Hepler has developed a technique of examining the sign of $[\partial^2 \phi_v^0 / \partial T^2]_p$ i.e. second derivative of partial molar volume with respect to temperature at constant pressure, for various solutes in terms of long range structure making and breaking capacity of the solutes in aqueous solutions using the general thermodynamic expression [23]:

$$[\partial C_P / \partial P]_T = - [\partial^2 \phi_v^0 / \partial T^2]_p \tag{7}$$

It is observed from relations (5) and (6) that $[\partial^2 \phi_v^0 / \partial T^2]_p$ for the solutions of both the alkaline earth metal chlorides is negative showing that both the alkaline earth metal chlorides behave as structure breakers in sucrose + water mixtures.

CONCLUSION

In the present study both the alkaline earth metals have been found as structure breakers in sucrose + water mixtures. Also the behavior of both the alkaline earth metal chlorides has been found similar to common electrolytes.

REFERENCES

[1] ML Parmar; RK Awasthi ; MK Guleria. *Indian J. Chem.,* **2004**, 116(1),33-38
[2] ML Parmar; MK Guleria, *J Indian Chem. Soc.,* **2005**, 82, 648.
[3] ML Parmar; RC Thakur, *Proc. Nat. Acad. Sci. India.,* **2006**, 76 (A), 183
[4] ML Parmar; RC Thakur. *J Mol Liq.*, **2006**, 128, 85-89.
[5] SJ Kharat. *J. Mol. Liq.,* **2008**, 140, 10-14.
[6] SL Oswal; SP Ijardar. *J Mol.Liq.*, **2009**, 144, 115-123.
[7] ML Parmar; P Sharma; MK Guleria. *Ind. J. Chem.,* **2009**, 48, 57-62.
[8] MN Roy; RS Sah; PP Pradhan; PK Roy. *Russian J. Phy. Chem. A*., **2009**, 83(11), 1887-1895.
[9] SD Deosarkar; AL Puyad. *Russian J. Phy. Chem. A.,* **2014**, 88(6), 946-950.
[10] RC Thakur; Sonika. *Research J. Pharma, Bio. and Chem., Sci.,* **2014**, 5(6) 1298-1305.
[11] RN Goldberg; YB Tewari. *J. Phys. Chem.Ref. Data.,* **1989**, 18, 809.
[12] J Boerio Goates. *J. Chem. Thermodyn.,* **1991**, 23, 403.
[13] RL Putnam; J Boerio-Goate. *J. Chem. Thermodyn.,* **1993**, 25, 607.
[14] RN Goldberg; YB Tewari. *J. Biol. Chem.,* **1989**, 264, 9897.
[15] RN Goldberg; YB Tewari; JC Ahluwalia. *J. Biol. Chem.,* **1989**, 264, 9901.
[16] YB Tewari; RN Goldberg. *Biophys. Chem.,* **1991**, 40, 59.
[17] GG Birch; SShamil. *J. Chem. Soc. Faraday Trans.I.,* **1988**, 84, 2635.
[18] T Arakawa; Y Kita; JF Carpenter. *Pharmcol. Res.,* **1991**, 8, 285.
[19] DP Miller; JJ de Pablo. *J. Phys. Chem.,* **2000**, B104, 8876.
[20] GK Ward; FJ Millero. *J Solution Chem.,* **1974**, 3,417.

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[21] AWeissberger; ES Proskaver. Techniques of organic chemistry (Inter Science. Publications, New York), Vol.VII (**1967**).

[22] FJ Millero. Structure and Transport Processes in water and Aqueous Solution, edited by R A Horne, (Wiley – inter Science, New York) **1971**, chap. 13, p 521.

[23] LG Hepler. *Can J Chem.,* **1969**, 47, 4613.

[24] FJ Millero. Structure and Transport Processes in Water and Aqueous Solutions, Ed. by R. A. Horne, John Wiley and Sons, Inc., Interscience Division, N.Y., 519-595.

[25] FJ Milllero; W.Hansen Drost., *J.Phys. Chem.* **1968**, **72** (6), 2251-2254.

[26] FJ Millero. *Chem.Rev.***1971**, **71** (2), 147-176.