Research Article

Transport studies of alkaline earth metal chlorides in binary aqueous mixtures of sucrose at different temperatures

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ABSTRACT

Viscosities 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 has also been studied by taking equidistant temperatures (298.15, 303.15, 308.15, 313.15 and 318.15K) for these electrolytes in 3% (w/w) sucrose + water. Viscosity data has been analysed by using Jones – Dole equation and B-coefficient values are determined. The obtained parameters have also been interpreted in terms of ion –ion and ion – solvent interactions. In the present study, magnesium chloride and calcium chloride act as structure breakers in sucrose + water system.

Keywords: B - coefficient, relative viscosity and structure breakers.
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INTRODUCTION

Viscosities of solutions of electrolytes are usually done to obtain information about structure and properties of solutions [1-4].There are different types of interactions existing between the ions in the electrolytic solutions and ion – ion and ion – solvent interactions are of current interest. A number of researchers found that the addition of an electrolyte either breaks or makes the structure of the liquid and these interactions help in the understanding of the nature of the solvent. The survey of literature [5-13] shows that many studies have been carried out for various electrolytic solutions but little attention has been paid to the behaviour of magnesium chloride and calcium chloride in different compositions of sucrose + water.

Recently much interest has also been shown for the study of sugars (carbohydrates) because of their biochemical and industrial importance [14-20]. In addition to their importance in the food, pharmaceutical and chemical industries, sugars have received considerable attention for their ability to protect biological macromolecules [21,22].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 solutions. Biologically magnesium is vital to the 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 salts of calcium and magnesium with aqueous sucrose solutions. Hence, the present study is an attempt to study the solute-solute and solute-solvent interactions in sucrose + water solvent systems.

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EXPERIMENTAL SECTION

Alkaline earth metal chlorides viz; 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] of analytical grade were used after drying over P_2O_5 desiccators. Double distilled water was used for the preparation of binary aqueous mixtures of sucrose. The binary aqueous mixtures of sucrose as well as the solutions of magnesium chloride and calcium chloride of different concentrations has been prepared by weight and the conversion of molal solutions (m) into molar solution (C) were made by using the following expression:

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

where d and M_2 is the density and molecular weight of the each of the salt. The densities of solutions of magnesium chloride and calcium chloride were measured with the help of an apparatus as described by the Ward and Millero [23].The glass sample cell had a Bakelite top with a hole in the centre and was placed in a water bath ($\pm 0.01^o$C).Density was calculated using the relation:

$$d = d_0 + \frac{w_0 - w}{d} \tag{2}$$

where d and d_0 are densities of sample solution and pure water respectively, w and w_0 are the weights of float in the sample solution and water, and V_f is float volume. The relative viscosities of the solutions of magnesium chloride and calcium chloride were determined with the help of Ostwald viscometer with the flow time of 289.89 seconds for water at 303.15K. Process was repeated until three successive determinations were obtained with in ± 0.1 seconds. No kinetic energy correction required, as the flow time was greater than 100 seconds. The relative viscosities of the solutions were determined by usual procedure [24-25].The density and viscosity studies were carried out in water thermostat (± 0.01K) in order to study the effect of temperature.

RESULTS AND DISCUSSION

The relative viscosities and densities of the solutions of magnesium chloride and calcium chloride in sucrose + water system in four different compositions 3,6,9 and 12% (w/w) were determined at 303.15K.The relative viscosity data has been analyzed by using Jones Dole equation[26].

$$\eta_{rel} = \frac{\eta}{\eta_0} = 1 + AC^{1/2} + BC \tag{3}$$

where, η and η_0 are the viscosities of solutions and solvent respectively. A and B are two constants parameters. A coefficient corresponds to ion- ion interactions and parameter B coefficient corresponds to ion – solvent interactions. These parameters A and B have been obtained by plotting a graph between $(\eta_r - 1)/\sqrt{C}$ verses $\sqrt{C}$ for both the alkaline earth metal chlorides in all the prepared compositions of sucrose + water at one temperature i.e 303.15 K. All these obtained values of A and B parameters were recorded in Table 1 and a sample plot of $(\eta_r - 1)/\sqrt{C}$ verses $\sqrt{C}$ shown in Figure.1 for calcium chloride.

TABLE 1 : Values of A and B Coefficients of the Jones Dole Equation for magnesium chloride and calcium chloride in different compositions of sucrose + water at 303.15K

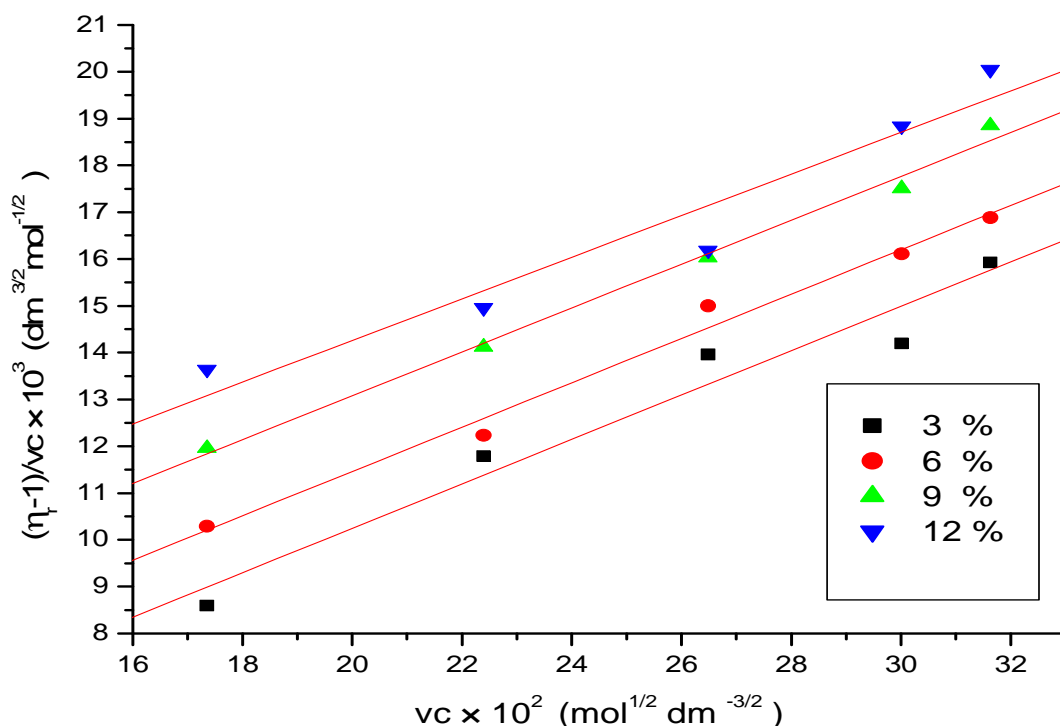| Composition of Sucrose+ Water [(w/w)%]	Magnesium Chloride		Calcium Chloride	
	A ($dm^{3/2}mol^{-1/2}$)	B (dm^3mol^{-1})	A ($dm^{3/2}mol^{-1/2}$)	B (dm^3mol^{-1})
3	0.933	0.398	0.763	0.474
6	1.972	0.391	1.978	0.466
9	2.824	0.385	3.676	0.458
12	4.103	0.377	5.315	0.431

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Figure 1: Plots of $(\eta_r\text{-}1)/\sqrt{c}$ Vs $\sqrt{c}$ for calcium chloride in different compositions of sucrose + water at 303.15 K

It is clear from, Table - 1 that the values of A increases with the increase in the content of sucrose in water indicating that ion- ion interactions are strengthened with the increase in the content of sucrose in water. It is also clear from Table - 1 that the values of B-coefficient for magnesium chloride and calcium chloride are positive, in the entire composition range of binary aqueous mixtures of sucrose at 303.15K, thereby showing the presence of strong ion –solvent interactions. Further values of B –coefficient decrease with the increase of sucrose content in water at 303.15K, for an individual salt, thereby showing that ion – solvent interactions are weakened with the increase of sucrose content in water. In other words ion –solvation decreases as the composition of sucrose in water increases, or it may be said that sucrose has less affinity for an electrolyte than that for water.

The viscosity data has also been analysed on the basis of transition state treatment of relative viscosity as proposed by Feakins*et al* [27].The parameter B in terms of transition state theory is given by the following relation:

$$B = \frac{\overline{V_1^0} - \overline{V_2^0}}{1000} + \frac{\overline{V_1^0}}{1000}\left[\frac{\Delta\mu_2^0 - \Delta\mu_1^0}{RT}\right] \tag{4}$$

Where,$\overline{V_1^0}$ is mean volume of the solvent, $\overline{V_2^0}$ is the partial molar volume of the alkaline earth metal chlorides,$\Delta\mu_1^{0^*}$ and $\Delta\mu_2^{0^*}$ are the free energies of activations per mole of pure solvent and alkaline earth metal chlorides respectively and were calculated by the following relations [28]:

$$\Delta\mu_1^{0^*} = RTIn\left(\eta_0\overline{V_1^0}/hN\right) \tag{5}$$

$$\Delta\mu_2^{0^*} = \Delta\mu_1^{0^*} + RT/\overline{V_1^0}\left[1000B - \left(\overline{V_1^0} - \overline{V_2^0}\right)\right] \tag{6}$$

Where R is the gas constant T is the absolute temperature η_0 is the viscosity of the solvent, h is the Planck's constant and N is the Avogadro number.

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The values of $\Delta\mu_1^{0^*}$ were calculated with the help of relation (5) and are given in Table 2 for mixed solvents, each solvent mixture was treated as pure and the molar volume taken as a mean volume given as:

$$\overline{V_1^0} = (x_1 M_1 + x_2 M_2)/d_1 \tag{7}$$

Where x_1, M_1 and x_2, M_2 are the mole fractions and molecular weights of the water and sucrose respectively and d_1 is the density of (sucrose + water) as solvent. The values of $\overline{V_2^0}$ for the alkaline earth metal chlorides calculated with the help of the density data and are recorded in Table 2. The values of $\Delta\mu_2^{0^*}$ and $\overline{V_1^0}$ calculated with the help of relations (6) and (7) and are also recorded in Table 2.

TABLE 2: Values of $\overline{V_1^0}$, $\overline{V_2^0}$, $\Delta\mu_1^{0^*}$ and $\Delta\mu_2^{0^*}$ for magnesium chloride and calcium chloride in different compositions of sucrose + water at 303.15K

Composition of Sucrose + Water (w/w %)	Magnesium Chloride				Calcium Chloride			
	$\overline{V_1^0}$ (dm³ mol⁻¹)	$\overline{V_2^0}$ (dm³ mol⁻¹)	$\Delta\mu_1^{0^*}$ (kJ mol⁻¹)	$\Delta\mu_2^{0^*}$ (kJ mol⁻¹)	$\overline{V_1^0}$ (dm³ mol⁻¹)	$\overline{V_2^0}$ (dm³ mol⁻¹)	$\Delta\mu_1^{0^*}$ (kJ mol⁻¹)	$\Delta\mu_2^{0^*}$ (kJ mol⁻¹)
3	18.42	55.14	61.49	120.98	18.42	77.62	61.49	134.46
6	18.70	39.20	61.72	117.20	18.70	72.66	61.72	131.82
9	19.15	24.49	61.94	113.31	19.15	71.11	61.94	129.06
12	19.65	11.66	62.21	109.54	19.65	63.30	62.21	123.09

It is clear from the table that the values of $\Delta\mu_1^{0^*}$ and $\overline{V_1^0}$ are practically constant in all the solvent compositions. Also the values of $\Delta\mu_1^{0^*}$ does not change much with the change in composition of sucrose in water at 303.15K. In other words it may be said that $\Delta\mu_1^{0^*}$ values for different compositions of sucrose +water at 303.15 K are practically constant and values of $\Delta\mu_2^{0^*}$ change with solvent composition for each electrolyte in sucrose +water at 303.15 K. Further the positive values of $\Delta\mu_2^{0^*}$ suggest that the transition state formation is less favoured in the presence of the alkaline earth metal chlorides. This indicates that the formation of transition state is followed by the breaking and distortions of the intermolecular bonds between sucrose and water.

Many workers intensified that instead of parameter B, $\frac{dB}{dT}$ is a better criterion for determining the structure making/breaking nature of any solute [29]. In order to analyse $\frac{dB}{dT}$ parameter, the effect of temperature must be studied.

Effect of temperature:
Since the behaviour of both the alkaline earth metal chlorides in different compositions 3%, 6%, 9% and 12% (w/w) of sucrose + water was found to be linear and identical at 303.15 K. So, only 3% (w/w) sucrose + water system has been selected for analysing the effect of temperatures (298.15K, 303.15K, 308.15K, 313.15K and 318.15 K). The plot of $(\eta_r - 1)/\sqrt{C}$ verses $\sqrt{C}$ has been found to be linear for both the alkaline earth metal chlorides at five temperatures (298.15K to 318.15K). A sample plot for calcium chloride in 3% w/w sucrose + water system is shown in Figure.2 at different temperatures. This is in accordance to the Jones – Doles equation. The plot of $(\eta_r - 1)/\sqrt{C}$ verses $\sqrt{C}$ has been fitted to least square fit method to obtain the values of A and B parameters.

TABLE 3: Values of A and B Coefficients of Jones Dole Equation for magnesium chloride and calcium chloride in 3% sucrose + water at different temperature

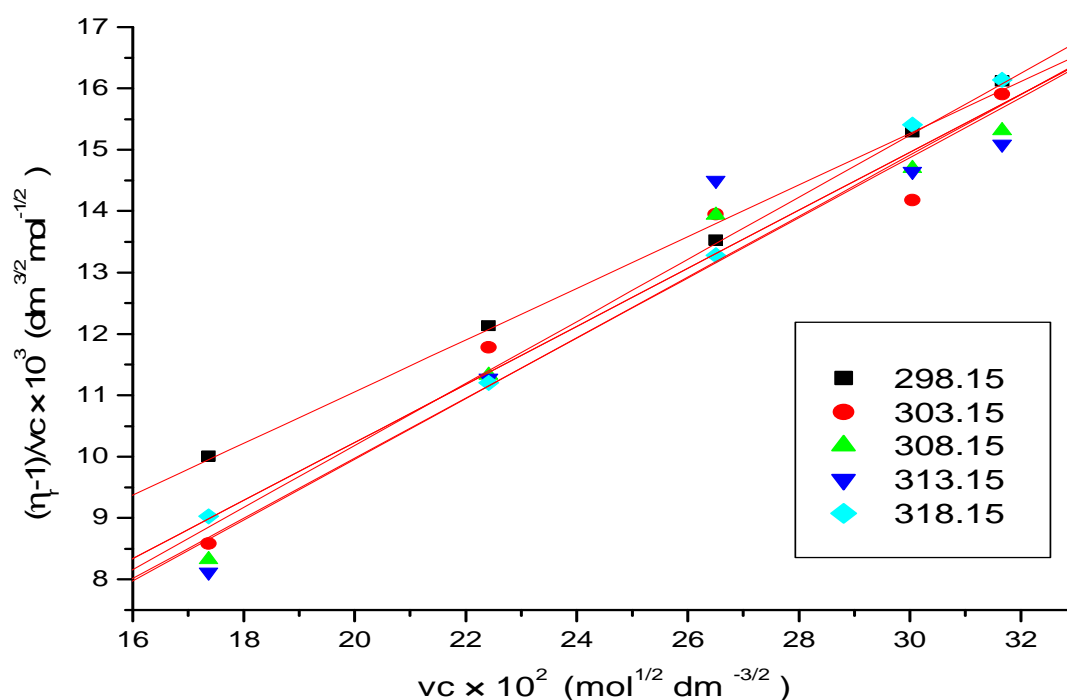| Temperature (K)	Magnesium Chloride		Calcium Chloride	
	A (dm³/² mol⁻¹/²)	B (dm³ mol⁻¹)	A (dm³/² mol⁻¹/²)	B (dm³ mol⁻¹)
298.15	2.150	0.384	2.632	0.421
303.15	0.933	0.398	0.763	0.474
308.15	0.171	0.407	0.152	0.492
313.15	0.104	0.418	0.035	0.498
318.15	0.027	0.426	0.026	0.511

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Figure 2: Plot of (η$_{r}$-1)/√c Vs √c for calcium chloridein 3% sucrose + water at different temperature

It is clear from Table 3, that the values of A parameter decreases with the rise in temperature in 3% w/w sucrose + water for both the alkaline earth metal chlorides. So, it suggests that ion- ion interactions are weakened with the rise of temperature. In order words, the presence of weak ion – ion interactions may attributes to increase in the solvation of alkaline earth metal ions in sucrose + water system. From Table 3, the values of B-coefficients are positive for both the alkaline earth metal chlorides in 3% w/w sucrose + water at all temperatures. These positive values indicate the presence of strong ion – solvent interactions. Further the values of B-coefficients increase with the rise in temperature which suggests that ion-solvent interaction are enhanced with rise in temperature for both these alkaline earth metal chlorides. The value of $\frac{dB}{dT}$ is positive for both the alkaline earth metal chlorides in 3% w/w sucrose + water. This indicates the structure breaking nature of magnesium chloride and calcium chloride in sucrose + water system. The data of viscosity B-coefficients at 298.15, 303.15, 308.15, 313.15 and 318.15 K has also been interpreted by applying the transition state theory. The values of $\Delta\mu_1^{0^*}$ and $\Delta\mu_2^{0^*}$ have been recorded in Table 4.

TABLE 4: Values of $\overline{V_1^0}$, $\overline{V_2^0}$, $\Delta\mu_1^{0^*}$ and $\Delta\mu_2^{0^*}$ for magnesium chloride and calcium chloride in 3% sucrose + water at different temperature

Temperature (K)	Magnesium Chloride				Calcium Chloride			
	$\overline{V_1^0}$, (dm³ mol⁻¹)	$\overline{V_2^0}$, (dm³ mol⁻¹)	$\Delta\mu_1^{0^*}$ (kJ mol⁻¹)	$\Delta\mu_2^{0^*}$ (kJ mol⁻¹)	$\overline{V_1^0}$, (dm³ mol⁻¹)	$\overline{V_2^0}$, (dm³ mol⁻¹)	$\Delta\mu_1^{0^*}$ (kJ mol⁻¹)	$\Delta\mu_2^{0^*}$ (kJ mol⁻¹)
298.15	18.39	52.02	60.74	117.03	18.39	80.43	60.74	125.85
303.15	18.42	55.14	61.49	120.97	18.42	77.62	61.49	134.45
308.15	18.42	104.33	62.24	130.80	18.42	101.07	62.24	142.17
313.15	18.45	114.07	62.94	135.42	18.45	109.64	62.94	146.09
318.15	18.49	153.81	63.74	144.04	18.49	128.73	63.74	152.61

According to Feakins model, $\Delta\mu_2^{0^*}$ increases with temperature for solutes having positive dB/dT which is nicely shown by both these salts[30].

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TABLE 5: Values of $(\Delta\mu_2^{0*} - \Delta\mu_1^{0*})$, $T\Delta S_2^{0*}$ and ΔH_2^{0*} for magnesium chloride and calcium in 3% sucrose + water at different temperature

Temperature (K)	Magnesium Chloride			Calcium Chloride		
	$(\Delta\mu_2^{0*} - \Delta\mu_1^{0*})$ (kJ mol^{-1})	$T\Delta S_2^{0*}$ (kJ mol^{-1})	ΔH_2^{0*} (kJ mol^{-1})	$(\Delta\mu_2^{0*} - \Delta\mu_1^{0*})$ (kJ mol^{-1})	$T\Delta S_2^{0*}$ (kJ mol^{-1})	ΔH_2^{0*} (kJ mol^{-1})
298.15	56.29	- 408.17	- 291.14	65.11	- 388.49	- 262.64
303.15	59.48	- 415.01	- 294.04	72.96	- 395.00	- 260.55
308.15	68.56	- 421.86	- 291.06	79.93	- 401.52	- 259.35
313.15	72.48	- 428.70	- 293.28	83.15	- 408.03	- 261.94
318.15	80.30	- 435.55	- 291.51	88.87	- 414.55	- 261.94

Also, It is clear from Table 5, that the quantity $(\Delta\mu_2^{0*} - \Delta\mu_1^{0*})$, the change in activation energy per mole of solute on replacing one mole of solvent by one more mole of solute at infinite dilution is positive and less for alkaline earth metal chlorides in 3% w/w sucrose + water at different temperatures so it may be said that transition state is less favoured in the presence of these alkaline earth metal chlorides in the entire temperature range studied
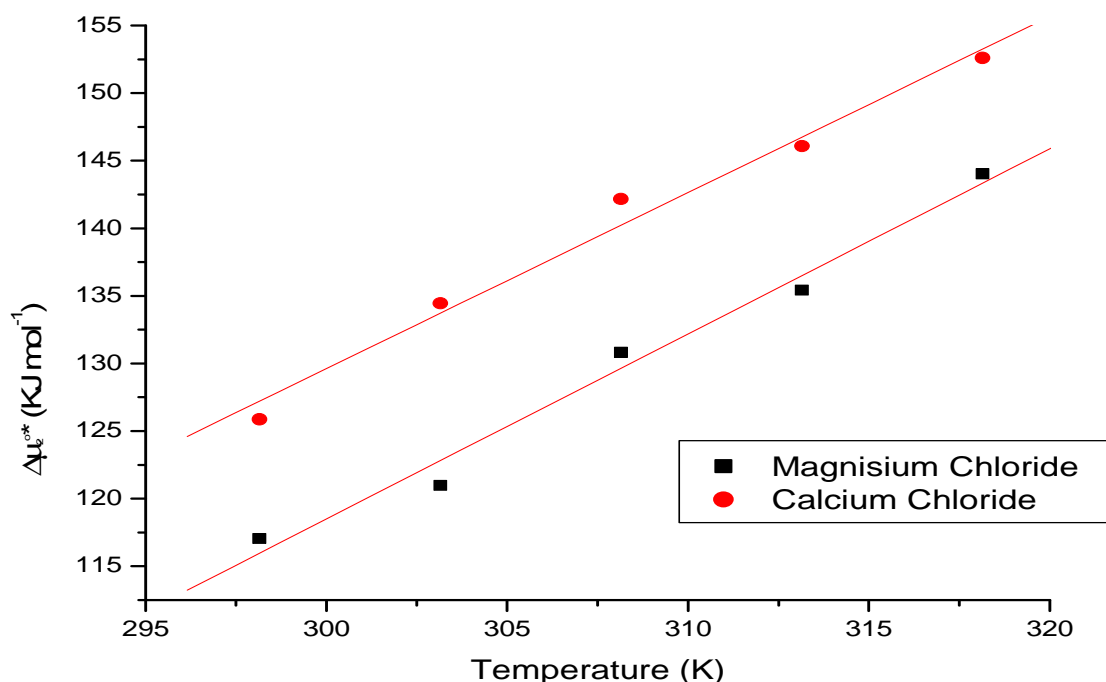
The entropy of activation ΔS_2^{0*} for both alkaline earth metal chlorides has been calculated from the following equations [27]:

$$\frac{d\left(\Delta\mu_2^{0*}\right)}{dT} = -\Delta S_2^{0*} \tag{8}$$

The values of ΔS_2^{0*} have been calculated from the slopes of linear plot of $\Delta\mu_2^{0*}$ verses T. The enthalpy of activation ΔH_2^{0*} has been calculated with the help of relationship [27]:

$$\Delta H_2^{0*} = \Delta\mu_2^{0*} + T\Delta S_2^{0*} \tag{9}$$

A sample plot has been shown in fig 3. The $T\Delta S_2^{0*}$ and ΔH_2^{0*} values at different temperatures are recorded in Table 5.

Figure 3: Plot for $\Delta\mu_2^{0*}$ Vs Temperature for magnesium chloride and calcium chloride in 3% Sucrose -Water

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It is clear from Table 5 that both parameters enthalpy and entropy of activation are negative for both the alkaline earth metal chlorides taken in the present study. These negative values of ΔH_2^{0*} and $T\Delta S_2^{0*}$ parameters indicates that the transition state is associated with bond breaking and increase in order.

CONCLUSION

In the present study the value of $\frac{dB}{dT}$ is positive for both the alkaline earth metal chlorides in 3% w/w sucrose + water. This indicates the structure breaking nature of magnesium chloride and calcium chloride in sucrose + water mixtures. Also values of thermodynamic activation parameters have been found negative, which indicates that the transition state is associated with bond breaking and increase in order.

REFERENCES

[1] RH Strokes; R. Mills. *Viscosity of electrolytes and related properties*", Pergamon Press, London , **1965.**
[2] RR Nightingale. *Chemical Physics of ionic solutions"* edited by B.E.Conway and R.G Barrades, (John Wiley, New York), **1965**, 295.
[3] R L Kay, *Water A Comprehensive Treatise*, ed. F. Franks, Plenum Press, New York, **1973**, volume 3, chapter 4.
[4] JE Desnoyers ; G Parron. *J Sol. Chem.*, **1972,** 1(3), 199-212.
[5] ML Parmar ; S Sharma. Res. *J Chem Environ.*, **1998**. 2, 17
[6] ML Parmar; DK Dhiman; RC Thakur. *Indian J Chem.,* **2002,** A41, 2032-2038.
[7] ML Parmar; RC Thakur. *Indian J Chem.*, **2006,** A45, 1631-1637.
[8] A Ali; Shahjahan. *J Iranian Chem. Society*, **2006,** 3, 340-350.
[9] MN Roy; V. K.Dakua; B.Sinha. *Int J Thermophys.* **2007,** 28, 1275–1284.
[10] SD Deosarkar; M.L. Narwade. *Rasayan J. Chem.,* **2010,** 3(1), 55-59 .
[11] SD Deosarkar; A.L Puyad. *Russian J Phy Chem.,* **2012,** A86, 775–778 .
[12] A Chen; M Liu; Y Zheng; D Sun; B Wang. *J Solution Chem.* **2013,** 42, 2213–2228.
[13] Riyazuddeen; Usmani, Mohd Amil.; *Thermochimica Acta.* **2014,** 575, 331– 335.
[14] RN Goldberg; YB Tewari. *J. Phys. Chem. Ref. Data.*, **1989,** 18, 809.
[15] J Boerio Goates; *J. Chem. Thermodyn.*, **1991,** 23, 403.
[16] RL Putnam; J.Boerio-Goate. *J. Chem. Thermodyn.,* **1993,** 25, 607.
[17] RN Goldberg; YB Tewari. *J. Biol. Chem.,* **1989,** 264, 9897.
[18] RN Goldberg, YB Tewari, J.C Ahluwalia*; J. Biol. Chem.,* **1989,**264, 9901.
[19] YB Tewari; RN Goldberg, *Biophys. Chem.,* **1991,** 40, 59.
[20] GG Birch ; S.Shamil. *J. Chem. Soc. Faraday Trans.I. ,* **1988,**84, 2635
[21] T Arakawa; Y. Kita; J.F. Carpenter. *Pharmcol. Res.*, **1991,** 8, 285.
[22] DP Miller; JJ de Pablo. *J. Phys. Chem.,* 2000, B104, 8876.
[23] GK Ward; FJ Millero. *J Solution Chem.* **1974,**3, 417
[24] ML Parmar; A Khanna. *J Phys Soc Japan*, **1986,** 55, 4122.
[25] ML Parmar; A Khanna; V. K. Gupta. *Indian J Chem.,* **1989,** 28A, 565.
[26] G Jones; M Dole. *J Am Chem Soc.* **1929,** 51, 2950.
[27] D Feakins; JD Freemental; K.G. Lawrence. *J Chem Soc Faraday Trans1.* **1974,**70,795.
[28] S Glastone; K Laidler; H.Eyring. *The Theory of Rate Processes*, McGraw Hill, New York, **1941,** p 477.
[29] TS Sharma; JC Ahluwalia. *Chem Soc Rev.*, **1973,** 2, 203-232.
[30] J Timmerman; *Physicochemical Constants of Pure Organic Compounds*, Elsevier Amsterdam**, 1950**, p 335-502.