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RESEARCH ARTICLE

Studies on Thermodynamic and Transport Properties of Calcium Chloride in Different Composition of Sorbitol in 0.01 m Aq. NaCl at Different Temperatures

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Abstract: The physical properties *i.e.* density, viscosity and conductance have been measured for calcium chloride in 2, 4 and 6 wt. % of sorbitol in 0.01 m aq. NaCl at 303.15, 308.15, 313.15 and 318.15 K. The experimental data was used for the evaluation of various thermodynamic parameters such as apparent molar volume (φ_v), limiting apparent molar volume (φ_v^o), its constant (S_v), apparent molar expansibilities (φ_E^o), viscosity coefficients A and B and limiting molar conductance (Λ_m^o) *etc.* by which molecular interactions *i.e.* solute-solvent and solute-solute has been interpreted. The structure making/breaking capacity of calcium chloride has been inferred from the sign of [$\partial^2\varphi_v^o / \partial T^2$], dB/dT and temperature dependence of Walden product d($\Lambda_m^o\eta_o$)/dT. The results showed that calcium chloride acts as structure-breaker in 2, 4 and 6 wt. % of sorbitol in 0.01 m aq. NaCl. The activation parameters of viscous flow were also determined and discussed by the application of transition state theory.

Keywords: Apparent molar volume, Viscosity coefficients, Limiting molar conductance, Structure-breaker, Transition state theory

Introduction

Solvation dynamics[1-2] has been the focus of research activities for the past few years. Experimental and theoretical studies have given rise to renewed interest in this field[3-4]. Measurement of some bulk properties like viscosity (η), density (ρ) and conductance (Λ) provides an insight into the intermolecular arrangements of the components in solutions and helps to understand the thermodynamic and transport properties of the solutions. Various types of interactions exist between the ions in the solutions and of these, ion-ion and ion-solvent interactions are of current interest. These interactions[5-8] help in better understanding of the nature of solute and solvent *i.e.* whether the added solute modifies or distorts the structure of the solvent. The solution structure is of great importance in understanding the nature of bioactive molecules in the body system. But the reports of the effects of electrolyte on the structure of water modified by sugar-alcohol are still scarce.

In the present work calcium chloride dihydrate, sorbitol and sodium chloride are being used. Calcium the most abundant mineral in the body is the major constituent of bones and teeth, it is also required for muscle contraction, blood clotting, secretion of hormones and enzymes and as a main buffer in the body to neutralize acids and maintain[9] proper pH. Sorbitol a hexahydroxy alcohol is used as a sweetener in some dietetic foods. It is also used in cosmetics, mouth wash and in toothpastes. Owing to the importance of calcium in human body and increasing use of sorbitol in daily life an attempt has been made to elucidate the molecular interactions of calcium chloride dihydrate in 2, 4 and 6 wt. % of sorbitol in 0.01 m Aq NaCl at 303.15, 308.15, 313.15 and 318.15 K temperatures by measuring density, viscosity and conductance of its solutions. The use of mixed solvent is important in the study of molecular interactions of bio-molecules because it helps in understanding the complex phenomena.

Experimental

Water used for solutions had specific conductance in the range 0.1-1.0x10^{-6} ohm^{-1} cm^{-1}. Calcium chloride dihydrate, sodium chloride and sorbitol (Anala R) were procured from Sd Fine-Chem. Limited, Mumbai and dried over anhydrous calcium chloride for more than 48 h and used as such. All the solutions were prepared by weight and conversion of molality to molarity was done by using the standard expression[10]. The concentration range of calcium chloride dihydrate in 2, 4 and 6 wt. % of sorbitol in 0.01 M aqueous sodium chloride was 0.01 to 0.12 m. The density was measured with the help of DSA (Density and Sound Analyser) 5000, Anton Paar, GmbH, Garz, Austria. Viscosity was determined with the help of capillary type viscometer[11]. The conductance was measured with the help of calibrated digital conductivity meter (HARCO Limited) at 50 Hz. All measurements were made in a water bath at 30, 35, 40 and 45 ^{0}C (±0.05).

Results and Discussion

The value of density (ρ), apparent molar volume (φ_v), viscosity (η) and conductance (Λ) for calcium chloride dihydrate in 2, 4 and 6 wt. % of sorbitol in 0.01 m aq. NaCl at different temperatures 303.15, 308.15, 313.15 and 318.15 K are given in Table 1.

Apparent molar volume studies

The apparent molar volume of calcium chloride dihydrate in 2, 4 and 6 wt. % of sorbitol in 0.01 m Aq sodium chloride solutions have been calculated from experimental values of density (Table 1) by using following equation[12];

$$\varphi_v = \frac{M_2}{\rho_o} - \frac{1000(\rho - \rho_o)}{C\rho_o} \tag{1}$$

Where ρ_o is the density of solvent, ρ is the density of solution, C is the concentration of solution and M_2 is the molecular weight of calcium chloride (*i.e.* 147.02). The values of limiting apparent molar volume (φ_v^o) and experimental slopes (S_v) at different temperatures have been obtained by extrapolating the plots of φ_v *versus* $\sqrt{C}$ using the Masson equation[13];

$$\varphi_v = \varphi_v^o + S_v\sqrt{C} \tag{2}$$

Table 1. Densities, apparent molar volumes, viscosity and molar conductance of calcium chloride in different compositions (2, 4 and 6 Wt. %) of sorbitol in 0.01 M aqueous sodium chloride at different temperatures

Concentration C x 10^2, mol L^{-1}	Density ρ x 10^{-3}, kg m^{-3}	Apparent Molar Volume φ_v x 10^6, m^3 mol^{-1}	Viscosity η x 10^3 (Pa s)	Molar Conductance Λ_m x 10^4, ohm^{-1} m^2 mol^{-1}
2 % Sorbitol in 0.01 M aqueous sodium chloride				
Temperature = 303.15 K				
0.0000	1.002701	-	0.83353	-
1.0021	1.003601	57.06	0.83706	342.46
2.0031	1.004482	57.95	0.83966	318.59
4.0013	1.006209	59.19	0.84433	284.53
5.9945	1.007899	60.15	0.84880	258.27
7.9826	1.009557	60.97	0.85322	235.97
9.9654	1.011193	61.64	0.85740	216.20
11.9430	1.012807	62.23	0.86158	198.89
Temperature = 308.15 K				
0.0000	1.001029	-	0.74507	-
1.0004	1.001918	58.10	0.74791	379.65
1.9997	1.002790	58.90	0.75021	351.43
3.9945	1.004498	60.11	0.75431	312.77
5.9842	1.006171	61.03	0.75831	283.36
7.9688	1.007814	61.81	0.76240	258.64
9.9481	1.009433	62.48	0.76627	236.54
11.9220	1.011029	63.08	0.77013	217.03
Temperature = 313.15 K				
0.0000	0.999146	-	0.66944	-
0.9986	1.000022	59.34	0.67162	413.19
1.9959	1.000881	60.14	0.67355	383.50
3.9868	1.002572	61.14	0.67727	340.93
5.9727	1.004232	61.92	0.68091	309.57
7.9534	1.005866	62.58	0.68456	282.05
9.9288	1.007481	63.13	0.68813	257.87
11.8989	1.009072	63.66	0.69169	236.73
Temperature = 318.15 K				
0.0000	0.996928	-	0.60359	-
0.9963	0.997799	59.78	0.60527	455.71
1.9914	0.998655	60.49	0.60695	421.62
3.9780	1.000339	61.46	0.61029	372.95
5.9594	1.001992	62.24	0.61362	337.11
7.9356	1.003621	62.87	0.61695	305.88
9.9066	1.005226	63.45	0.62027	279.18
11.8723	1.006812	63.96	0.62358	254.80
4 % Sorbitol in 0.01 M aqueous sodium chloride				
Temperature = 303.15 K				
0.0000	1.009607	-	0.84207	-

Contd…

1.0090	1.010485	59.43	0.84560	330.54
2.0168	1.011352	59.92	0.84815	305.89
4.0286	1.013064	60.63	0.85290	267.74
6.0353	1.014752	61.18	0.85735	240.69
8.0367	1.016414	61.73	0.86183	216.60
10.0331	1.018058	62.19	0.86604	195.99
12.0242	1.019695	62.52	0.87026	170.16
		Temperature = 308.15 K		
0.0000	1.007896	-	0.75810	-
1.0073	1.008740	62.49	0.76085	364.60
2.0132	1.009576	62.83	0.76309	337.07
4.0213	1.011225	63.49	0.76726	294.59
6.0240	1.012852	63.99	0.77139	264.02
8.0213	1.014465	64.37	0.77541	238.17
10.0134	1.016067	64.66	0.77929	214.66
12.0001	1.017654	64.94	0.78318	193.58
		Temperature = 313.15 K		
0.0000	1.005987	-	0.68637	-
1.0053	1.006801	65.13	0.68853	399.81
2.0093	1.007608	65.43	0.69044	369.86
4.0132	1.009209	65.81	0.69426	323.28
6.0117	1.010795	66.12	0.69788	289.25
8.0048	1.012370	66.36	0.70141	259.25
9.9924	1.013927	66.63	0.70497	233.15
11.9744	1.015474	66.87	0.70854	210.10
		Temperature = 318.15 K		
0.0000	1.003902	-	0.61014	-
1.0032	1.004706	65.79	0.61202	437.16
2.0051	1.005502	66.14	0.61368	403.81
4.0048	1.007084	66.48	0.61698	353.09
5.9990	1.008649	66.80	0.62028	314.77
7.9877	1.010208	66.98	0.62334	284.79
9.9710	1.011756	67.16	0.62664	256.18
11.9486	1.013286	67.39	0.62994	230.56
		6 % Sorbitol in 0.01 M aqueous sodium chloride		
		Temperature = 303.15 K		
0.0000	1.016702	-	0.85925	-
1.0160	1.017533	65.18	0.86334	304.53
2.0307	1.018353	65.66	0.86601	282.42
4.0560	1.019972	66.33	0.87106	249.53
6.0758	1.021566	66.88	0.87568	225.12
8.0899	1.023139	67.36	0.87853	205.77
10.0985	1.024698	67.74	0.88447	187.08
12.1014	1.026241	68.09	0.88864	170.46
		Temperature = 308.15 K		
0.0000	1.014939	-	0.77138	-
1.0043	1.015748	67.03	0.77466	339.28

Contd…

2.0271	1.016546	67.51	0.77699	315.26
4.0487	1.018124	68.11	0.78127	276.99
6.0646	1.019682	68.56	0.78541	249.69
8.0748	1.021217	69.02	0.78953	228.00
10.0792	1.022737	69.39	0.79339	207.52
12.0777	1.024233	69.80	0.79723	189.15
		Temperature = 313.15 K		
0.0000	1.012988	-	0.68580	-
1.0123	1.013775	68.87	0.68817	374.21
2.0232	1.014555	69.16	0.69012	346.84
4.0406	1.016098	69.64	0.69380	306.78
6.0524	1.017629	69.92	0.69748	276.63
8.0583	1.019142	70.23	0.70098	252.39
10.0586	1.020650	70.42	0.70456	229.99
12.0530	1.021380	70.68	0.70806	208.73
		Temperature = 318.15 K		
0.0000	1.010849	-	0.61670	-
1.0101	1.011624	69.72	0.61835	410.32
2.0189	1.012392	70.01	0.61999	379.57
4.0319	1.013911	70.49	0.62328	335.17
6.0392	1.015415	70.83	0.62656	301.66
8.0407	1.016903	71.14	0.62971	274.52
10.0363	1.018384	71.35	0.63311	248.75
12.0260	1.019845	71.62	0.63639	226.03

Where φ_v^o and S_v are the intercept and slope respectively. The values of limiting apparent molar volume (φ_v^o) and experimental slopes (S_v) are listed in Table 2. The limiting apparent molar volume (φ_v^o) is a measure of solute-solvent interactions[14]. The high positive value of φ_v^o showed strong solute-solvent interactions in 2, 4 and 6 wt. % of sorbitol in 0.01 m Aq NaCl.

The φ_v^o values for calcium chloride increases with increase in percentage composition of sorbitol in 0.01 m Aq sodium chloride. This may be due to structure-breaking effect of both sodium chloride[15] and sorbitol[16]. The φ_v^o values for calcium chloride dihydrate in 2, 4 and 6 wt. % of sorbitol in 0.01 m Aqsodium chloride solutions increases with increase in temperature, suggesting larger electrostriction at higher temperatures[17]. The increase in φ_v^o may also be attributed to the increase in solvation.

A perusal of Table 2 also reveals that S_v values are small and positive in all the solutions. Since S_v is a measure of solute-solute interactions[18-19] low and positive values accounts for weak solute-solute interactions in 2, 4 and 6 wt. % of sorbitol in 0.01 m aq. sodium chloride solutions and these interactions further decreases with a rise in temperature. The temperature dependence of φ_v^o for calcium chloride dihydrate in 2, 4 and 6 wt. % of sorbitol in 0.01 m aq sodium chloride solutions can be expressed as

$$\varphi_v^o = a + bT + cT^2 \quad (3)$$

Table 2. Limiting apparent molar volume (φ_v^o) and experimental slope (S_v) for calcium chloride in different compositions (2, 4 and 6 Wt. %) of sorbitol in 0.01 M aqueous sodium chloride at different temperatures

Temp. K	φ_v^o x 10^6, m^3 mol^{-1}	S_v x 10^6, m^3 $L^{1/2}$ $mol^{-3/2}$
2 % Sorbitol in 0.01 M aqueous sodium chloride		
303.15	54.95	0.212
308.15	56.04	0.204
313.15	57.64	0.175
318.15	58.07	0.171
4 % Sorbitol in 0.01 M aqueous sodium chloride		
303.15	58.20	0.124
308.15	61.44	0.102
313.15	64.20	0.077
318.15	65.21	0.063
6 % Sorbitol in 0.01 M aqueous sodium chloride		
303.15	63.97	0.119
308.15	65.91	0.110
313.15	68.14	0.074
318.15	68.94	0.073

Where, the temperature T is expressed in Kelvin (K). Values of the coefficients a, b and c of the above equation for different calcium chloride solutions are reported in Table 3. The limiting apparent molar expansibilities (φ_E^o) can be obtained by the following equation:

$$\varphi_E^o = \left(\frac{\partial \varphi_v^o}{\partial T}\right)_P = b + 2cT \tag{4}$$

Table 3. Values of various coefficients of Eq.3 for calcium chloride in different compositions (2, 4 and 6 Wt. %) of sorbitol in 0.01 M aqueous sodium chloride at different temperatures

Sorbitol, Wt. %, in 0.01 m NaCl	a x 10^6, m^3 mol^{-1}	b x 10^6, m^3 mol^{-1} K^{-1}	c x 10^6, m^3 mol^{-1} K^{-2}
2	-622.501	4.220	-0.007
4	-2221.143	14.279	-0.022
6	-1127.654	7.413	-0.012

The values of φ_E^o for different solutions of the calcium chloride dihydrate at 303.15, 308.15, 313.15 and 318.15 K are reported in Table 4. The values of φ_E^o decreases with increase in temperature for calcium chloride dihydrate in 2, 4 and 6 wt. % of sorbitol in 0.01 m aqsodium chloride indicates the absence of "caging effect"[20] and its behaviour is just like common electrolyte[21].

According to Hepler, the sign of $\left[\partial^2 \varphi_v^o / \partial T^2\right]_P$ is a criterion for characterizing the long-range structure-making and breaking capacity[22] of the electrolytes in solution. The general thermodynamic expression is as follows

$$\left(\frac{\partial \overline{C_P^O}}{\partial P}\right)_T = -T\left(\frac{\partial^2 \varphi_V^O}{\partial T^2}\right)_P \tag{5}$$

Table 4. Limiting apparent molar expansibilities (φ_E^o) and $[\partial^2\varphi_v^o/\partial T^2]_P$ for calcium chloride in different compositions (2, 4 and 6 Wt. %) of sorbitol in 0.01 M aqueous sodium chloride at different temperatures

Sorbitol Wt. %, in 0.01 m NaCl	φ_E^o x 10^6, $m^3 mol^{-1} K^{-1}$				$[\partial^2\varphi_v^o/\partial T^2]_P$ x 10^{12} $m^6 mol^{-2} K^{-2}$
	303.15 K	308.15 K	313.15 K	318.15 K	
2	0.25	0.18	0.12	0.06	-0.013
4	0.76	0.54	0.31	0.09	-0.045
6	0.45	0.33	0.22	0.10	-0.023

Where $\overline{C_P^o}$ is the partial molar heat capacity at infinite dilution. If the sign of $[\partial^2\varphi_v^o/\partial T^2]_P$ is negative, the electrolyte is a structure breaker; otherwise it is a structure maker. From equation (4) it is clear that

$$\left(\frac{\partial^2\varphi_v^o}{\partial T^2}\right)_P = 2c \tag{6}$$

As evident from Table 4 the value of $[\partial^2\varphi_v^o/\partial T^2]_P$ is negative for calcium chloride dihydrate in 2, 4 and 6 wt. % of sorbitol in 0.01 m aq. sodium chloride solutions thus it behaves as structure breaker in 2, 4 and 6 wt. % of sorbitol in 0.01 m aq. sodium chloride.

Viscosity studies

The viscosity data of solutions for calcium chloride dihydrate in 2, 4 and 6 wt. % of sorbitol in 0.01 m aq.sodium chloride mixtures have been analysed using the Jones-Dole[23] equation;

$$\frac{\eta}{\eta_O} = 1 + A\sqrt{C} + BC \tag{7}$$

$$\left(\frac{\frac{\eta}{\eta_o}-1}{\sqrt{C}}\right) = A + B\sqrt{C} \tag{8}$$

Where η_o and η are the viscosities of solvent/solvent mixtures and solution, respectively. C is the molar concentration of a solution and A and B are constants. The value of A and B have been determined from the intercept and slopes of linear plots of $\left(\frac{\eta}{\eta_o}-1\right)/\sqrt{C}$ *versus* $\sqrt{C}$ by applying the methods of least square fit. The values of A and B are recorded in Table 5.

Parameter A of Jones-Dole equation represents the contribution from solute-solute interactions[24]. A perusal of Table 5 shows that the values of the A-coefficient decreases with increase in temperature for calcium chloride dihydrate in studied media which may be due to more solvation of solute ions.

The B-parameter *i.e.* Jones-Dole coefficient[25] reflects the effects of ion-solvent interactions on solution viscosity. The viscosity B-coefficient is a valuable tool to provide information concerning the solvation of the solutes and their effects on the structure of the solvent in the local vicinity of the solute molecules.

Table 5. Values of parameters of Jones Dole Equation, limiting molar conductance, Λ_m^o and Walden product for calcium chloride in different compositions (2, 4 and 6 Wt. %) of sorbitol in 0.01 M aqueous sodium chloride at different temperatures

Temp. K	A $(L\ mol^{-1})^{1/2}$	B, $L\ mol^{-1}$	Λ_m^o x 10^4, $ohm^{-1}\ m^2\ mol^{-1}$	$\Lambda_m^o \eta_o$ x 10^5, $ohm^{-1}\ m^2\ mol^{-1}$ Pa s
	2 % Sorbitol in 0.01 M aqueous sodium chloride			
303.15	2.00	0.224	401.43	3.34
308.15	1.422	0.241	445.37	3.32
313.15	0.669	0.260	485.20	3.25
318.15	0.050	0.277	537.31	3.24
	4 % Sorbitol in 0.01 M aqueous sodium chloride			
303.15	1.928	0.223	393.69	3.32
308.15	1.188	0.242	434.91	3.30
313.15	0.643	0.252	478.69	3.29
318.15	0.490	0.256	522.07	3.19
	6 % Sorbitol in 0.01 M aqueous sodium chloride			
303.15	2.595	0.209	359.21	3.09
308.15	1.970	0.221	400.78	3.09
313.15	1.015	0.240	441.67	3.06
318.15	-0.017	0.265	485.53	2.99

It has been reported in a number of studies[26-27] that dB/dT is a better criterion for determining the structure-making / breaking nature of any solute rather than the *B*-coefficient. Viscosity study of a number of electrolytes has shown that structure-maker will have negative dB/dT and structure- breaker will have positive dB/dT[28]. It is found from Table 5 that the value of the B-coefficient increase with a rise in temperature (positive dB/dT), suggesting the structure-breaking tendency of calcium chloride dihydrate in studied media. This conclusion is in excellent agreement with our earlier view drawn from sign of $\left[\partial^2 \varphi_v^o / \partial T^2\right]_P$ illustrated earlier. The sample plot of B *vs*. T for 2% sorbitol in 0.01 m aq. NaCl is shown in Figure 1.

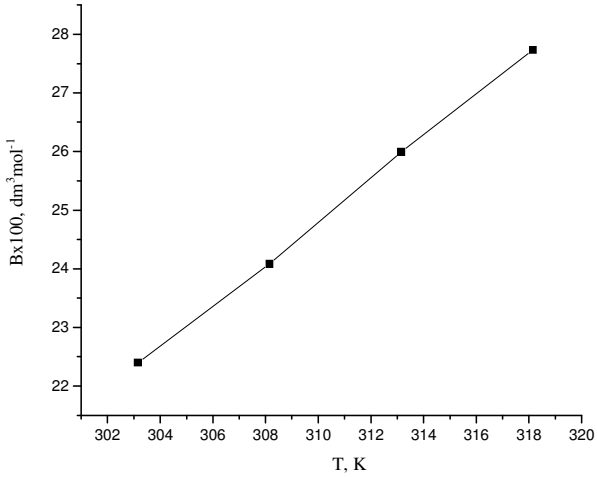

Figure 1. Plot of Bx100 *vs.* T for calcium chloride in 2% sorbitol in 0.01M aqueous sodium chloride

The viscosity data have also been analysed on the basis of transition state theory of relative viscosity of the electrolytes as suggested by Feakins *et al*[29] using the following equation;

$$\Delta\mu_2^{0\neq} = \Delta\mu_1^{0\neq} + \frac{RT}{V_1^0}\left[1000B - \left(\overline{V}_1^{\,0} - \varphi_v^0\right)\right] \quad (9)$$

Where $\Delta\mu_2^{o\neq}$ is the contribution per mole of the solute to the free energy of activation of viscous flow of the solutions, $\overline{V_1^o}$ and φ_v^o are the partial molar volumes of the solvent and solute, respectively.

The free energy of activation of viscous flow per mole of the pure solvent ($\Delta\mu_1^{o\neq}$) is given by relation[29-30].

$$\Delta\mu_1^{o\neq} = \Delta G_1^{o\neq} = RT\ln(\eta_o \overline{V_1^o}/hN_A) \quad (10).$$

Where N_A is the Avogadro's number, h is the Planck's constant, η_o is the viscosity of the solvent, R is the gas constant and T is the absolute temperature. For mixed solvents, each solvent mixture was treated as pure and molar volume taken as a mean volume defined[31] as

$$\overline{V_1^o} = [x_1M_1 + x_2M_2 + x_3M_3]/d_o \quad (11)$$

Where (x_1, M1), (x_2, M_2) and (x_3, M_3) are the mole fractions and molecular weights of water, NaCl and sorbitol respectively. The values of $\overline{V_1^o}$, $\Delta\mu_1^{o\neq}$ and $\Delta\mu_2^{o\neq}$ are recorded in Table 6.

Table 6. Values of $\overline{V_1^o}$, $\Delta\mu_1^{o\neq}$, $\Delta\mu_2^{o\neq}$, $T\Delta S_2^{o\neq}$ and $\Delta H_2^{o\neq}$ for calcium chloride in different compositions (2, 4 and 6 Wt. %) of sorbitol in 0.01 M aqueous sodium chloride at different temperatures

Temp. K	$\overline{V_1^o} \times 10^6$ $m^3\,mol^{-1}$	$\Delta\mu_1^{o\neq}$ $kJmol^{-1}$	$\Delta\mu_2^{o\neq}$ $kJmol^{-1}$	$T\Delta S_2^{o\neq}$ $kJmol^{-1}$	$\Delta H_2^{o\neq}$ $kJmol^{-1}$
2 % Sorbitol in 0.01 M aqueous sodium chloride					
303.15	18.29	9.18	45.11	-189.10	-143.99
308.15	18.32	9.05	48.01	-192.22	-144.21
313.15	18.35	8.92	51.37	-195.34	-143.97
318.15	18.39	8.80	54.38	-198.46	-144.08
4 % sorbitol in 0.01 M aqueous sodium chloride					
303.15	18.50	9.24	45.02	-138.12	-93.10
308.15	18.53	9.12	48.46	-140.39	-91.93
313.15	18.57	9.02	50.68	-142.67	-91.99
318.15	18.61	8.86	51.87	-144.95	-93.08
6 % sorbitol in 0.01 M aqueous sodium Chloride					
303.15	18.72	9.32	43.51	-195.93	-152.42
308.15	18.76	9.20	45.80	-199.19	-153.38
313.15	18.79	9.05	49.09	-202.42	-153.33
318.15	18.83	8.92	53.19	-205.65	-152.46

Table 6 shows that $\Delta\mu_1^{o\ddagger}$ is practically constant at all solvent compositions implying that $\Delta\mu_2^{o\ddagger}$ is dependent mainly on B-coefficient and ($\overline{V_1^o}$ - φ_v^o) terms. It is also clear from Table 6 that the values of $\Delta\mu_2^{o\ddagger}$ are positive and larger than $\Delta\mu_1^{o\ddagger}$ which suggest that the formation of the transition state is less favoured in the presence of calcium chloride, meaning thereby that the formation of transition state is accompanied by the breaking and distortion of the intermolecular bonds between solvent.

According to Feakins model[29] $\Delta\mu_2^{o\ddagger}$ increases with increase in temperature for solutes having positive value of dB/dT. This is shown by calcium chloride dihydrate which act as structure-breaker in 2, 4 and 6 wt. % of sorbitol in 0.01 m aq. Sodium chloride solutions. The activation entropy for calcium chloride has also been calculated from the following relation[29]

$$d\,(\Delta\mu_2^{o\ddagger})/dT = -\Delta S_2^{o\ddagger} \tag{12}$$

The values of $\Delta S_2^{o\ddagger}$ have been calculated from the slopes of $\Delta\mu_2^{o\ddagger}$ *vs*. T by using the least squares method. The values of T $\Delta S_2^{o\ddagger}$ at different temperatures are listed in Table 6. The activation enthalpy ($\Delta H_2^{o\ddagger}$) has been calculated with the help of following expression[29].

$$\Delta H_2^{o\ddagger} = \Delta\mu_2^{o\ddagger} + T\Delta S_2^{o\ddagger} \tag{13}$$

And the values are also recorded in Table 6. It is evident from Table 6 that both enthalpy and entropy of activation are negative for calcium chloride dihydrate in 2, 4 and 6 wt. % of sorbitol in 0.01 m aq. Sodium chloride mixtures at different temperatures, which suggest that the transition state is associated with bond-breaking and increase in order. Although a detailed mechanism for this cannot be easily advanced, it may be suggested that the slip-plane is in the disordered state[32].

Conductance studies

The limiting molar conductance Λ_m^o for calcium chloride dihydrate in 2, 4 and 6 wt. % of Sorbitol in 0.01 m aq. Sodium chloride solutions was obtained by extrapolating the linear plots of Λ_m (Table 1) *versus* $\sqrt{c}$ to zero concentration. The limiting molar conductance Λ_m^o for calcium chloride dihydrate in 2, 4 and 6 wt. % of sorbitol in 0.01 m aq. sodium chloride solutions at 303.15, 308.15, 313.15 and 318.15 K temperatures are given in Table 5, which shows that limiting molar conductance increases with increase in temperature, which may be due to increase in ionic mobility of free Ca^{2+}, Cl^-, Na^+ and Cl^- ions at infinite dilution.

The structure making/breaking nature of solute can be determined from temperature coefficient of Walden product *i.e.* [d ($\Lambda_m^o\eta_o / dT$)[33]. The Walden product data ($\Lambda_m^o\eta_o$) have been recorded in Table 5. From this data it is found that Walden product decreases with increase in temperature for calcium chloride dihydrate in 2, 4 and 6 wt. % of sorbitol in 0.01 m aq. sodium chloride solutions which indicates that calcium chloride behaves as structure-breaker in these solvents. The sample plot of $\Lambda_m^o\eta_o$ *vs*. T for calcium chloride in 2wt. % of sorbitol in 0.01m aq. NaCl is shown in Figure 2.

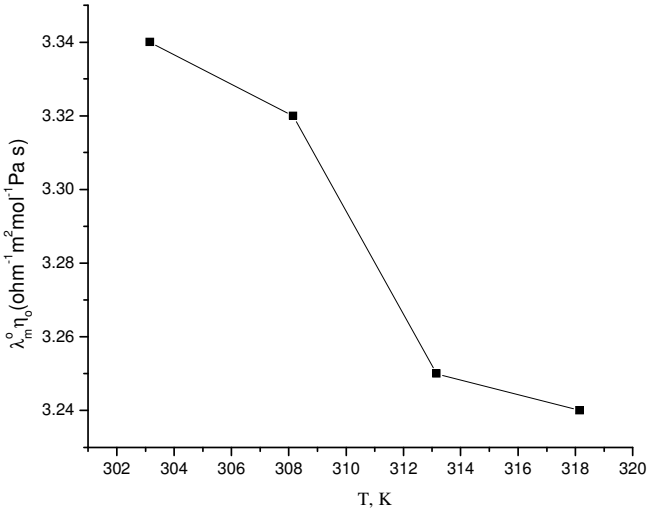

Figure 2. Plot of $\Lambda^o_m \eta_o$ *vs*. T for calcium chloride in 2% sorbitol in 0.01 M aqueous sodium chloride at different temperatures

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