

Apparent Molar Volume, Viscometric and Conductance Studies of Sodium Chloride in Different Composition of Lactose

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Abstract: Molar volume, viscosity and conductance of sodium chloride in 2, 4 and 6 wt. % of lactose solutions have been evaluated from density, viscosity and conductance data respectively at temperatures 303.15 K, 308.15 K, 313.15 K and 318.15 K. The solute-solvent interactions for sodium chloride in 2, 4 and 6 wt. % of lactose solutions have been inferred from ϕ_v° , B - coefficient of Jones-Dole equation and Λ_m° values. The structure making/breaking behavior of sodium chloride in different composition of lactose is inferred from the sign of $[\partial^2 \phi_v^\circ / \partial T^2]_p$, dB/dT , transition state theory *i.e.* free energy contribution per mole of solute ($\Delta\mu_2^\circ$) and free energy contribution per mole of solvent ($\Delta\mu_1^\circ$) values and temperature coefficient of Walden product *i.e.* $d(\Lambda_m^\circ \eta_o)/dT$. It has been found that sodium chloride behaves as structure-breaker in 2, 4 and 6 wt. % of lactose solutions from molar volume, viscosity and conductance studies.

Keywords: Molar volume, Viscosity, Conductance, Sodium chloride, Lactose

Introduction

The study of apparent molar volumes of electrolytes at infinite dilution, B parameter of Jones-Dole equation and their dependence on temperature, transition state theory, molar conductance at infinite dilution and Walden product studies can furnish useful information on the nature of solute-solvent interactions. The behavior of electrolytes in aqueous carbohydrates and carbohydrates containing small quantity of ions which are present in body fluids has recently been subject of interest¹⁻⁸. The study of sodium chloride in 2, 4 and 6 wt. % of lactose at 303.15 K, 308.15 K, 313.15 K and 318.15 K temperatures was carried out to understand the nature of solute-solute and solute-solvent interactions by measuring the density and molar conductance of their solutions.

Experimental

Water used for solutions had specific conductance in range $0.1- 1.0 \times 10^{-6} \Omega^{-1} \text{ cm}^{-1}$. Sodium chloride and lactose (AnalaR) were 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 expression⁹. The concentration range of sodium chloride in 2, 4 and 6 wt. % of lactose solutions was 0.01 to 0.12 m. The density was measured with the help of DSA (Density and Sound Analyzer) 5000, Anton Paar, GmbH, Garz, Austria. Viscosity was determined with the help of capillary type Viscometer¹⁰. The conductance was measured with the help of calibrated Digital conductivity meter, CM 180, Elico Limited. All measurements were made in a water bath maintained at 30, 35, 40 and 45 °C (± 0.05).

Results and Discussion

The apparent molar volume of sodium chloride in 2, 4 and 6 wt. % of lactose have been calculated from density data (Table 1) by using eq. (1)

$$\phi_v = \frac{M_2}{d^0} - \frac{1000(d-d^0)}{md^0} \quad (1)$$

Where d^0 is the density of solvent, d is the density of solution, m the molality of solution and M_2 the molecular weight of sodium chloride. Errors in ϕ_v were calculated from eq. (2).

Table 1. Densities, apparent molar volumes, viscosities and molar conductance of sodium chloride in different compositions of lactose (2, 4 and 6%) solutions at different temperatures

Molality, m	$\rho \times 10^{-3}$, kg m ⁻³	$\Phi_v \times 10^6$, m ³ mol ⁻¹	$\eta \times 10^3$, Pa s	$\Lambda_m \times 10^4 \Omega^{-1} m^2 mol^{-1}$
Sodium chloride in 2% aqueous Lactose				
Temperature = 303.15 K				
0.00	1.0030	-	0.8246	-
0.01	1.0036	-8.43	0.8261	175.46
0.02	1.0042	-1.92	0.8270	168.49
0.04	1.0050	7.33	0.8285	161.07
0.06	1.0056	14.34	0.8298	155.01
0.08	1.0060	20.27	0.8310	149.80
0.10	1.0062	25.76	0.8322	145.34
0.12	1.0063	30.36	0.8333	141.26
Temperature = 308.15 K				
0.00	1.0013	-	0.7441	-
0.01	1.0019	-1.28	0.7454	187.75
0.02	1.0024	4.25	0.7462	181.78
0.04	1.0032	11.94	0.7475	171.86
0.06	1.0037	17.86	0.7487	164.63
0.08	1.0042	22.89	0.7498	158.33
0.10	1.0044	27.27	0.7508	153.02
0.12	1.0046	31.22	0.7519	148.03
Temperature = 313.15 K				
0.00	0.9994	-	0.6702	-
0.01	1.0000	3.11	0.6713	204.12
0.02	1.0004	7.96	0.6720	196.14
0.04	1.0012	15.00	0.6731	184.72
0.06	1.0017	20.27	0.6742	175.65
0.08	1.0021	24.43	0.6752	168.17
0.10	1.0024	28.59	0.6762	161.55
0.12	1.0026	31.88	0.6772	155.85

Contd...

Temperature = 318.15 K				
0.00	0.9973	-	0.6158	-
0.01	0.9978	6.71	0.6166	218.61
0.02	0.9982	11.28	0.6172	209.62
0.04	0.9989	17.20	0.6182	196.17
0.06	0.9994	22.04	0.6192	186.09
0.08	0.9999	25.97	0.6201	177.10
0.10	1.0001	29.49	0.6211	169.76
0.12	1.0003	32.78	0.6220	163.08
Sodium chloride in 4% aqueous Lactose				
Temperature = 303.15 K				
0.00	1.0106	-	0.8483	-
0.01	1.0112	-3.86	0.8503	166.24
0.02	1.0117	2.31	0.8515	160.31
0.04	1.0125	10.73	0.8536	150.48
0.06	1.0131	17.15	0.8555	142.97
0.08	1.0134	22.54	0.8572	136.56
0.10	1.0137	27.36	0.8589	131.18
0.12	1.0138	31.72	0.8606	126.15
Temperature = 308.15 K				
0.00	1.0089	-	0.7631	-
0.01	1.0094	3.20	0.7648	180.40
0.02	1.0099	8.16	0.7659	173.49
0.04	1.0106	15.16	0.7677	162.16
0.06	1.0112	20.53	0.7694	154.16
0.08	1.0116	24.92	0.7710	147.49
0.10	1.0118	28.92	0.7726	141.36
0.12	1.0120	32.50	0.7741	136.00
Temperature = 313.15 K				
0.00	1.0070	-	0.6875	-
0.01	1.0075	7.83	0.6888	196.64
0.02	1.0079	12.26	0.6897	187.74
0.04	1.0086	18.31	0.6914	176.40
0.06	1.0091	23.27	0.6929	166.74
0.08	1.0095	27.12	0.6944	158.99
0.10	1.0097	30.70	0.6958	152.01
0.12	1.0099	33.87	0.6973	145.91
Temperature = 318.15 K				
0.00	1.0043	-	0.6299	-
0.01	1.0047	10.79	0.6309	215.11
0.02	1.0051	14.75	0.6316	207.18
0.04	1.0058	20.24	0.6331	194.83
0.06	1.0063	24.65	0.6345	185.49
0.08	1.0067	28.23	0.6358	177.90
0.10	1.0069	31.53	0.6371	170.81
0.12	1.0071	34.29	0.6385	164.48

Contd...

Sodium chloride in 6% aqueous Lactose				
Temperature = 303.15K				
0.00	1.0183	-	0.8867	-
0.01	1.0188	0.49	0.8890	161.06
0.02	1.0193	5.98	0.8904	154.20
0.04	1.0201	13.61	0.8927	144.45
0.06	1.0206	19.19	0.8948	137.32
0.08	1.0210	23.98	0.8968	130.87
0.10	1.0213	28.11	0.8987	125.47
0.12	1.0214	32.02	0.9005	120.94
Temperature = 308.15 K				
0.00	1.0165	-	0.7856	-
0.01	1.0170	8.13	0.7876	175.12
0.02	1.0175	12.24	0.7888	168.26
0.04	1.0182	18.17	0.7908	157.02
0.06	1.0187	22.72	0.7926	149.41
0.08	1.0191	26.59	0.7943	142.21
0.10	1.0194	29.88	0.7960	136.37
0.12	1.0196	32.92	0.7976	131.03
Temperature = 313.15 K				
0.00	1.0146	-	0.7059	-
0.01	1.0151	13.20	0.7074	183.35
0.02	1.0154	16.79	0.7085	175.50
0.04	1.0161	21.48	0.7103	162.27
0.06	1.0166	25.20	0.7119	152.35
0.08	1.0170	28.22	0.7135	143.98
0.10	1.0173	30.99	0.7151	136.64
0.12	1.0176	33.46	0.7166	130.46
Temperature = 318.15 K				
0.00	1.0124	-	0.6459	-
0.01	1.0128	17.33	0.6470	203.51
0.02	1.0132	20.24	0.6478	193.68
0.04	1.0138	24.10	0.6494	180.94
0.06	1.0143	27.12	0.6510	171.82
0.08	1.0147	29.61	0.6525	163.62
0.10	1.0150	31.82	0.6540	156.57
0.12	1.0153	33.87	0.6554	150.43

$$\Delta\phi_v = \left(\frac{2\Delta d}{d^2} \right) \left(\frac{1000}{m + M_2} \right) \quad (2)$$

Eq. (2) assumes error to be associated with the density of solution (d) and solvent (d^0). Moreover, errors associated with determination of solution concentration are not the limiting factor while calculating the apparent molar volumes. The error in apparent molar volume as derived from eq. (2) was estimated to range from $\pm 0.06 \text{ cm}^3 \text{ mol}^{-1}$ at 0.01 m concentration to $\pm 0.10 \text{ cm}^3 \text{ mol}^{-1}$ at 0.12 m concentration. The densities of various solutions of sodium chloride in 2, 4 and 6 wt. % of lactose obey Root's equation and justify the use of Masson's eq. (3) for the estimation of the limiting apparent molar volume.

$$\phi_v = \phi_v^0 + S_v \sqrt{C} \quad (3)$$

Where ϕ_v° and S_v are calculated from the intercept and slope from the extrapolation of the plots of ϕ_v versus \sqrt{C} . The sample plot of ϕ_v versus \sqrt{C} for sodium chloride in 2 wt. % of lactose solutions is shown in Figure 1. The values of limiting apparent molar volume and slopes S_v are recorded in Table 2. The slope S_v in Masson's equation may be attributed to be as a measure of ion-ion or solute-solute interactions¹¹⁻¹³, low and positive values accounts for weak solute-solute interactions in 2, 4 and 6 wt. % of lactose. There is a decrease in inter ionic interactions with increase in temperature for sodium chloride in 2, 4 and 6 wt. % of lactose, which may be due to more solvation of solute ions with rise in temperature.

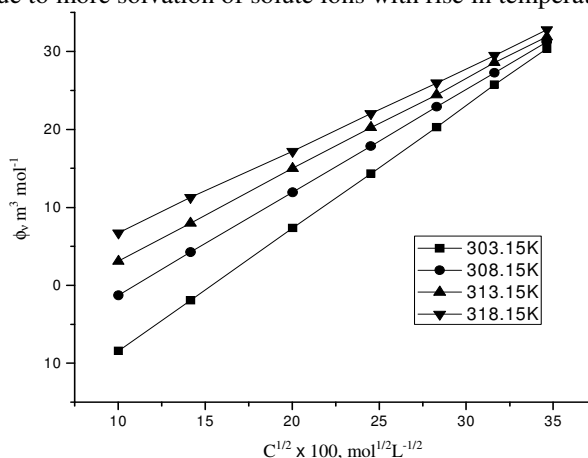


Figure 1. The plot of ϕ_v versus \sqrt{C} for sodium chloride in 2 wt. % of lactose solutions

The ϕ_v° is a measure of solute-solvent interactions¹⁴. The ϕ_v° values for sodium chloride are low and negative and increase with a rise in both the temperature and concentration in 2, 4 and 6 wt. % of lactose. This indicates the presence of ion-solvent interactions and these interactions are further strengthened at higher temperatures and higher concentrations suggesting larger electrostriction at higher temperatures. A quantitative comparison of the magnitude of values shows ϕ_v° values are much greater in magnitude than S_v values, for all the solutions. This suggests that ion-solvent interactions dominate over ion-ion interactions in all the solutions and at all experimental temperatures¹⁵. The partial molar volumes (ϕ_v°) were fitted to a polynomial of the following type in terms of absolute temperature (T):

$$\phi_v^\circ = a + bT + cT^2 \quad (4)$$

Values of the coefficients a, b and c of the above equation for different concentrations of sodium chloride in 2, 4 and 6 wt. % of lactose are reported in Table 3.

Table 2. Limiting apparent molar volume ϕ_v° , S_v and apparent molar expansibility (ϕ_E°) and Values of A and B parameters of Jones - Dole equation of sodium chloride in different compositions of lactose (2, 4 and 6%) solutions at different temperatures

Temperature K	$\phi_v^\circ \times 10^6$ $\text{m}^3 \text{mol}^{-1}$	$S_v \times 10^6$ $\text{m}^3 \text{L}^{1/2} \text{mol}^{3/2}$	$\phi_E^\circ \times 10^6$ $\text{m}^3 \text{mol}^{-1} \text{K}^{-1}$	A $\text{dm}^{3/2} \text{mol}^{1/2}$	B $\text{dm}^3 \text{mol}^{-1}$
Sodium chloride in 2% aqueous Lactose					
303.15	-24.266	1.577	2.457	1.465	0.046

Contd...

308.15	-14.481	1.321	1.455	1.247	0.051
313.15	-8.577	1.174	0.455	1.013	0.057
318.15	-3.791	1.057	-0.545	0.616	0.066
Sodium chloride in 4% aqueous Lactose					
303.15	-18.192	1.436	2.458	1.672	0.072
308.15	-8.688	1.186	1.341	1.394	0.079
313.15	-2.761	1.056	0.226	1.033	0.088
318.15	1.169	0.957	-0.889	0.484	0.099
Sodium chloride in 6% aqueous Lactose					
303.15	-12.133	1.266	2.474	1.927	0.073
308.15	-2.012	1.002	1.574	1.732	0.076
313.15	5.075	0.815	0.675	1.207	0.091
318.15	10.697	0.666	-0.225	0.596	0.105

Table 3. Values of a, b, c for sodium chloride in different compositions of lactose (2, 4 and 6%) solutions

Solvent System	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
NaCl in 2% aq. Lactose	-9957.82	63.08	-0.100
NaCl in 4% aq. Lactose	-11008	70.05	-0.111
NaCl in 6% aq. Lactose	-9032.3	57.04	-0.090

The partial molar expansibilities (ϕ_E^o) can be obtained by the following equation:

$$\phi_E^o = \left(\frac{\partial \phi_V^o}{\partial T} \right)_p \quad (5)$$

The values of ϕ_E^o for different solutions of the studied electrolyte at 303.15, 308.15, 313.15 and 318.15 K are reported in Table 2. The values of ϕ_E^o decreases with increase in temperature for sodium chloride in 2, 4 and 6 wt. % of lactose solutions indicates the absence of “caging effect”¹⁶, and its behavior is just like common electrolytes¹⁷⁻¹⁸. The structure making/ breaking capacity of sodium chloride may be interpreted with the help of Hepler’s reasoning¹⁹, *i.e.* on the basis of sign of $(\partial^2 \phi_V^o / \partial T^2)_p$. It has been shown from general thermodynamic eq. (6)

$$\left(\frac{\partial \bar{C}_p^o}{\partial P} \right)_T = -T \left(\frac{\partial^2 \phi_V^o}{\partial T^2} \right)_p \quad (6)$$

Where \bar{C}_p^o is the partial molar heat capacity at infinite dilution. From eq. (6), it is clear that structure making electrolytes should have a positive value of $(\partial^2 \phi_V^o / \partial T^2)_p$ and structure breaking electrolytes should have negative value of $(\partial^2 \phi_V^o / \partial T^2)_p$. For sodium chloride in 2, 4 and 6 wt. % of lactose solutions sign of $(\partial^2 \phi_V^o / \partial T^2)_p$ has been found negative, which suggests that it acts as structure- breaker in 2, 4 and 6 wt. % of lactose solutions.

Viscosity studies

The viscosity data (Table 1) has been analyzed on the basis of Jones- Dole equation²⁰.

$$\eta_s / \eta_0 = 1 + A\sqrt{C} + BC \quad (7)$$

Where η_s and η_0 are viscosities of solution and solvent respectively, C is the molar concentration, A and B are constants. The values of A and B have been determined from the intercept and slope of linear plots of $(\eta_s/\eta_0 - 1)/\sqrt{C}$ versus \sqrt{C} . The sample plots of $(\eta_s/\eta_0 - 1)/\sqrt{C}$ versus \sqrt{C} for sodium chloride in 2 wt. % of lactose is shown in Figure 2. The values of A and B of different solutions are recorded in Table 2.

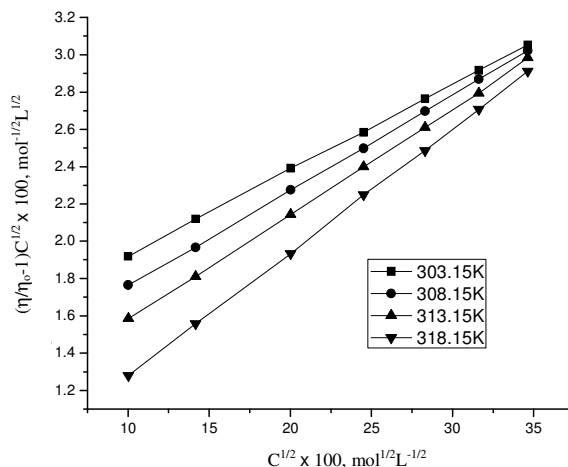


Figure (2). The plot of $(\eta_s/\eta_0 - 1)/\sqrt{C}$ versus \sqrt{C} for sodium chloride in 2 wt. % of lactose solutions

Parameter A of Jones-Dole equation represents the contribution from solute-solute interactions²¹. The values of A , shows that ion-ion interactions for sodium chloride in 2, 4 and 6 wt. % of lactose solutions decreases with increase in temperature, which may be due to more solvation of solute ions.

The B parameter which measures the structure making/breaking capacity of an electrolyte in a solution also contain a contribution from structural effects and is responsible for solute-solvent interactions in a solvent²². It has been emphasized by a number of workers that dB/dT is more important criteria²³ for determining solute-solvent interactions. 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 . The temperature effect on B coefficient for sodium chloride in 2, 4 and 6 wt. % of lactose solutions shows a positive sign of dB/dT thus behaves as structure-breaker in 2, 4 and 6 wt. % of lactose solutions. The sample plot of B versus T for sodium chloride in 2 wt. % of lactose solution is shown in Figure 3. Viscosity data has also been analyzed on the basis of transition state theory of relative viscosity of electrolytic solutions as suggested by Feakins *et al.*²⁴⁻²⁵. The values of $\Delta\mu_1^0$ (Free energy of activation per mole of solvent) and $\Delta\mu_2^0$ (Free energy of activation per mole of solute) is calculated by using the following relations:

$$\Delta\mu_1^0 = RT \ln (\eta_0 \bar{V}_1^0 / hN) \quad (8)$$

$$\Delta\mu_2^0 = \Delta\mu_1^0 + RT / \bar{V}_1^0 [1000B - (\bar{V}_1^0 - \phi^0)] \quad (9)$$

In the earlier prediction it suggested that for structure maker normally $\Delta\mu_1^0 < \Delta\mu_2^0$ and for breaker $\Delta\mu_1^0 > \Delta\mu_2^0$ ²⁴⁻²⁶. From the Table 4 it is found that $\Delta\mu_1^0 < \Delta\mu_2^0$ for sodium chloride in 2, 4 and 6 wt. % of lactose solutions. It suggests that sodium chloride behave as structure-breaker in 2, 4 and 6 wt. % of lactose solutions. This may be due to increase in interactions of solute ions by the solvent molecules as a result of weakening of forces among solvent molecules at transition state.

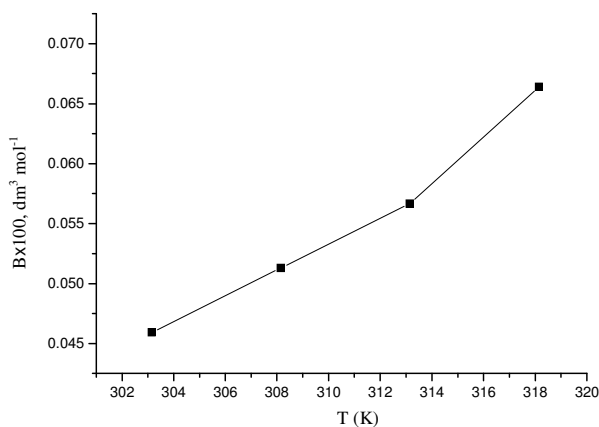


Figure 3. The plot of B versus T for sodium chloride in 2 wt. % of lactose solutions

Where R, h and N are gas constant, Planck constant and Avogadro's number respectively; T is absolute temperature and \bar{V}_1^0 is partial molar volume of solvent. The values of \bar{V}_1^0 , $\Delta\mu_1^0$ and $\Delta\mu_2^0$ are recorded in Table 4.

Table 4. Values for \bar{V}_1^0 , Φ_v^0 , $\Delta\mu_1^0$ and $\Delta\mu_2^0$ for sodium chloride in different composition of lactose at different temperatures

Temperature, K	$\bar{V}_1^0 \times 10^6, \text{m}^3 \text{mol}^{-1}$	$\Delta\mu_1^0, \text{kJ mol}^{-1}$	$\Delta\mu_2^0, \text{kJ mol}^{-1}$
Sodium Chloride in 2 % Lactose			
303.15	18.29	61.40	61.86
308.15	18.32	62.15	64.74
313.15	18.35	62.89	67.11
318.15	18.39	63.68	70.04
Sodium Chloride in 4 % Lactose			
303.15	18.49	61.49	66.29
308.15	18.52	62.24	69.40
313.15	18.55	62.99	72.34
318.15	18.60	63.77	75.43
Sodium Chloride in 6 % Lactose			
303.15	18.68	61.63	67.33
308.15	18.71	62.34	69.90
313.15	18.75	63.08	73.76
318.15	18.79	63.86	77.48

Conductance studies

The limiting molar conductance Λ_m^0 for sodium chloride in 2, 4 and 6 wt. % of lactose solutions were obtained by extrapolating the linear plots of Λ_m versus \sqrt{C} to zero concentration (Table 1). The sample plot of Λ_m versus \sqrt{C} for sodium chloride in 2 wt. % of lactose is shown in Figure 4. The limiting molar conductance for sodium chloride in 2, 4 and 6 wt. % of lactose solutions at 303.15, 308.15, 313.15 and 318.15 K temperatures are recorded in Table 5, shows that limiting molar conductance increases with increase in temperature, which may be due to increase in ionic mobility of ions at infinite dilution.

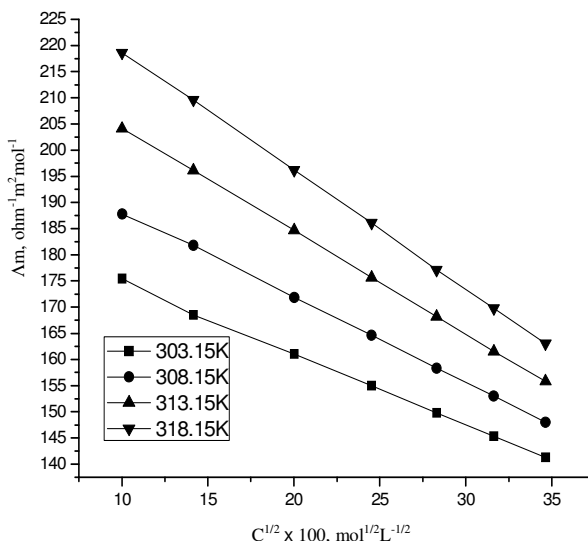


Figure 4. The plot of Λ_m versus \sqrt{C} for sodium chloride in 2 wt. % of lactose solutions

The Walden product data ($\Lambda_m^o \eta_0$) have been recorded in Table 5. The structure making/breaking nature of solute has been determined from temperature coefficient of Walden product *i.e.* $[d(\Lambda_m^o \eta_0) / dT]^{27}$. The negative temperature coefficient of Walden product for sodium chloride in 2, 4 and 6 wt. % of lactose solutions indicate that sodium chloride behaves as structure-breaker in 2, 4 and 6 wt. % of lactose solutions. The sample plot of $\Lambda_m^o \eta_0$ versus T for sodium chloride in 2 wt. % of lactose is shown in Figure 5.

Table 5. Values of limiting molar conductance (Λ_m^o), Viscosity of solvent (η_0) and Walden Product for sodium chloride in different compositions of lactose (2, 4 and 6%) solutions at different temperatures

Temperature, K	$\Lambda_m^o \times 10^4$ $\Omega^{-1} \text{m}^2 \text{mol}^{-1}$	$\eta \times 10^3$ Pa s	$\Lambda_m^o \eta_0 \times 10^7$ $\Omega^{-1} \text{m}^2 \text{mol}^{-1} \text{Pa s}$
Sodium chloride in 2% aqueous Lactose			
303.15	188.56	0.8246	155.48
308.15	204.39	0.7441	152.08
313.15	223.97	0.6702	150.12
318.15	241.53	0.6158	148.74
Sodium chloride in 4% aqueous Lactose			
303.15	183.17	0.8483	155.38
308.15	198.75	0.7631	151.67
313.15	217.22	0.6875	149.34
318.15	236.09	0.6299	148.72
Sodium chloride in 6% aqueous Lactose			
303.15	177.36	0.8867	157.26
308.15	193.39	0.7856	151.93
313.15	205.70	0.7059	145.21
318.15	224.40	0.6459	144.94

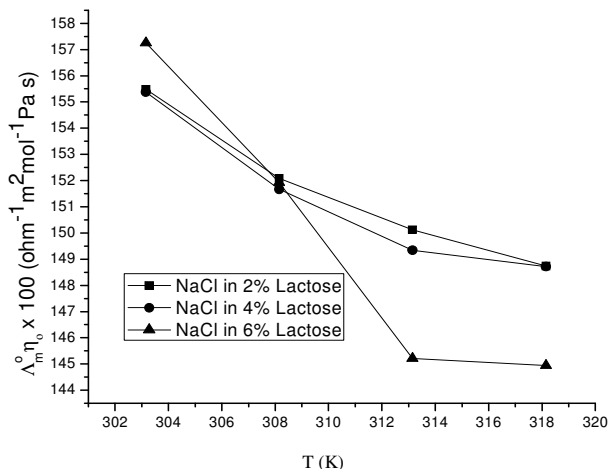


Figure 5. The plot of $\Delta_m^\circ \eta_0$ versus T for sodium chloride in 2 wt. % of lactose solutions

Conclusion

This study reveals that ion–solvent interactions are predominant over ion–ion interactions for sodium chloride in different composition of lactose at all experimental temperatures. Also, the electrolyte under study was found to act as a structure breaker in the solvent mixtures studied. Density, viscosity and conductance have been measured for NaCl in different composition of lactose at 303.15, 308.15, 313.15 and 318.15 K. The variation in density, viscosity and conductance and other related thermodynamic parameters of NaCl at various concentrations and temperatures in aqueous lactose shows the variation to be increase and decrease non-linear. The non linearity confirms the presence of solute-solvent, ion-ion interactions. On the basis of above study, it has been concluded that NaCl behaves as structure-breaker in different composition of lactose.

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