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Thermodynamic study of monovalent and divalent cations in mixed solvent system by conductance method

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The ionic conductivities of potassium chloride (KCl) and calcium chloride (CaCl_2) solutions in aqueous ethanol (0 to 50% mixtures) were measured at various concentrations (0.50×10^{-3} to 50×10^{-3} M) and at different temperatures (25 to 45°C) respectively. The viscosities of v/v aqueous ethanol compositions (0 to 50%) at different temperatures (25 to 45°C) were also measured. The conductivity data have been analyzed by various equations to evaluate molar conductivity at infinite dilution (λ_m^0), degree of dissociation (α), dissociation constant (K_d), Walden constant, and energy of activation (E_a). The values of ion–ion interactions (A) and ion–solvent interactions (B) have been calculated by the Debye–Huckel relation. The increase in value of B with rising temperature led to conclusion that potassium chloride (KCl) and calcium chloride (CaCl_2) behave as structure breaker in aqueous ethanol mixtures. The thermodynamic parameters such as free energy change of activation (ΔG^\ddagger), enthalpy change of activation (ΔH^\ddagger) and entropy change of activation (ΔS^\ddagger) have also been calculated.

Keywords: Conductivity; Ion–ion interactions; Ion–solvent interactions; Walden constant

1. Introduction

Conductance measurement have been credited as one of the most useful techniques to study various types of interactions occurring in solutions [1–5]. The study of variation of conductance with concentrations and viscosities provides valuable information about the behavior of solutions. Different equations for conductivities and viscosities of 1:1 and 2:1 electrolytes in solutions have been deduced and subjected to test using the data available in literature [5–10]. In previous papers conductance of number of salts were reported in both aqueous and mixed solvents and the interpretation of ionic processes in solution is the subject of many discussions [11–16]. The present investigation has been undertaken with a view to test the applicability of conductivity and viscosity data for evaluation of different parameters, the behavior and nature of electrolytes in mixed solvent system and the nature of solvent must be taken under consideration.

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The physical properties such as dielectric constant, dipole moment, attraction forces, ionic interactions of mixed solvents are quite different from that of water. In solutions the medium does not remain stationary and all the ions are generally solvated and carry with them solvent molecules associated with ionic atmosphere. When they move in a direction opposite to motion of solvated positive ion it is thus forced to swim against the current. This counter current makes more difficult for the ion to move through the solution and thus slows down the velocity of the ion. The additional retardation arising in this manner is called the electrophoretic effect. Under the influence of these effects, the molar conductivities at infinite dilution λ_m^0 have been determined by the Debye–Huckel relation [2]:

$$\lambda_m = \lambda_m^0 - (A + B \lambda_m^0) \sqrt{C} \quad (1)$$

where λ_m is the molar conductivity, λ_m^0 is the molar conductivity at infinite dilution, A and B are coefficients which represent ion–ion and ion–solvent interactions respectively.

$$A = \frac{82.4}{(DT)^{1/2} \eta^0} \quad (2)$$

$$B = \frac{8.20 \times 10^5}{(DT)^{1/2}} \quad (3)$$

where D is dielectric constant, η^0 is viscosity of solvent and T is the absolute temperature and C represents molar concentration of solution. Walden product relates molar conductivity at infinite dilution to viscosity of that solvent as [2,3]:

$$\lambda_m^0 \eta^0 = \text{Constant}/r \quad (4)$$

where r is radius of ion. Walden product of ion is inversely proportional to the effective radius of the ion in a given solvent [1].

Viscosities of v/v solvent compositions have been measured by relation [9]:

$$\eta^0 = \frac{d_{\text{sol}}}{d_w} \times \frac{t_{\text{sol}}}{t_w} \times \eta_w \quad (5)$$

where d_{sol} and d_w are densities of solvent and water in g ml^{-1} , t_{sol} and t_w are time of flow of solvent and water in seconds respectively and η_w is viscosity of water in poise.

2. Experimental

Potassium chloride (KCl) and calcium chloride (CaCl_2) (E. Merck) were used without further purification. Ethanol of Analar grade extra pure was used as solvent. Double distilled water having conductivity 0.06 mS cm^{-1} was used for preparation of different percentages (v/v) of mixed solvent system.

Conductivities were measured by digital direct reading conductivity meter model 103, range 0 to 20.00 $\text{K}\mu\text{S cm}^{-1}$ manufactured by Jenco Electronic Ltd. A dip type conductivity cell with platinised electrode was calibrated having cell constant 0.999 cm^{-1} was used for quick response. An Ostwald viscometer type Techniconomial constant 0.05 CS/C capillary ASTM 445 manufactured by USA was used to measure the viscosity. A stopwatch (Advance-85 Quartz) having a least count of 0.5 s was used for determination of time of flow of solvents. Densities were determined by specific gravity bottle with capacity of 10 mL by volume. A thermostatic bath (type Haake-13 manufactured by Haake Korlsruhe, Germany) was used to maintain the constant temperature during the experimental work. Solutions of KCl and CaCl_2 were prepared in the concentration ranges from 0.50×10^{-3} to $5.0 \times 10^{-2}\text{ mol dm}^{-3}$ in aqueous and aqueous ethanol 10 to 50% (V/V) solvents. Density and conductivity of each solution were measured at fixed temperature by placing a known volume of each solution of salt in water bath for at least twenty minutes to attain required temperature. Reproducibility in the results was also checked by taking each measurement three times. The uncertainty in the experimental data for conductivity, viscosity and density was found to be $\pm 0.5\text{ mS cm}^{-1}$, ± 0.002 millipoise and $\pm 0.001\text{ g mL}^{-1}$ respectively.

3. Results and discussion

The interpretation of ionic processes in solution is the subject of many discussions. One of the most difficult problems encountered in studying electrolyte solution is that concerning the nature of ion-solvent interaction. The results hitherto have referred specially to solutions in water. A large number of theoretical and experimental works have been done on studying the association of 2:1 electrolyte in water, but those papers with interest in studying electrolytic phenomena in mixed solvents are rather few.

The molar conductivity values of potassium chloride (KCl) and calcium chloride (CaCl_2) in aqueous and 10 to 50% (v/v) aqueous ethanol mixtures at different temperatures 25 to $45 \pm 0.1^\circ\text{C}$ are tabulated in tables 1 and 2 for potassium chloride

Table 1. Molar conductivity (λ_m) of KCl at different temperatures in 0–50% (v/v) aqueous ethanol.

Temperature ($^\circ\text{C}$)	Molar conductivity ($\text{S cm}^2\text{ mol}^{-1}$) in aqueous ethanol mixtures (% v/v)					
	0	10	20	30	40	50
	[KCl] = 3.0×10^{-3} (mol dm^{-3})					
25	144.67	113.67	90.33	77.67	67.67	62.00
30	141.67	113.33	91.67	73.33	62.00	59.73
35	136.67	114.33	92.00	80.33	64.00	58.50
40	132.33	118.00	97.33	74.00	66.33	61.00
45	139.67	117.67	98.00	78.00	68.70	61.53
	[KCl] = 5.0×10^{-3} (mol dm^{-3})					
25	121.60	99.20	72.00	71.60	53.00	45.60
30	111.60	83.80	78.00	67.20	48.40	48.20
35	100.00	98.20	79.00	68.00	48.80	49.80
40	107.00	84.00	80.20	68.40	52.20	50.83
45	108.00	87.40	81.40	69.00	53.20	51.40

Table 2. Molar conductivity (λ_m) of CaCl_2 at different temperatures in 0–50% (v/v) aqueous ethanol.

Temperature (°C)	Molar conductivity ($\text{S cm}^2 \text{mol}^{-1}$) in aqueous ethanol mixtures (% v/v)					
	0	10	20	30	40	50
	$[\text{CaCl}_2] = 3.0 \times 10^{-3} \text{ (mol dm}^{-3}\text{)}$					
25	211.33	162.00	128.67	104.00	95.33	69.33
30	220.00	159.67	131.67	102.33	99.67	70.67
35	201.00	157.33	136.00	103.00	100.00	70.00
40	203.33	159.33	138.33	108.00	104.00	68.33
45	202.33	162.33	140.33	111.30	106.67	79.67
	$[\text{CaCl}_2] = 5.0 \times 10^{-3} \text{ (mol dm}^{-3}\text{)}$					
25	145.00	120.40	78.40	76.60	59.00	47.80
30	138.20	118.60	79.00	75.40	61.00	47.00
35	135.00	115.40	85.60	75.00	61.20	44.20
40	136.80	115.00	85.80	78.60	63.00	45.00
45	139.00	115.60	87.20	80.40	64.80	52.20

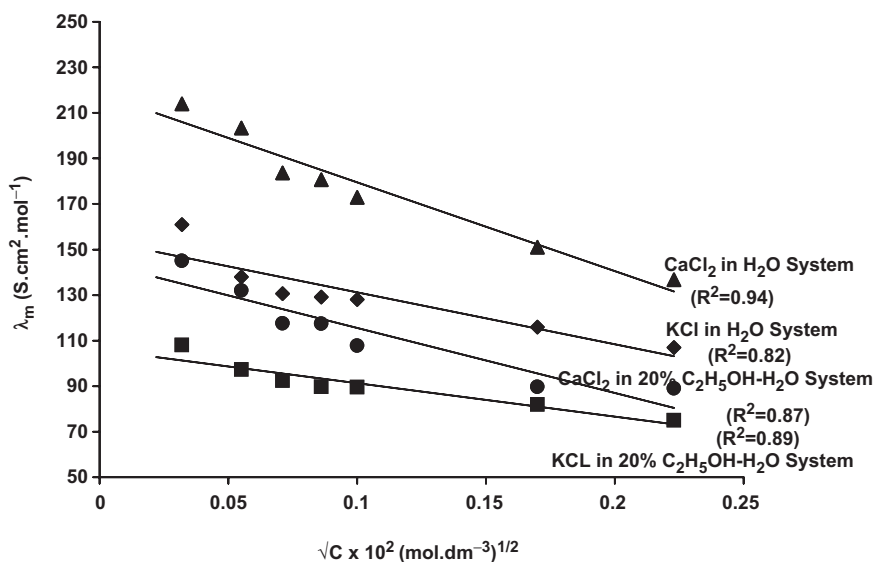
Table 3. Viscosity (η_0) of aqueous ethanol (% v/v) compositions at different temperatures.

Temperature (°C)	Viscosities (mp) of different (% v/v) aqueous ethanol					
	0	10	20	30	40	50
25	8.90	11.38	14.57	19.23	21.89	25.44
30	7.98	9.11	11.81	14.45	18.13	19.94
35	7.19	8.74	10.94	12.96	14.64	15.16
40	6.53	7.57	9.45	10.90	12.20	13.09
45	5.96	6.92	8.70	9.77	10.77	11.53

and calcium chloride respectively. The viscosities of 0 to 50% (v/v) aqueous ethanol mixtures are summarized in table 3. Results show that molar conductivities decrease with increase of concentration both for potassium chloride (KCl) and calcium chloride (CaCl_2) at all solvent compositions. With this increase in temperature there is decrease in molar conductance in aqueous medium while an increase in molar conductance was observed in 10 to 50% v/v aqueous ethanol compositions with some exceptions. With the increase of v/v aqueous ethanol composition from 0 to 50% results show a decrease in molar conductance. It is also found that molar conductivities values for calcium chloride (CaCl_2) are higher than potassium chloride (KCl) at fixed temperature and fixed solvent composition. The values of viscosity of solvent decreased with the increase of temperature are summarized in table 3. Molar conductivity at infinite dilution (λ_m^0) were determined by intercept of representative plot of λ_m versus \sqrt{C} and the values for potassium chloride and calcium chloride are shown in table 4. The value of λ_m^0 for KCl in water at 298 K was found $150.71 \text{ S cm}^2 \text{mol}^{-1}$, which is close to the reported value of $149.8 \text{ S cm}^2 \text{mol}^{-1}$ shows the validity of results. The representative plot of λ_m versus \sqrt{C} is linear as shown in figure 1, for both potassium chloride and calcium chloride. These values show that with the increase in temperature there is an increase in molar conductance at infinite dilution. This indicates an increase in ionic mobility or a decrease in viscosity. Molar conductance at infinite dilution has been regarded as a measure of solute–solvent interactions, the greater the magnitude of molar conductance at infinite dilution the greater would be the solute–solvent interaction. Molar conductance at

Table 4. Molar conductivity at infinite dilution (λ_m^0) of KCl and CaCl₂ at different temperatures in 0–50% (v/v) aqueous ethanol.

Temperature (°C)	Molar conductivity at infinite dilution (S cm ² mol ⁻¹) in aqueous ethanol mixtures (% v/v)					
	0	10	20	30	40	50
	Salt = KCl					
25	150.71	121.26	104.01	79.16	70.74	65.82
30	152.28	126.70	109.43	74.43	66.56	66.29
35	148.89	122.18	98.64	83.40	69.61	65.10
40	145.39	129.82	99.58	79.40	68.76	66.77
45	145.49	129.61	104.95	80.09	70.97	70.08
	Salt = CaCl ₂					
25	228.19	170.81	131.33	119.67	113.82	74.46
30	229.62	172.07	145.92	117.45	119.52	75.52
35	230.41	169.74	152.48	120.75	115.48	75.65
40	251.82	171.13	147.39	142.67	119.85	73.17
45	220.81	175.49	150.31	129.83	124.58	86.05

Figure 1. Plot of λ_m vs. \sqrt{C} for KCl and CaCl₂ in aqueous and 20% aqueous ethanol at 35°C.

infinite dilution decreases with increase of solvent compositions because solvent–solute interactions have been decreased.

Degree of dissociation (α) was calculated by using relation [10]:

$$\alpha = \lambda_m / \lambda_m^0 \quad (6)$$

Values of degree of dissociation are tabulated in table 5 for potassium chloride and calcium chloride respectively. Results show that the degree of dissociation decreases with increase of concentration, % composition of aqueous ethanol and temperature for both salts. It was also found that the values of degree of dissociation for calcium chloride are lower than those for potassium chloride.

Table 5. Values of dissociation constant (K_d), Walden constant and degree of dissociation for KCl and CaCl₂ in aqueous ethanol (% v/v) at 35°C.

Aqueous-ethanol (% v/v)	Dissociation constant (K_d) $\times 10^2$	Walden constant $\times 10^8$	Degree of dissociation (α)
Salt = KCl			
0	4.41	1.43	0.84
10	7.20	1.42	0.89
20	5.82	1.44	0.87
30	6.45	1.44	0.88
40	2.58	1.36	0.77
50	4.82	1.31	0.85
Salt = CaCl ₂			
0	2.25	1.64	0.75
10	3.73	1.47	0.82
20	1.63	1.65	0.70
30	2.25	1.55	0.75
40	3.20	1.67	0.80
50	2.58	1.14	0.77

The values of dissociation constant (K_d) of potassium chloride and calcium chloride in aqueous ethanol solvent at different temperatures were calculated by [10]:

$$K_d = [\alpha^2/1 - \alpha]C. \quad (7)$$

The results tabulated in table 5 for potassium chloride and calcium chloride respectively show that with the increase of concentration there is an increase in dissociation constant as it is directly related to concentration, while with the increase of solvent composition values of dissociation constant decrease. Calcium ions have high positive charge compared to potassium which have low solute-solvent interactions but high solute-solute interactions, and have low values of dissociation constant for calcium chloride. Values of dissociation constant decrease with the increase of temperature. This shows that potassium chloride or calcium chloride causes a reduction in the thickness of ionic atmosphere surrounding the polar species and reduces repulsion between them, thus resulting in an increase in aggregation number and formation of micelles. In a mixed solvent system, decrease in hydration of ions led to a decrease in a value of dissociation constant [3,15].

Walden constant values are tabulated in table 5 for potassium chloride and calcium chloride respectively. Its value decreases with an increase of temperature while increases with increase of solvent composition. Increase in value of Walden constant indicates maximum interaction between water and ethanol. The increase also indicates weak solvation of ion. The decrease in value of Walden constant indicates an increase of hydrophobic solvation with increasing concentration of ethanol. As the ethanol contents increases, progressive disruption of water structure occurs and ions become solvated with other component of solvent mixture [3]. Walden constant values for calcium chloride are higher than potassium chloride because effective radius of calcium is smaller than potassium, due to large size and high positive charge.

The mobility of ions in aqueous ethanol mixture was also determined in terms of ionic interactions A and B , which are constants characteristic of electrolyte. The A -coefficient represents the contribution from interionic electrostatic forces,

Table 6. Ion-ion interaction (A) and ion-solvent interaction (B) for KCl and CaCl₂ in aqueous ethanol (% v/v) compositions at different temperatures.

Aqueous-ethanol (% v/v)	Ion-ion and ion-solvent interactions	
	A	B
	Salt = KCl	Temperature = 35°C
0	187.02	0.22
10	88.90	0.26
20	82.65	0.30
30	72.70	0.34
40	49.12	0.39
50	48.64	0.47
	Salt = CaCl ₂	Temperature = 45°C
0	343.70	0.21
10	272.73	0.27
20	237.51	0.30
30	213.89	0.35
40	205.90	0.41
50	120.59	0.48

the B -coefficient measures order or disorder introduced by ions into solvent structure. B coefficient is specific and an additive property of the ions of strong electrolyte at a given temperature. The results of A and B are tabulated in table 6. The values of ion-ion interaction (A) decrease with increase of solvent composition for both salts, while with the increase of temperature value of ion-ion interaction (A) for potassium chloride (KCl) decreases and a reverse behavior was observed for calcium chloride (CaCl₂). The results show with the rise of temperature the solubility of calcium chloride decreases in aqueous ethanol system [13]. The values of ion solvent interaction (B) increase with increases of solvent composition and temperature shows that potassium chloride (KCl) and calcium chloride (CaCl₂) act as a structure breaker in aqueous ethanol mixtures. The potassium ion or calcium ion strongly orders the solvent in co-sphere about the ion, with increasing temperature the solvent ordering is perturbed by the increase in thermal energy and the B -coefficient for potassium or calcium ion increased.

Energy of activation ($E_a^\#$) was calculated from slope of plot $\log \lambda_m^0$ against $1/T$ by relation [3,10]:

$$\log \lambda_m^0 = \log A - \frac{E_a^\#}{2.303RT} \quad (8)$$

where A is constant or frequency factor, R is the gas constant, T is the absolute temperature. Representative plot of $\log \lambda_m^0$ versus $1/T$ is shown in figure 2 and values of activation energy ($E_a^\#$) are tabulated in table 7. Results show that the values of activation energy ($E_a^\#$) decrease with the increase of solvent composition for potassium chloride whereas a reverse order was observed for calcium chloride. It shows that the degree of dissociation is lower in high content of ethanol. It was also found that the values of activation energy ($E_a^\#$) are lower for calcium chloride as compared to potassium chloride in aqueous ethanol mixtures. Values of free energy change of activation ($\Delta G^\#$), enthalpy change of activation ($\Delta H^\#$) and entropy change of activation

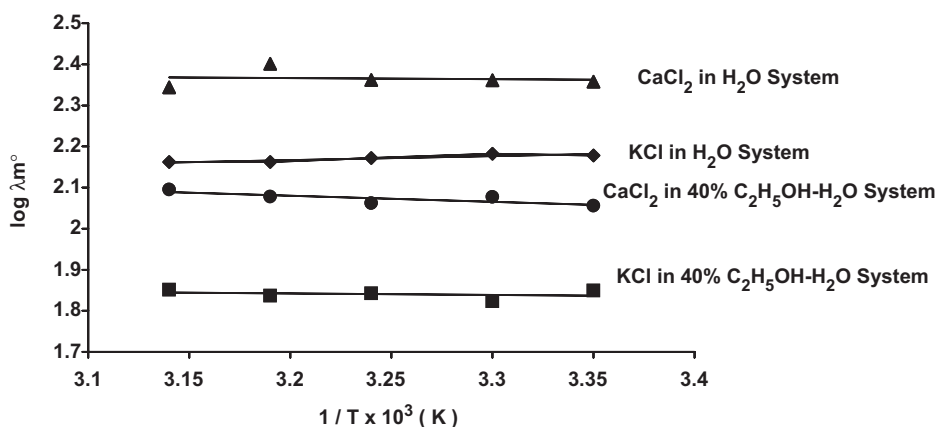


Figure 2. Plot of $\log \lambda_m^0$ vs. $1/T$ for KCl and CaCl_2 in aqueous and 40% aqueous ethanol.

Table 7. Thermodynamic parameters for KCl and CaCl_2 in aqueous ethanol at 40°C.

Aqueous ethanol (% v/v)	Energy of activation ($E_a^\#$) (kJ mol^{-1})	Enthalpy change of activation ($\Delta H^\#$) (kJ mol^{-1})	Free energy change of activation ($\Delta G^\#$) (kJ mol^{-1})	Entropy change of activation ($\Delta S^\#$) ($\text{JK}^{-1} \text{mol}^{-1}$)
$[\text{KCl}] = 10 \times 10^{-3} \text{ (mol dm}^{-3}\text{)}$				
0	36.34	33.74	-4.43	122.00
10	26.02	23.42	-8.15	101.00
20	14.57	11.97	-6.53	59.59
30	10.47	7.87	-7.91	50.40
40	6.36	3.76	-7.67	34.00
50	21.50	18.90	-7.67	85.00
$[\text{CaCl}_2] = 10 \times 10^{-3} \text{ (mol dm}^{-3}\text{)}$				
0	1.93	-0.67	-10.85	32.50
10	0.71	-1.89	-8.75	21.90
20	1.92	-0.68	-10.25	30.60
30	2.94	0.34	-10.75	31.40
40	3.07	0.47	-11.33	37.70
50	6.34	3.74	-9.53	42.40

($\Delta S^\#$) are expressed as:

$$\Delta G^\# = 2.303RT \log K_d \quad (9)$$

$$\Delta H^\# = E_a^\# - RT \quad (10)$$

$$\Delta S^\# = \frac{\Delta H^\# - \Delta G^\#}{T} \quad (11)$$

The values of activation parameters are tabulated in table 7. Results show that free energy change of activation ($\Delta G^\#$) become more negative with increase of concentration of salts but become less negative with increase of temperature. Enthalpy change of activation ($\Delta H^\#$) values for potassium chloride decrease with increase of temperature and solvent composition up to 40% while increase 50% in aqueous ethanol. For calcium chloride the values increases from negative to positive with increase

in ethanol composition. Enthalpy values for calcium chloride are found less negative than potassium chloride. Entropy change of activation values for potassium chloride decreased with the increase in temperature and concentration of salt. For calcium chloride entropy change of activation (ΔS^\ddagger) increased with increase of temperature and concentration of salt. Entropy values for calcium chloride were found higher than potassium chloride in aqueous system and lower with increase in ethanol content in aqueous ethanol system.

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