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## Ionic interaction of electrolyte with dilute solution of poly(vinyl alcohol) at different temperatures

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The ionic interactions of  $\text{ZnSO}_4 \cdot 7\text{H}_2\text{O}$  were studied, using dilute solution of polymer as a solvent. The ionic conductance of  $\text{ZnSO}_4 \cdot 7\text{H}_2\text{O}$  in aqueous and mixed solvent systems of aqueous poly(vinyl alcohol) (0–0.9%) was measured in concentration range ( $2 \times 10^{-3}$  to  $10 \times 10^{-2} \text{ m dm}^{-3}$ ) at different temperatures (25–45°C), respectively. Conductance data were analyzed by Ostwald dilution law to get the limiting molar conductance ( $\lambda_{\text{m}}^\circ$ ). The limiting molar conductance ( $\lambda_{\text{m}}^\circ$ ) decreased with the increase in the composition of polymer showing decreased ion–solvent interaction. Walden product, degree of dissociation and dissociation constant were also calculated using conductance data. Thermodynamic parameters such as free energy change of activation ( $\Delta G^*$ ), enthalpy change of activation ( $\Delta H^*$ ) and entropy change of activation ( $\Delta S^*$ ) were also calculated at various temperatures as function of concentration of electrolyte in aqueous and mixed solvent systems.

**Keywords:** Conductivity; Polymer; Electrolyte; Ion–ion interaction; Ion–solvent interaction; Thermodynamic parameters

### 1. Introduction

Poly(vinyl alcohol) (PVOH) is a film forming and the largest volume synthetic water-soluble resin produced in the world. The resin has a wide range of applications in several industries. It is an industrially important polymer, and this is shown by the fact that its production increases every year [1–3]. Conductance studies of electrolytes in mixed solvents have received considerable attention in recent years. It is a simple, accurate and reliable method to study the solvents effects, modification in the structure of a solvent due to the presence of an ion and ionic movement in a solution. The study of variation in molar conductance with temperature and solvent composition provides information about ionic mobility and solvent viscosity, hydrogen bonding capability, dielectric constant and its specific interaction with ions. The influence of various temperatures on conductivity measurement can give detailed information of ion–ion

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and ion–solvent interaction for different electrolytes solution [4–7]. The interaction of salts into solvents is used to study the solvent property like structural behavior of water has been extensively studied. It is important to investigate the polymers and their interactions with the electrolytes in solution form. Realizing this important aspect, some researchers have reported the solution properties of water-soluble polymers, whereas others tried to give some theoretical background about these polymers [8,9]. In general, properties such as conductance can be measured very precisely at low concentrations and reliable values of infinite dilution are readily obtained. It is hoped that a systematic coverage of properties of typical ions and solvents or mixed solvents will give an overall view of the main aspects of solvation [10,11]. The physical properties of the mixed solvents are very different from that of water. Thermodynamic investigations play an important role in understanding the type and extent of patterns of molecular associations that exist in liquid mixtures and their sensitivities to variations in composition, temperature, pressure and chemical nature [12,13].

## 2. Experimental

All glassware used were of Pyrex ‘A’ grade quality. PVOH (<98% from Merck) average molecular weight  $\approx 46861.80 \text{ g mol}^{-1}$  was used without further purification. Different compositions (0–0.9%) of aqueous PVOH was prepared by taking w/v of polymer in a known volume of hot ( $80 \pm 0.1$ )°C double-distilled water having a conductivity of  $0.06 \mu\text{S cm}^{-1}$ . The solution was constantly stirred when a clear solution was formed; the solution was cooled to room temperature and made up to the mark. Zinc sulfate heptahydrate ( $\text{ZnSO}_4 \cdot 7\text{H}_2\text{O}$  of E. Merck, 99% pure) was used without further purification. Stock solutions of  $0.01 \text{ (mol dm}^{-3}\text{)}$  zinc sulfate ( $\text{ZnSO}_4 \cdot 7\text{H}_2\text{O}$ ) were prepared by dissolving calculated amounts in aqueous and aqueous PVOH solutions ranging from (0 to 0.9% w/v). Solutions in various concentration ranges from  $2 \times 10^{-3}$  to  $8 \times 10^{-2} (\pm 0.001) \text{ (mol dm}^{-3}\text{)}$  were prepared from stock solutions. Conductivities were measured by digital direct reading conductivity meter (HI-9813, HANNA instruments) having range  $0.001\text{--}4.00 \text{ mS cm}^{-1}$  connected with an electrode having cell constant  $0.99 \text{ cm}^{-1}$  at various temperatures ranging  $25\text{--}45^\circ\text{C}$  with a difference of  $5^\circ\text{C}$ . The temperature was kept constant with the help of thermostatic water bath. The solutions were kept in a thermostatic bath for 15–20 min to attain constant temperature. Conductivity of solutions was measured at particular temperatures with the help of a digital conductometer. To check reproducibility, this procedure was repeated three times for each solution.

## 3. Results and discussion

Conductivities of various concentrations of electrolyte ranging from  $2 \times 10^{-3}$  to  $10 \times 10^{-2} \text{ mol dm}^{-3}$  in aqueous and aqueous PVOH (0–0.9% w/v) at different temperatures ( $25\text{--}45^\circ\text{C}$ ) with a difference of  $5^\circ\text{C}$ . The molar conductivities were measured at different temperatures as shown in table 1. The increase in molar conductance with temperature shows high mobility of  $\text{ZnSO}_4 \cdot 7\text{H}_2\text{O}$  ions.

Table 1. Molar conductivity ( $\lambda_m$ ) of  $8 \times 10^{-3}$  (mol dm $^{-3}$ ) ZnSO $_4 \cdot 7$ H $_2$ O in aqueous poly(vinyl alcohol) systems at different temperatures.

Percentage composition of PVOH (w/v)	Molar conductivity $\times 10^{-3}$ (mS cm $^2$ mol $^{-1}$ ) at temperatures ( $^{\circ}$ C)				
	25	30	35	40	45
0.0	112	113	114	115	116
0.1	116	118	119	120	122
0.3	118	120	121	122	123
0.5	124	126	127	128	130
0.7	130	131	132	135	136
0.9	133	135	136	137	138

Table 2. Molar conductance at infinite dilution ( $\lambda_m^{\circ}$ ) for ZnSO $_4 \cdot 7$ H $_2$ O in aqueous poly(vinyl alcohol) systems at different temperatures.

Temperature ( $^{\circ}$ C)	Molar conductance at infinite dilution $\times 10^{-3}$ (S cm $^2$ mol $^{-1}$ ) in aqueous PVOH (w/v) (%)					
	0	0.1	0.3	0.5	0.7	0.9
25	137	146	161	173	186	198
30	142	152	165	177	189	201
35	146	156	169	181	193	206
40	150	159	173	185	197	210
45	152	162	176	188	202	214

Resultant data were analyzed by Ostwald dilution law to obtain molar conductance at infinite dilution ( $\lambda_m^{\circ}$ ).

$$\lambda_m = \lambda_m^{\circ} - [A + B\lambda_m^{\circ}]C^{1/2} \quad (1)$$

where,  $\lambda_m$  is the molar conductivity and  $\lambda_m^{\circ}$  is the molar conductivity at infinite dilution.

These results of limiting molar conductance ( $\lambda_m^{\circ}$ ) tabulated in table 2 have been calculated from intercept of plot between  $\lambda_m$  versus  $\sqrt{C}$  as shown in figure 1, it is clear that, molar conductance at infinite dilution increased with the increase in the temperature for all the compositions of PVOH indicating less solvation resulting in high mobility of available ions. The increase in the number of ions due to higher frequency and bond breaking causes an increase in translational and vibrational degree of freedom at high temperature and decrease in viscosity of solvent [16]. The observed variation in ( $\lambda_m^{\circ}$ ) with solvent composition explained by the three-dimensional structure of water which gets disturbed with the addition of PVOH due to hydrophobic interaction or formation of H-bonding with water molecules. This decreased the size of solvation shell, thereby increasing conductivity.

Walden product, is the product of limiting molar conductance ( $\lambda_m^{\circ}$ ) and viscosity of the solvent which is inversely proportional to the effective radius of ion or species in a given solvent.

$$\lambda_m^{\circ} \eta_o = \frac{\text{Constant}}{r} \quad (2)$$

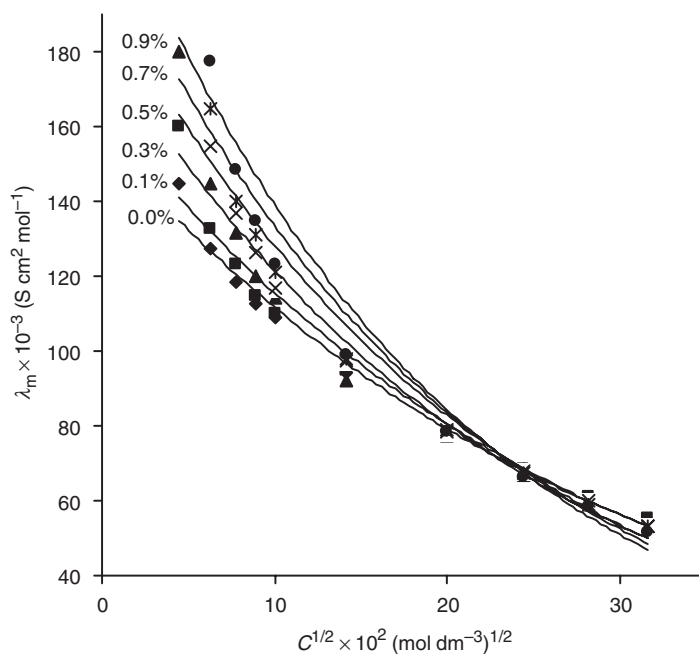


Figure 1. Limiting molar conductance of  $\text{ZnSO}_4 \cdot 7\text{H}_2\text{O}$  at  $30^\circ\text{C}$  in aqueous poly(vinyl alcohol).

Table 3. Walden constant of  $\text{ZnSO}_4 \cdot 7\text{H}_2\text{O}$  in aqueous poly(vinyl alcohol) systems at different temperatures.

Temperature ( $^\circ\text{C}$ )	Walden constant $\times 10^2$ ( $\text{S cm}^3 \text{mol}^{-1} \text{Poise}$ ) in aqueous PVOH (w/v) (%)					
	0	0.1	0.3	0.5	0.7	0.9
25	0.900	0.991	1.250	1.711	1.866	2.200
30	0.839	0.983	1.105	1.386	1.635	1.879
35	0.780	0.873	1.011	1.263	1.494	1.619
40	0.728	0.820	0.940	1.163	1.398	1.493
45	0.672	0.770	0.874	1.050	1.262	1.376

where,  $r$  is the radius of an ion and  $\eta_o$  is the viscosity of the solvent. The values for Walden constant are tabulated in table 3 for zinc sulfate ( $\text{ZnSO}_4 \cdot 7\text{H}_2\text{O}$ ). The values of Walden constant increases with the increase of percent compositions (0–0.9% w/v) of PVOH because viscosity of solvent increases. The value of Walden product decreases with the increase of temperature because with increase in temperature viscosity of solvent decreases which increases the mobility of ions. The decrease in viscosity overweighs the effect of conductivity, which results in the decrease in values of Walden product. Increased values of Walden product indicated weak solvation while decreased values of Walden product indicated strong solvation [1].

Degree of dissociation is the ratio of molar conductance at given concentration to molar conductance at infinite dilution given by:

$$\alpha = \frac{\lambda_m}{\lambda_m^\circ} \quad (3)$$

Table 4. Degree of dissociation ( $\alpha$ ) of  $8 \times 10^{-3}$  (mol dm $^{-3}$ ) ZnSO $_4 \cdot 7$ H $_2$ O in aqueous poly(vinyl alcohol) systems at different temperatures.

Percent composition of PVOH (w/v)	Degree of dissociation at temperature ( $^{\circ}$ C)				
	25	30	35	40	45
0.0	0.8167	0.7910	0.7759	0.7620	0.7620
0.1	0.7851	0.7773	0.7637	0.7538	0.7518
0.3	0.7370	0.7244	0.7157	0.7068	0.7003
0.5	0.7129	0.7092	0.7018	0.6951	0.6883
0.7	0.6970	0.6920	0.6841	0.6839	0.6731
0.9	0.6686	0.6693	0.6605	0.6536	0.6463

Table 5. Dissociation constant ( $K_d$ ) of  $8 \times 10^{-3}$  (mol dm $^{-3}$ ) ZnSO $_4 \cdot 7$ H $_2$ O in aqueous poly(vinyl alcohol) at different temperatures.

Percent composition of PVOH (w/v)	Dissociation constant $\times 10^2$ (mol dm $^{-3}$ ) at temperatures ( $^{\circ}$ C)				
	25	30	35	40	5
0.0	2.91	2.39	2.13	1.95	1.95
0.1	2.29	2.17	1.97	1.84	1.82
0.3	1.65	1.52	1.43	1.36	1.30
0.5	1.41	1.38	1.32	1.26	1.21
0.7	1.28	1.24	1.18	1.18	1.10
0.9	1.07	1.08	1.02	0.98	0.94

$\alpha$  is the degree of dissociation, values of degree of dissociation tabulated in table 4 showed the decrease in values with the increase in concentration of electrolytes i.e. ZnSO $_4 \cdot 7$ H $_2$ O. As with the increase in concentration, the molar conductance decreases (molar conductance increases at infinite dilution) so degree of dissociation decreases. With the increase of percent composition of PVOH, degree of dissociation decreased as dielectric constant of the solvent decreased, but dielectric constant of water favors the dissociation of electrolytes i.e. salt, because in aqueous PVOH medium solvent-solvent interactions are higher than the ion-solvent interactions.

The state of equilibrium between ionized and un-ionized molecule in solution was determined by:

$$K_d = \left[ \frac{\alpha^2}{1 - \alpha} \right] C \quad (4)$$

where,  $K_d$  is the dissociation constant and  $1 - \alpha$  is the remaining fraction of an electrolyte undissociated. The values of dissociation constant for zinc sulfate (ZnSO $_4 \cdot 7$ H $_2$ O) tabulated in table 5 showed a decrease in dissociation constant with the increase in percent composition of PVOH. The variation of dissociation constant with percentage composition and temperature were observed due to the selective solvation of the ions by the solvent. The decreased values of dissociation constant with increase in temperature also indicated the endothermic nature of the dissociation process of the zinc sulfate in aqueous-PVOH solvent mixture. The variation in values of dissociation constant with percent composition is primarily due to change in dielectric constant. It was also indicated that the electrolyte caused reduction in the thickness of the ionic

environment surrounding ionic species, which reduced the repulsion between different ionic species by increasing the aggregation number capacity. It showed that due to bulky organic molecules, either entered the solvation shell or came out of it during the movement of the solvated ion in the bulk of the solution. In mixed solvent system, decrease in hydration of ions also led to decrease in values of dissociation constant.

The effect of temperature on the conductance of an ion depends on its rate of movement, it seems reasonable to treat conductance in a manner analogous to that employed for other processes which took place at a definite rate, which increased with temperature [16] and thus the relation between conductivity and temperature has been expressed as:

$$\log \lambda_m^\circ = \log A - \frac{E_a}{2.303 RT} \quad (5)$$

where,  $R$  is the molar gas constant,  $E_a$  is the energy of activation which determines the rate of movement of ions,  $A$  is the frequency factor and  $T$  is the absolute temperature. Energy of activation was calculated by Arrhenius plot of  $\log \lambda_m^\circ$  versus  $1/T$  as a function of solvent compositions. There was decrease in values of  $E_a$  which

Table 6. Energy of activation ( $E_a$ ) for  $\text{ZnSO}_4 \cdot 7\text{H}_2\text{O}$  in aqueous poly(vinyl alcohol) systems.

Energy of activation ( $\text{kJ mol}^{-1}$ ) in aqueous PVOH (w/v) (%)					
0	0.1	0.3	0.5	0.7	0.9
4.135	3.829	3.618	3.274	3.216	3.178

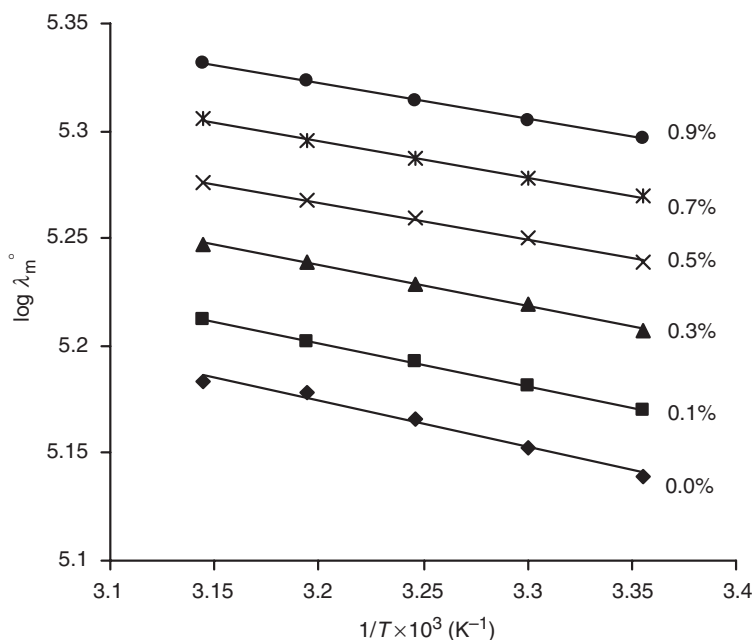


Figure 2. Energy of activation ( $E_a$ ) for  $\text{ZnSO}_4 \cdot 7\text{H}_2\text{O}$  in aqueous poly(vinyl alcohol).

are shown in table 6. It was observed that when the rate of movement was slow in high concentration of aqueous PVOH the energy of activation decreased, while rate of movement of ions was fast in low concentration of solvent. Representative plot of  $\log \lambda_m^\circ$  versus  $1/T$  is shown in figure 2.

$$\Delta G^* = -2.303 RT \log K_d \quad (6)$$

where,  $\Delta G^*$  is the free energy change of activation. Table 7 shows the results of  $\Delta G^*$  for zinc sulfate ( $\text{ZnSO}_4 \cdot 7\text{H}_2\text{O}$ ). There was an increase in values of  $\Delta G^*$  by increasing percent composition (0–0.9% w/v) aqueous PVOH and temperature. By the increase in temperature there occurred more association of ions than dissociation, thus ion–ion interaction increased. The increased values of  $\Delta G^*$  showed endothermic nature of zinc sulfate in aqueous PVOH.

Enthalpy change of activation ( $\Delta H^*$ ) was calculated by plotting  $\log K_d$  versus  $1/T$ , representative plot is shown in figure 3. The values of  $\Delta H^*$  are shown in table 8

Table 7. Free energy change of activation ( $\Delta G^*$ ) of  $8 \times 10^{-3}$  ( $\text{mol dm}^{-3}$ )  $\text{ZnSO}_4 \cdot 7\text{H}_2\text{O}$  in aqueous poly(vinyl alcohol) systems at different temperatures.

Percent composition of PVOH (w/v)	Free energy change of activation ( $\text{kJ mol}^{-1}$ ) at temperatures ( $^\circ\text{C}$ )				
	25	30	35	40	45
0.0	8.764	9.404	9.854	10.24	10.41
0.1	9.358	9.649	10.05	10.39	10.58
0.3	10.16	10.54	10.87	11.18	11.48
0.5	10.55	10.79	11.08	11.38	11.67
0.7	10.78	11.05	11.37	11.55	11.90
0.9	11.24	11.40	11.74	12.03	12.34

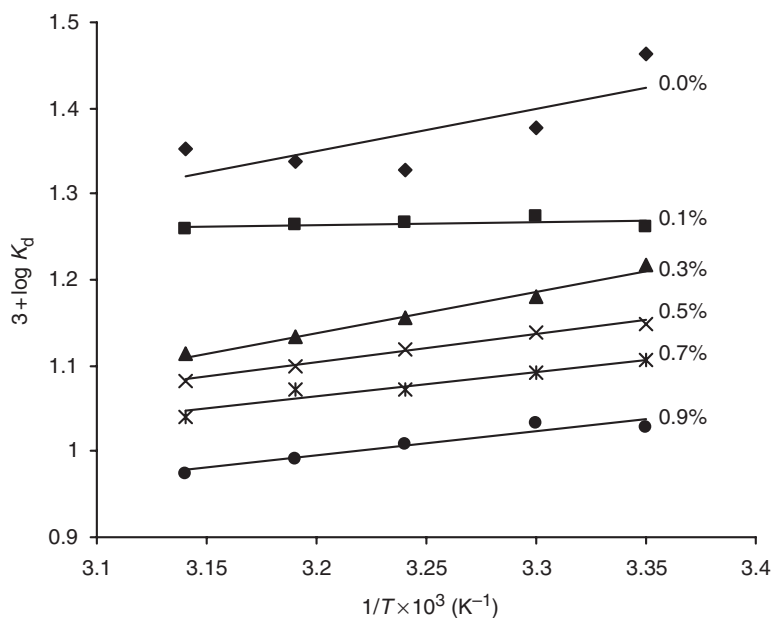


Figure 3. Enthalpy change of activation ( $\Delta H^*$ )  $8 \times 10^{-3}$  ( $\text{mol dm}^{-3}$ )  $\text{ZnSO}_4 \cdot 7\text{H}_2\text{O}$  in aqueous poly(vinyl alcohol).



Table 8. Enthalpy change of activation ( $\delta H^*$ ) of  $8 \times 10^{-3}$  (mol dm $^{-3}$ ) ZnSO $_4 \cdot 7H_2O$  in aqueous poly(vinyl alcohol) systems at different temperatures.

Enthalpy change of activation (kJ mol $^{-1}$ ) in aqueous PVOH (w/v) (%)					
0.0	0.1	0.3	0.5	0.7	0.9
0.830	0.620	0.484	0.326	0.290	0.287

Table 9. Entropy change of activation ( $\Delta S^*$ ) of  $8 \times 10^{-3}$  (mol dm $^{-3}$ ) ZnSO $_4 \cdot 7H_2O$  in aqueous poly(vinyl alcohol) systems at different temperatures.

Percent composition of PVOH (w/v)	Entropy change of activation $\times 10^2$ (kJ K $^{-1}$ mol $^{-1}$ ) at temperatures ( $^{\circ}$ C)				
	25	30	35	40	45
0.0	-2.93	-2.91	-2.99	-3.05	-3.06
0.1	-2.66	-2.82	-2.92	-3.00	-3.01
0.3	-3.24	-3.32	-3.37	-3.41	-3.95
0.5	-3.43	-3.45	-3.49	-3.53	-3.56
0.7	-3.52	-3.55	-3.59	-3.59	-3.65
0.9	-3.67	-3.67	-3.71	-3.75	-3.79

for zinc sulfate. Results indicated a decrease in the values of  $\Delta H^*$  with the increased in percent composition of PVOH ranging from 0–0.9%, also expressed endothermic nature of ionic process. The low values of  $\Delta H^*$  showed that ion-dissociation decreased and ion-association increased, in high compositions of PVOH solvent.

$$\Delta S^* = \frac{\Delta H^* - \Delta G^*}{T} \quad (7)$$

Entropy change of activation decreased with the increase of temperature (25–45 $^{\circ}$ C) and percent composition 0–0.9% (w/v) was tabulated (table 9). It was observed that randomness decreased because with the increase in percent composition an increase in the association of the solvent resulted, which caused more hindrance to the flow of the ions that resulted in a decreased randomness of zinc sulfate in aqueous PVOH.

#### 4. Conclusion

It was concluded that conductivity of zinc sulfate in aqueous poly(vinyl alcohol) solutions increased with the increase in temperature and concentration of poly(vinyl alcohol) as mobility of ions increased due to weak solvation of polymer. Increased values of Walden constant with increased concentration of poly(vinyl alcohol) also showed strong interaction of polymer with water molecules. This strong interaction decreased the dielectric constant of water, as a result, degree of dissociation decreased. Activation parameters also confirmed ionic association.

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