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Ionic Interactions of NaCl in Aqueous Polyvinyl Alcohol and Cross-Linked Polyvinyl Alcohol with Glutaraldehyde

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Electrical conductivity serves as the primary measure for assessing electrolytic interactions in solvents. Studies on conductivity in mixed solvents offer valuable insights into solute-solute and solute-solvent interactions, as well as solvent structure. Fewer studies have explored this phenomenon in mixed solvent systems. Therefore, the current study aims to demonstrate how the addition of a cross-linking agent impacts solvent system properties through conductivity analysis. Monovalent electrolyte NaCl blend with polyvinyl alcohol as polymer in the presence of cross linking agent glutaraldehyde were prepared using solution casting technique in the temperature range of 303–318K. The conductivity of solution of NaCl were measured to evaluate limiting molar conductance (Λ°_m), degree of dissociation (α), dissociation constant (K_d), walden product, and energy of activation (E_a) for transport process as a function of concentration, solvent composition and temperature. The behavior of these parameters suggests strong ion-ion interactions in solvents. These measurements had been used to study the activation parameters for association of molar concentration of NaCl in aqueous polymer and cross-linked polymer of varying proportion. The different activation parameters such as energy of activation (E_a), enthalpy of activation (ΔH^*), entropy of activation (ΔS^*) and the Gibbs free energy of activation (ΔG^*) for NaCl were estimated and compared the result of polymeric solvent system within temperature range of 303–318K.

Keywords: Conductivity, Cross linking, Molar conductance, Thermodynamic parameters, Walden product

Introduction

The nature of aqueous solutions of a solute indicates its interaction with the hydrogen-bonded structure of water. This also applies for aqueous solutions of polymers.[1] The molecular structure of solvent is affected by the ion-solvent interaction in a solution. The interesting properties of polymer has enhanced its commercial applications which led to discover their chemical structure and behaviour with various solvents.[2] Polyvinyl Alcohol (PVA) is a polyhydroxy hydrophilic polymer which is biodegradable in nature. The characteristics of PVA can be altered by varying conditions of synthesis and extent of its hydrolysis.[3–8] Polymer possess low conductivity, therefore different methods are adopted to enhance conductivity as polymer blending, crosslinking etc. Crosslinking is found to be more efficient and cost friendly. Cross-linking is a noteworthy stabilization process to obtain polymer (natural or synthetic) of improved properties.[9] This process leads to elognation of polymeric chain in various dimensions producing a network structure. Adding cross-links between polymers chains containing electrolytes impacts the physical characteristics of polymer including viscosity and density depending upon the degree of cross-linking and concentrations of electrolytes. Cross-linking causes increase in conductivity, reduces the viscosity and solubility of the polymer.[10] The crosslinking in PVA increases its applications in new areas of sciences.[9] The hydrophilic nature of PVA enables it to crosslink through different methods such as chemical, thermal. But commonly chemical crosslinkers are used. There are broad range of cross-linking agents available for PVA to improve its properties, such as sulfosuccinic acid, boronic acid, and glutaraldehyde. The hydroxyl group of PVA react with glutaraldehyde to form cross linked polymer through formation of acetal bonds.[11] The ion association and ion-mobility of this system are interesting subject, to investigate. Conductivity is the principal parameter used to measure the electrolytic interaction, which can explain the factors affecting the thermodynamic and kinetic stability. Liquid electrolytes possess high dielectric constants (more dissociation of ions) as low viscosity ease ion movement. Electrical conductivity of an electrolyte solution is usually improved by using

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mixed solvents instead of one component.[12] The practical importance has promoted extensive studies on the conductivity of many electrolytes of sodium salts and their dependency on salt content, solvent composition and temperature. Conductivity studies in mixed solvents provide valuable information on solute-solute and solute-solvent interactions and solvent structure. Wide studies have been made on the influence of ion association on the electrolytic conductance, but very few studies in mixed solvents are reported earlier.[13–23] The electrical conductance of nicotinium dichromate was assessed across a spectrum of compositions of water-N,N-dimethylformamide mixtures within the temperature range of 283 to 313K.[13] The ionic interaction of nicotinic acid was observed in aqueous PVOH and the degree of dissociation, the partial molar volume of nicotinic acid in the polyvinyl alcohol aqueous solution, and the B-coefficient of viscous flow were assessed.[14] Similarly, the ionic interactions of $ZnSO_4.7H_2O$ in aqueous and aqueous PVOH were studied over wide range of temperatures and concentrations of salt. The result concluded diminished ion-solvent interactions with increase in polymer content.[15] The Ionic conductivities of alkali salts (KCl and $CaCl_2$) solutions in aqueous ethanol mixtures (ranging from 0% to 50%) were measured across concentrations from 0.50×10^{-3} to 50×10^{-3} polyvinyl alcohol and aqueous polyacrylamide, at concentrations ranging from 2×10^{-3} to 10×10^{-3} $mol \cdot dm^{-3}$ and temperatures from 25 to 45°C.[16] The ionic conductivities of sodium chloride (NaCl) and potassium chloride (KCl) in aqueous polyvinyl alcohol and aqueous polyacrylamide, at concentrations ranging from 2×10^{-3} to 10×10^{-3} $mol \cdot dm^{-3}$, were measured across temperatures ranging from 298 to 318K.[17] Molar conductance of transition metal sulfates $MnSO_4$, $CoSO_4$, and $CuSO_4$ was measured in aqueous, aqueous-methanol (30% v/v), aqueous-polyvinyl alcohol (0.1%, 0.5%, and 0.9% w/v), and mixed solvent systems of aqueous-polyvinyl alcohol-methanol. The observed changes in Λ with solvent composition indicate relatively stronger polymer interactions with solvents (aqueous and methanol) compared to transition metal sulfates.[18] Conductivity measurements of potassium nitrate were conducted in aqueous and aqueous ethanol mixture at temperatures range of 303.15−313.5K, with concentrations varying from ~0.010 to ~0.10 $mol \cdot dm^{-3}$. The decrease in conductivity with increasing ethanol content is attributed to the reduced relative permittivity of the ethanol-water mixed solvent phase, facilitating the formation of ion pairs in the solution phase.[19] The impact of a crosslinking agent on the interaction between transition metal salts and polyvinyl alcohol was analyzed using conductometric. Specific conductance measurements of transition metal salts such as $CoSO_4.7H_2O$, $NiSO_4.6H_2O$, $CuSO_4.5H_2O$, and $ZnSO_4.7H_2O$ were conducted at different temperatures in aqueous polyvinyl alcohol, aqueous ethyl acetate, and mixed solvent systems of aqueous polyvinyl alcohol + borax + ethyl acetate.[20] By employing both steady-state and time-resolved spectroscopy techniques, the reinforcement of hydrogen bonding (H-bond) networks and the transition from a tetrahedral-like water network to a zigzag chain structure of alcohol were investigated with increasing alcohol concentration in ethanol-water and tertiary butanol (TBA) – water mixtures.[21]

Conductivities of ammonium formate, ammonium benzoate, sodium formate, and sodium benzoate in aqueous alcohol mixtures (methanol, ethanol, glycerol)) were measured at temperatures ranging from 293 to 308K.[22] Conductivities of tap water, underground water, sewage, and canal water were computed and investigated for temperature variations from 40 to 70°C. Additionally, electrical conductivity of different water sources was compared with that of a typical NaCl electrolyte solution at concentrations ranging from 2.5 to 20%.[23]

The purpose of the current work is to show how electrolytic interactions affects the properties of solvent systems by adding cross-linking agent using conductivity data.

Experimental Section

Washed, dried glasswares of Pyrex “A” grade quality were used throughout the experiment. Sodium chloride, polyvinyl alcohol and glutaraldehyde of E. Merck quality were used. De-ionized water of 0.6 $\mu S \cdot cm^{-1}$ electrical conductivity was used as a solvent. All solutions were prepared in de-ionized water.

The conductivities of the solutions were measured by digital conductivity meter of Jenway-4510 (least count of 0.01 $mS \cdot cm^{-1}$). Ostwald viscometer was used to determine the viscosities of solvents. Thermostatic water bath (YCW-0.1, Taiwan R.O.C.) was used to maintain the temperature within ±0.01K. The mass of solids were determined using analytical balance (Sartorius, Germany (least count of ±0.001 g).

Stock solution of 1% PVA was prepared by dissolving 1g of PVA in approximately 80 mL of warm deionized water with continuous stirring and heating at about 80°C. After all solids dissolve the volume of the solution was made up to 100 mL with deionized water. The dilutions of 0.1 and 0.3 % w/v of PVA were made from the 1% PVA stock solution.

Stock of 1% v/v of Glu was prepared by taking 4 mL of 50% Glu having density 1.13 g·mL^{-1} and made up to 100 mL. Dilutions of 0.1% and 0.3% were prepared from the stock solution

The blend of 0.1 PVA and 0.1% Glu was prepared by taking equal volume of 1% of both solutions with constant stirring.

Stock solution of 0.1 mol·dm^{-3} NaCl was prepared by adding calculated amount of NaCl in 1% PVA and 1% PVA + 1% Glu solutions respectively. The electrolyte concentrations ranges from 0.001 to 0.01 mol·dm^{-3} were prepared from stocks in respective solvent. Conductivity of solutions was measured at temperature ranges from 303–318K with difference of 5K.

Results and Discussion

Specific conductance of different concentrations of NaCl ranging from 1 × 10^{-3} to 1 × 10^{-2} mol·dm^{-3} was measured in aqueous, aqueous PVA (0.1 and 0.3%w/v) and cross-linked polymer (0.1 and 0.3%) at various temperatures from 303–318K. The plots of specific conductance as a function of solvent composition, salt concentration and temperature are shown in Figs 1–3 respectively. The rise in the values of specific conductance was observed as the concentration of NaCl and temperature was increased.

The significant higher values of specific conductance of NaCl was observed in aqueous medium as the water is polar solvent, having higher dielectric constant favors more dissociation of ions which resulted in greater conductance values. The values of specific conductance increase with the increase in concentration of aqueous polymer and cross-linked polymer (0.3% > 0.1%). The rise in values is attributed to the rise in number of ions per unit area of conductor. While in aqueous polymer and cross-linked polymer, the specific conductance follows the order:

0.3% Aqueous PVA + 0.3% Aqueous Glu > 0.1% Aqueous PVA + 0.1% Aqueous Glu > 0.3% Aqueous PVA > 0.1% Aqueous PVA

The measured values of specific conductance were used to calculate molar conductance using the relation as given in Eq. 1:

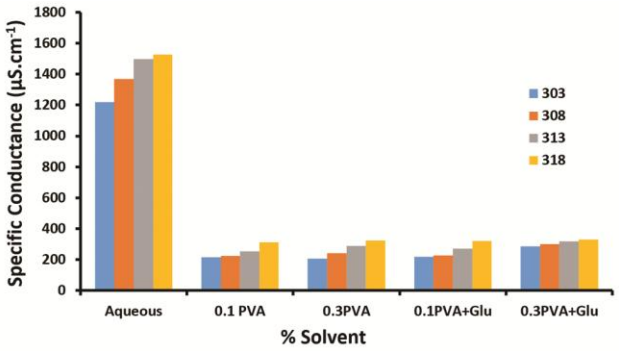


Fig. 1 — Plot of specific conductance of 0.001 mol·dm^{-3} mol·dm^{-3} NaCl in aqueous, aqueous PVA and aqueous PVA + Glu at different temperatures

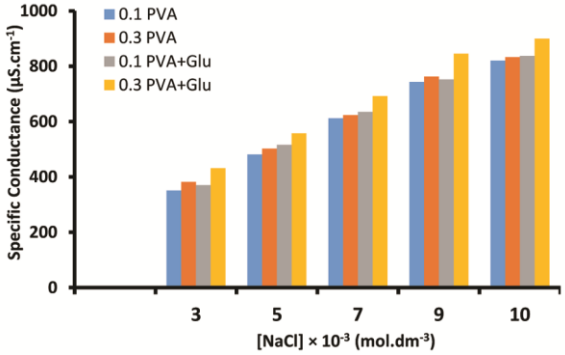


Fig. 2 — Plot of specific conductance against different concentration of NaCl in aqueous PVA and aqueous PVA + aqueous Glu at 303 K

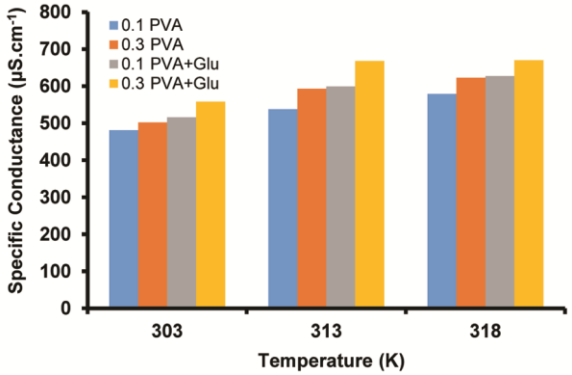


Fig. 3 — Plot of specific conductance against different temperatures in aqueous PVA and aqueous PVA + Glu at [NaCl] = 0.005 mol·dm^{-3}

$$\Lambda_m = \frac{K \times 1000}{C} \quad \ldots (1)$$

where, Λ_m is the molar conductance, K is the specific conductance and C is the molar concentration of electrolyte. The values of molar conductance are tabulated in Table 1.

The increase in molar conductance with increase in temperature was observed which indicates the

Table 1 — Molar conductance (Λ_m) of NaCl in aqueous PVA and aqueous PVA+Glu at different temperatures

[NaCl] $\times10^{-3}$ (mol·dm^{-3})	Molar Conductance Λ_m (S·cm^{-2}·mol^{-1}) at Temperatures (K)			
	303	308	313	318
	0.1 g·dL^{-1} Aqueous PVA			
3	117.0	119.3	126.0	134.0
5	96.20	101.0	107.6	115.8
7	87.43	93.14	100.0	106.8
9	82.55	87.44	98.22	103.8
10	82.00	88.00	95.70	106.1
	0.3 g·dL^{-1} Aqueous PVA			
3	127.3	135.0	146.3	153.0
5	100.4	111.0	118.6	124.6
7	89.00	97.00	106.1	114.0
9	84.77	94.00	99.44	103.4
10	83.30	92.40	99.30	102.9
	0.1 g·dL^{-1} Aqueous PVA + 0.1 g·dL^{-1} Aqueous GLU			
3	123.3	128.0	141.3	147.3
5	103.2	109.0	119.8	125.4
7	90.71	92.57	106.4	114.4
9	83.67	92.00	100.3	103.1
10	83.70	93.40	99.90	103.9
	0.3 g·dL^{-1} Aqueous PVA+0.3 g·dL^{-1} Aqueous GLU			
3	144.0	155.3	171.0	175.6
5	111.6	118.4	133.6	134.0
7	98.86	104.6	117.7	120.2
9	93.89	98.11	111.3	119.5
10	90.00	94.00	102.0	111.0

relatively higher movement of ions of electrolytes. The rise in temperature lowers the viscosity of the solvent which enables free movement of ions towards their respective electrodes.[17]

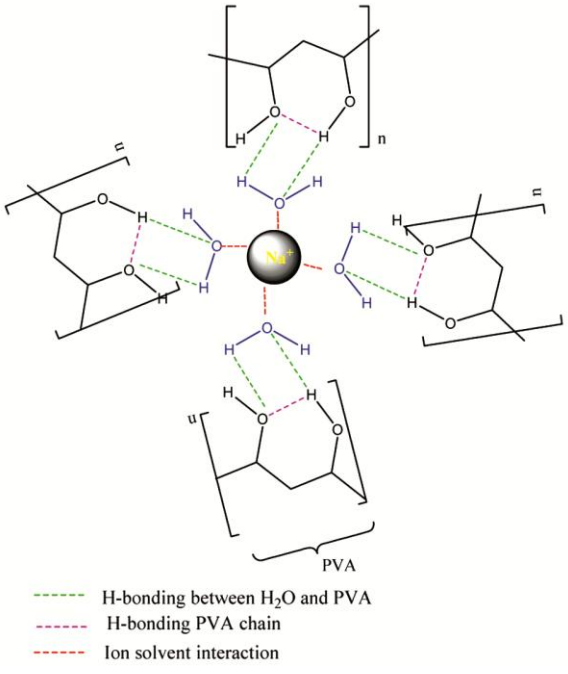
Molar conductance decreases with the increase in concentration of electrolyte (NaCl). Interionic forces govern the motion of ions within a solution. In concentrated solution of electrolyte interionic forces are greater which retard the flow of ions, hence resulting in lowering of molar conductance.

The molar conductivities of NaCl were found to increase with the gain in polymer content in the solvent. The trend of molar conductance in aqueous polymer and cross-linked polymer is shown as:

0.3% Aqueous PVA + 0.3% Aqueous Glu > 0.1% Aqueous PVA+0.1% Aqueous Glu > 0.3% Aqueous PVA > 0.1% Aqueous PVA.

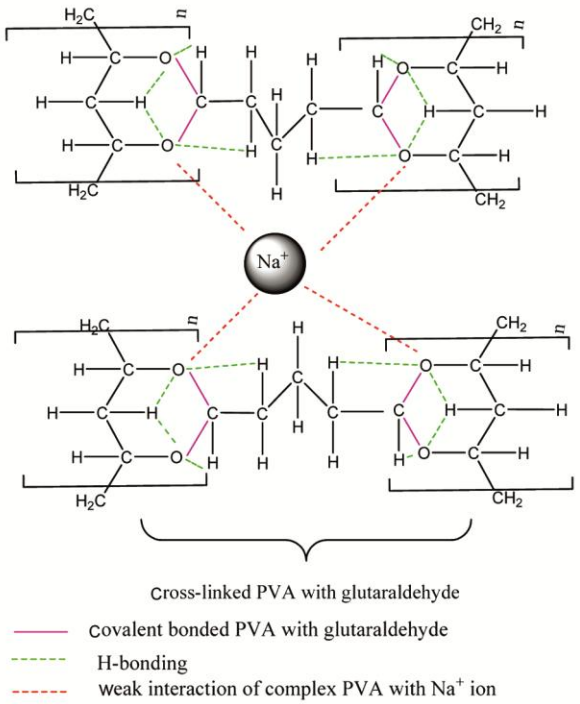
In aqueous polymer the PVA interaction with water increases through H-bonding (Scheme 1), as a result solvation of ion with aqueous PVA decreases and ions becomes free to move in solution. Hence, mobility of ions becomes greater with the rise in concentration of PVA.

Molar conductance in cross-linked polymer was observed higher than the aqueous PVA as the cross-linking agent glutaraldehyde forms covalent bond



Scheme 1 — Solvation of Na^+ with aqueous PVA

with PVA chains. The intramolecular H-bonding between the cross-linked polymers also formed (Scheme 2). Due to intramolecular H-bonding between cross-linked polymer weak interaction occurs



Scheme 2 — Solvation of Na^+ with cross linked PVA with glutaraldehyde

between Na^+ ion and cross-linked polymer. This causes the free movement of electrolyte. The number of hydroxyl group reduces, which causes weak hydrogen bonding between cross-linked PVA and water than in PVA and water.Therefore the interaction of water with cross-linked polymer decreases due to which aqueous medium becomes available to ions and concentration of electrolyte increases in water hence causing increase in molar conductance. The FTIR spectra of crosslinked polymer with electrolyte (Fig. 4) confirmed the interaction of electrolyte with crosslinked polymer shown in scheme 2.

The values of molar conductance in aqueous PVA and aqueous PVA polymer has the following trend:

0.3% Aqueous PVA + Glu > 0.1% Aqueous PVA + Glu > 0.3% Aqueous PVA > 0.1% Aqueous PVA

Molar conductance at infinite dilution (Λ_m°) is a measure of ion-solvent interactions. It is calculated from the relation:

$$\Lambda_m = \Lambda_m^\circ - (A + B\Lambda_m^\circ)C^{1/2} \quad \ldots (2)$$

where, Λ_m° and C is molar conductance, molar conductance at infinite dilution, and concentration of electrolyte. While A and B in the Eq. (2) are constants which depend on the nature of solvent. Λ_m° depends on solvation of ions and dielectric constant of the

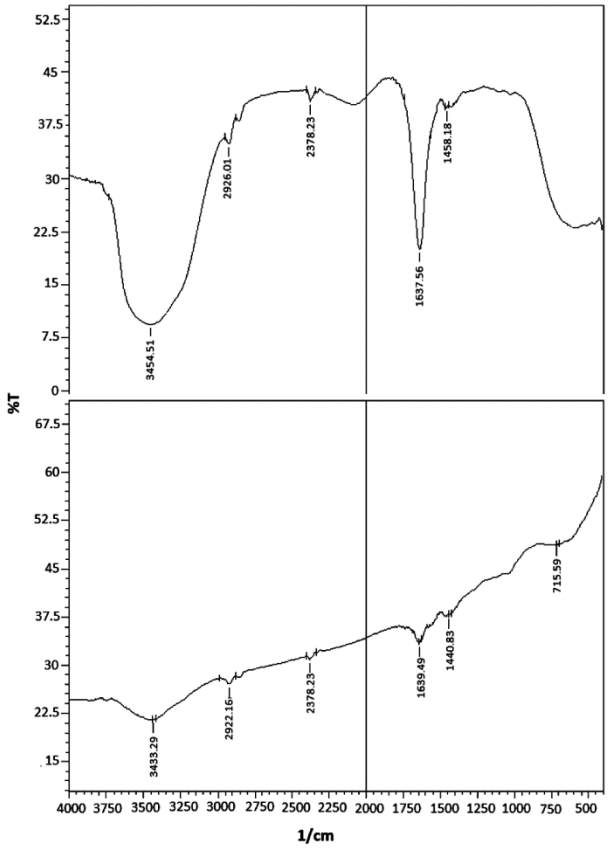


Fig. 4 — FTIR spectra of a) aqueous PVA and b) elctrolyte in aqueous PVA + Glu

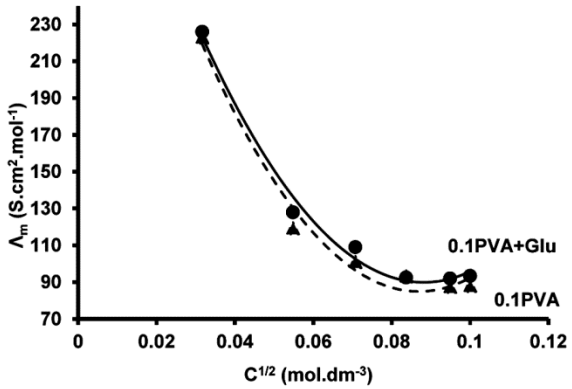


Fig. 5 — Plot of $C^{1/2}$ against molar conductance (Λ_m) of NaCl in aqueous PVA and aqueous PVA + Glu at 308 K

solvent. The intercept of linear plot of Λ_m and $C^{1/2}$ (Fig. 5) gives the values of Λ_m° as tabulated in Table 2.

Molar conductance at infinite dilution are observed to increase as the content of PVA increases indicating weak solute-solute interactions at infinite dilution as there are more solvent molecules around the ions and ions are far apart. Therefore the movement of ions are

Table 2 — Limiting Molar Conductance $\Lambda°_m$($S·cm^{-2}·mol^{-1}$) of NaCl in aqueous PVA and aqueous PVA + Glu at different temperatures (K)

Solvents ($g·dL^{-1}$)	Limiting Molar Conductance $\Lambda°_m$ ($S·cm^{-2}·mol^{-1}$) at Temperatures (K)			
	303	308	313	318
0.1 Aqueous PVA	211.00	249.21	279.74	339.00
0.3 Aqueous PVA	240.74	278.32	327.41	364.68
0.1 Aqueous PVA + 0.1 Aqueous Glu	250.05	255.39	304.80	358.61
0.3 Aqueous PVA + 0.3 Aqueous Glu	303.20	315.84	356.02	349.30

restricted by its interaction with solvent molecules surrounding them. The values of Λ_m° for aqueous PVA + Glu are greater than aqueous PVA as weak interaction of Na^+ with cross-linked polymer as compared to PVA, so electrolyte solvated more with water hence can easily flow causing increase in Λ_m°. When cross-linked polymer solvate Na^+, steric hindrance due to bulky molecules occurs. The steric hindrance and intramolecular H-bonding causes less interactions of cross-linked polymer with Na^+. Therefore, ions are less solvated. Consequently, ion-ion interactions increased in the cross-linked polymer as compared to ion-solvent interactions.

The degree of dissociation (α) explains dissociation of electrolyte ion and can be calculated by Eq. (3)

$$\propto = {}^{\Lambda_m}/_{\Lambda_m^\circ} \quad \text{... (3)}$$

The values of degree of dissociation as reported in Table 3 are found to decrease with increase in temperature. The lowering value of degree of dissociation with rise in temperature indicates ion-pair formation at higher temperature.

It reduced as the PVA content was increased owing to the polarity of solvent decreases causing decrease in dissociation of ions. The trend in aq PVA and cross-linked PVA with glutarladehyde is as follow:

0.1 % Aqueous PVA > 0.3 % Aqueous PVA > 0.1 % Aqueous PVA + 0.1 % Aqueous Glu > 0.3 % Aqueous PVA + 0.3 % Aqueous Glu

The degree of dissociation was lower in cross-linked PVA as compared to aqueous PVA. This shows that solvent interactions with Na^+ ion are weaker than polymer-water interactions i.e. weak ion-solvent interactions than solvent-solvent interactions. The high solvent-solvent interaction results in association instead of dissociation of Na^+ ions. The dissociation constant is determined by Eq. 4:

Table 3 — Degree of dissociation (α) and dissociation constant (K_d) of 7×10^{-3} $mol·dm^{-3}$ NaCl in aqueous PVA and aqueous PVA+Glu at different temperatures (K)

Solvents ($g·dL^{-1}$)	Degree of dissociation α	Dissociation Constant $K_d \times 10^3$($mol·dm^{-3}$)
	308K	
0.1 Aqueous PVA	0.373	1.55
0.3 Aqueous PVA	0.348	1.30
0.1 Aqueous PVA + 0.1 Aqueous Glu	0.362	1.44
0.3 Aqueous PVA + 0.3 Aqueous Glu	0.331	1.14
	318K	
0.1 Aqueous PVA	0.345	1.01
0.3 Aqueous PVA	0.312	1.00
0.1 Aqueous PVA + 0.1 Aqueous Glu	0.319	1.05
0.3 Aqueous PVA + 0.3 Aqueous Glu	0.344	1.26

$$K_d = \frac{\propto^2 C}{1-\propto} \quad \text{... (4)}$$

where, K_d is the dissociation constant.

Values of dissociation constant as tabulated in Table 3 follows decreasing trend with increase in temperature and solvent composition. The values of dissociation constant are higher in PVA than cross-linked PVA. This shows that after crosslinking the association of ions increased and dissociation decreased. The increase in temperature also favors ion-association phenomenon.

Walden product provides information of ion-solvent interaction in the solution. The degree of solvation and size of solvation shell are determined by the nature of solvent. The greater the solvation of ion, lower will be the walden product. It is calculated from the expression:

$$\text{walden Product} = \Lambda_m^\circ \, \eta^\circ \quad \text{... (5)}$$

where, $\eta°$ is the viscosity of the solvent.

Walden product increased with the increase in concentration of polymer. At lower concentration of polymer solvation of ions is favored, but with the rise in concentration of polymer, solvation decreased causing increase in walden product.[20] Higher values of walden product observed (Table 4) in cross-linked polymer indicate weak solvation (ion-solvent interactions). On crosslinking glutaraldehyde is covalently bonded with PVA chain. The large bulky molecule of cross-linked polymer has less available hydroxyl group to H-bond with water. And steric hindrance of cross-linked polymer reduces solvation

Table 4 — Walden product of solvent in aqueous PVA and aqueous PVA + Glu at different temperatures (K)

Solvents $g \cdot dL^{-1}$	Waldon product × 10^3 $\Lambda^\circ_m\eta^\circ$ ($S.cm^2 \cdot mol^{-1}$.poise) at different temperatures (K)			
	303K	308K	313K	318K
0.1 Aqueous PVA	2.29	2.10	2.04	2.03
0.3 Aqueous PVA	2.51	2.33	2.29	2.11
0.1 Aqueous PVA+ GLU	2.27	2.11	2.09	2.04
0.3 Aqueous PVA+ GLU	3.18	2.61	2.43	2.19

of ions resulting in free movement of ions. This increased the walden product in cross-linked polymer.

The walden product depends on molar conductance at infinite dilution (Λ°_m) and viscosity of solvents. Walden product increased with the increase in concentration of aqueous PVA, this was due to increase in both conductance and viscosity with the increase in solvent concentration. The Walden product in cross linked polymer was greater as compared to that in aqueous PVA because of higher $\mathbf{\Lambda^\circ_m}$ values in cross linked polymer. Walden product gave an idea about strong and weak solvation of ions by solvent molecules, the lower the value of Walden product higher the ion solvation. Thus ion solvation was favored at low concentration of PVA and decreased with increase in concentration of aqueous PVA. In cross linked polymer, higher values of Λ°_m indicating weakest solvation of Na^+ ions with cross linked polymer.

It decreased with the elevation in temperature, due to lowering of viscosity of solvent with rise in temperature. This outweighs the effect of increase in Λ°_m values with rise in temperature.

The energy of activation E_a was calculated by Arrhenius relation

$$\log \Lambda^\circ_m = \log A - \frac{E_a}{2.303RT} \quad \text{... (6)}$$

where, R is gas constant, A is the frequency factor and T is temperature in Kelvin. The representative plot of log Λ°_m and 1/T is shown in Fig. 6 and the values of energy of activation are reported in Table 5. The decrease trend in E_a was observed with rise in concentration of polymer, which indicates lower rate of flow of ions in dilute solution as compared to concentrated solution.

Thermodynamic parameters are fundamental properties used to describe the behavior of systems undergoing physical or chemical transformations. These parameters provide insights into the energetics and spontaneity of processes, aiding in the prediction and understanding of system behavior. Key thermodynamic parameters include enthapy change of

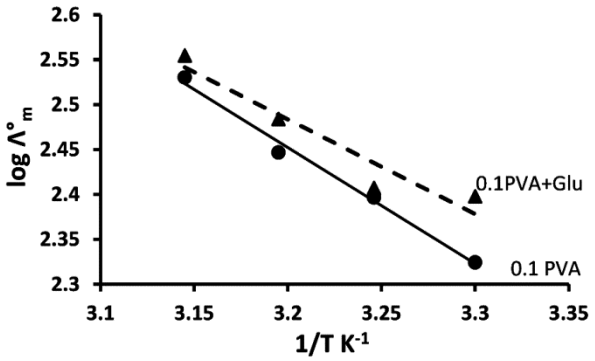


Fig. 6 — Plot of log molar conductance at infinite dilution (log Λ°_m) against 1/K in aqueous PVA and aqueous PVA+Glu

activation (ΔH^*), entropy of activation (ΔS^*) , free energy change of activation (ΔG^*) and their values are reported in Table 5.

The enthapy change of activation ΔH^* was determined by the relation as given in Eq. 7.

$$\Delta H^* = E_a - RT \quad \text{... (7)}$$

Enthalpy change decrease with the increase in polymer content, which show ion association increased and ion-dissociation decreased at high concentration of PVA. Higher value of enthalpy change is observed in PVA than in cross-linked polymer, indicating crosslinking favors more ion-association. The positive value of enthalpy change indicae ion-ion interactions in solution.

The entropy of activation was evaluated by the Eq. 8.

$$\Delta S^* = \frac{(\Delta H^* - \Delta G^*)}{T} \quad \text{... (8)}$$

A decrease in entropy change was observed with the rise in polymer content in solvent owing to increase in viscosity i.e. association of solvent which restrict free movement of ions causing decrease in randomness of ions in aqueous PVA. The disordered ions disturbed the structure of solvent causing change in entropy. The high values of entropy change observed in PVA than cross-linked PVA shows NaCl ions disturbed the structure of PVA more than the

Table 5 — Thermodynamic parameters of NaCl in aqueous PVA and aqueous PVA+Glu at different temperatures

Temperature K	Energy of Activation E_a* (kJ·mol)	Enthalpy change of activation ΔH*(kJ·mol)	Entropy change of activation ΔS*(kJ·mol^{-1}·K^{-1})	Free energy change of activation ΔG*(kJ·mol)
		0.1 g·dL^{-1} Aq-PVA		
303	24.7687	22.249	22.195	16.300
308		22.208	22.154	16.569
313		22.166	22.112	16.838
318		22.124	22.071	17.107
		0.3 g·dL^{-1} Aq- PVA		
303	20.1772	20.189	20.134	16.743
308		20.147	20.092	17.020
313		20.106	20.050	16.743
318		20.064	20.000	17.296
		0.1 g·dL^{-1} Aq- PVA + Glu		
303	22.7085	17.658	17.603	16.486
308		17.616	17.562	16.758
313		17.574	17.520	17.030
318		17.533	17.479	17.302
		0.3 g·dL^{-1} Aq- PVA + Glu		
303	7.2854	5.036	5.249	17.074
308		5.264	5.208	17.356
313		5.223	5.166	17.638
318		5.181	5.125	17.919

cross-linked polymer. i.e the structure of cross linked PVA was highly ordered and well associated. The decrease in entropy change was also observed with the rise in tempearature in both PVA and crosslinked PVA which also confirms ions association at high temperatures.

The values of free energy change of activation (ΔG^*) were evaluated by the following relation:

$$\Delta G^* = -2.303RT \log K_d \quad \ldots (9)$$

Gibbs free energy gives information about spontaneity of reaction. The increase in ΔG^* values with the increase in concentration of aqueous PVA and temperature, confirmed the association of ions with the solvent system at higher concentrations. The values of ΔG^* for Na^+ ion was comparatively higher in cross linked PVA because of comparatively greater association of Na^+ ion in cross linked complex.

The positive values of Gibbs free energy indicate dissociation process is non-spontaneous and endothermic process.[17]

Conclusions

The crosslinking of polymer changed the physical properties of polymer due to increase in its intermolecular H-bonding. Altering the composition of polymer through cross-linking renders them viable for facilitating the transport of ionic species. The increment of molar conductance in cross-linked polymer than aqueous polymer indicated weak ion solvation. The reduce values of degree of dissociation and dissociation constant of Na^+ in cross-linked polymer as compared to aqueous polymer solvent also show stronger ion-ion interaction than solvent-solvent interaction. The low values of dissociation constant in cross-linked polymer show weak ion-solvation between Na^+ ion and cross-linked polymer. This weak ion-solvent interactions enables the cross-linked polymer to liberate ions which makes them applicable in medication, for drug delivery systems. The presence of interactions within cross-linked units, particularly involving ionic moieties, make them suitable as ion storage membranes, ion sensors, actuators, ion diffusion membranes in batteries and fuel cells and the removal of excess ions in waste treatment processes.

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