



# Ionic Interaction of Transition Metal Salts with Polyvinyl Alcohol-Borax-Ethyl Acetate Mixtures

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## ABSTRACT

The effect of crosslinking agent (borax) on the interaction of transition metal salt with polyvinyl alcohol was analyzed in liquid and solid form by conductometric and FTIR spectroscopy. The specific conductance of transition metal salts i.e.,  $\text{CoSO}_4 \cdot 7\text{H}_2\text{O}$ ,  $\text{NiSO}_4 \cdot 6\text{H}_2\text{O}$ ,  $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$  and  $\text{ZnSO}_4 \cdot 7\text{H}_2\text{O}$  at different temperatures were measured, in aqueous polyvinyl alcohol, in aqueous ethyl acetate, and in mixed solvent systems of aqueous polyvinyl alcohol + borax + ethyl acetate. The experimental data was used to evaluate the interactions between transition metal salt and polymeric solvent system in the presence of crosslinking agent (borax) by conductometric method and FTIR analysis. It was observed that the values of  $\Lambda_m^\circ$  in mixed solvent systems were greater than in aqueous polyvinyl alcohol and aqueous ethyl acetate. It was also investigated through conductometric data that the association of transition metal salt with polymeric solvent was favorable in the presence of crosslinking agent. The association of crosslinking complexes of transition metal salts with polyvinyl alcohol in the presence of crosslinking agent was found to be in the order of  $\text{Co (II)} > \text{Cu (II)} > \text{Ni (II)} \approx \text{Zn (II)}$  which was further confirmed by FTIR analysis of complexes through KBr sampling technique.

**Key words:** Polyvinyl alcohol, Borax, Crosslinking, Conductivity, Transition metal salts.

## 1. INTRODUCTION

The study of conducting polymers and the advancement in the conduction behavior of polymers is a subject of great interest from fundamental point of view such as in analyzing various types of interactions offered by polymer substrate in the absence and presence of conducting entity. For application purpose, approach towards the enhancement of conductivity leads to the utilization of conducting polymeric material in different aspects such as a material of electrode, separator in electrochemical and fuel cells e.t.c. Polymers are usually preferred for the processing and fabrication of devices because of flexibility, stability, strength, light-weighting and biodegradability. One of the methods of improving the processability of polymers is the crosslinking of polymer which is a process of chemically joining two or more molecules by covalent bonding. Different experiments were performed [1-5] in which cross-linking agents were used to enhance the various physical properties of polymers such as thermal, mechanical, flame retardant, tensile strength, viscoelasticity. Various methods were adopted [6-7] in order to increase the conductivity of polymer electrolytes by either increasing the amorphous contents of the system or by increasing the chain mobility of the polymer electrolyte. Plasticization of polymers after crosslinking enhances the electrical conductivity of the polymers electrolytes were also reported [8]. Electrical conductance also varies depending upon the nature of crosslinking agent [9].

Polyvinyl alcohol (PVOH) forms a cage structure on treatment with crosslinking agent such as borax [10]. In certain researches [11-19] polymers are crosslinked using compounds of boron where boron acts as a central metal. The confirmation of crosslinked product can be done by observing the shifts in peaks in crosslinked product spectra and the pure polymer

spectra through XRD and FTIR technique e.t.c. While the characterization of crosslinked product can be done by studying the peaks shifting in the spectra of crosslinked product. Change in conductivity can be used to evaluate the various ionic interactions [20-25] which lead to the confirmation of formation of crosslinked product.

Present research concerns with the effect of crosslinking agent (borax) on the interactions of transition metal salts in PVOH in liquid and solid form by conductance and FTIR method. For the study of ionic interactions of transition metal salts in polyvinyl alcohol + borax (crosslinking agent) crystallization occur. Therefore ethyl acetate was added to keep the solution in liquid state. The behavior of interaction of crosslinking complexes was studied by FTIR technique. Thermodynamics parameters also confirmed the mode of interaction in the presence of solvent systems by determining the thermodynamic nature, spontaneity and order of thermodynamic process.

## 2. EXPERIMENTAL

All the glassware of pyrex A grade quality were used. Double distilled water having conductivity  $0.06 \mu\text{S}\cdot\text{cm}^{-1}$  was used for experimental purpose. PVOH E. Merck, (< 98 % hydrolyzed), having average molecular weight 65075.11 Da. Ethyl acetate Scharlau, (99 % pure), Sodium tetraborate decahydrate borax ( $\text{Na}_2\text{B}_4\text{O}_7 \cdot 10\text{H}_2\text{O}$ ) E. Merck, 98 % pure was used as crosslinking agent. Cobalt Sulphate heptahydrate ( $\text{CoSO}_4 \cdot 7\text{H}_2\text{O}$ ), Nickel Sulphate hexahydrate ( $\text{NiSO}_4 \cdot 6\text{H}_2\text{O}$ ), Copper Sulphate pentahydrate ( $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ ) and Zinc Sulphate heptahydrate ( $\text{ZnSO}_4 \cdot 7\text{H}_2\text{O}$ ) E. Merck, (99 % pure), were used without further purification. Stock solution of PVOH was prepared by dissolving required amount % of PVOH in double distilled water at  $(353 \pm 0.1 \text{ K})$ .



Different compositions 0.1, 0.5 and 0.9 g.dL<sup>-1</sup> of aqueous PVOH systems was prepared from the stock solution. Stock solution of 5 g.dL<sup>-1</sup> aqueous ethyl acetate was prepared by diluting pure ethyl acetate. Mixed solvent system (0.1 g.dL<sup>-1</sup> aqueous PVOH + 0.01 mol.dm<sup>-3</sup> borax + 5 g.dL<sup>-1</sup> aqueous ethyl acetate) was prepared by adding aqueous ethyl acetate in aqueous PVOH + borax mixture prepared by dissolving required amount of borax in aqueous PVOH. The stock solutions of transition metal salts were prepared by dissolving the required amount in aqueous polyvinyl alcohol, in aqueous ethyl acetate, and in mixed solvent systems of aqueous polyvinyl alcohol + borax + ethyl acetate. Different compositions of transition metal salts ( $2 \times 10^{-3}$ -  $2 \times 10^{-2}$  mol.dm<sup>-3</sup>  $\sigma \pm 7.0 \times 10^{-5}$ ) were prepared by diluting the stock solutions.

Specific conductance for different concentrations of transition metal salts in aqueous polyvinyl alcohol, in aqueous ethyl acetate, and in mixed solvent systems of aqueous polyvinyl alcohol + borax + ethyl acetate, were measured at different temperatures 298 - 318 K with (5 K intervals  $\pm 0.1$  K) using a digital conductometer (Jenway, 4510 conductivity meter) having (accuracy  $\pm 0.5$  %) was connected with electrode having cell constant (1.0 cm<sup>-1</sup>).

Crosslinking complexes of polyvinyl alcohol, with sulphates of Co (II), Ni (II), Cu (II) and Zn (II) using borax as a crosslinking

agent prepared in a total volume of  $50 \pm 0.1$  cm<sup>3</sup>. The crosslinking cage of PVOH-borax was prepared in 40 cm<sup>3</sup> by dissolving calculated amount of borax in  $40 \pm 0.1$  cm<sup>3</sup> of 0.1 g.dL<sup>-1</sup> PVOH, using magnetic stirrer such that total volume contains 0.02 mol.dm<sup>-3</sup> of borax. In  $10 \pm 0.1$  cm<sup>3</sup> of 0.1 g.dL<sup>-1</sup> PVOH calculated amount of transition metal salt were dissolved such that total volume contain 0.02 mol.dm<sup>-3</sup> concentration. On pouring the second solution into first solution precipitates were obtained. These precipitates were allowed to settle down and filtered using filter paper. The crystals were than dried in oven.

FTIR spectroscopy studies of solid samples were carried out using solid sampling KBr technique by FTIR Spectrometer (Shimadzu, IR Prestige-21).

### 3. RESULTS AND DISCUSSIONS

Specific conductance ( $K$ ) of different concentrations of transition metal salts  $2 \times 10^{-3}$ -  $2 \times 10^{-2}$  mol dm<sup>-3</sup> was measured in aqueous polyvinyl alcohol, in aqueous ethyl acetate, and in mixed solvent systems of aqueous polyvinyl alcohol + borax + ethyl acetate at different temperatures from 298 - 318 K with 5 K intervals. The observations for specific conductance of transition metal salt in particular solvents are reported in table (1).

**Table 1: Specific conductance  $K$  (mS.cm<sup>-1</sup>) of transition metal salts in different solvent systems at different temperatures**

Solvent system (g.dL <sup>-1</sup> )	$T$ (K)				
	298	303	308	313	318
	<b>[CoSO<sub>4</sub>.7H<sub>2</sub>O] = 6.0x 10<sup>-3</sup> mol.dm<sup>-3</sup></b>				
0.1 aq-PVOH	0.756	0.797	0.848	0.893	0.963
0.5 aq-PVOH	0.779	0.830	0.890	0.949	1.019
0.9 aq-PVOH	0.833	0.876	0.941	0.981	1.040
5 aq-ethyl acetate	0.864	0.921	0.983	1.077	1.182
Mixed solvent	1.752	1.858	2.030	2.200	2.350
	<b>[NiSO<sub>4</sub>.6H<sub>2</sub>O] = 6.0x 10<sup>-3</sup> mol.dm<sup>-3</sup></b>				
0.1 aq-PVOH	0.728	0.776	0.813	0.857	0.915
0.5 aq-PVOH	0.765	0.818	0.860	0.935	0.986
0.9 aq-PVOH	0.798	0.847	0.900	0.965	1.046
5 aq-ethyl acetate	0.867	0.912	0.959	1.012	1.074
Mixed solvent	1.704	1.821	1.942	2.110	2.260
	<b>[CuSO<sub>4</sub>.5H<sub>2</sub>O] = 6.0x 10<sup>-3</sup> mol.dm<sup>-3</sup></b>				
0.1 aq-PVOH	0.708	0.747	0.785	0.843	0.892
0.5 aq-PVOH	0.742	0.784	0.831	0.891	0.964
0.9 aq-PVOH	0.769	0.801	0.855	0.906	0.974
5 aq-ethyl acetate	0.867	0.897	0.934	0.998	1.088
Mixed solvent	1.498	1.590	1.718	1.882	2.050
	<b>[ZnSO<sub>4</sub>.7H<sub>2</sub>O] = 6.0x 10<sup>-3</sup> mol.dm<sup>-3</sup></b>				
0.1 aq-PVOH	0.740	0.776	0.828	0.880	0.970
0.5 aq-PVOH	0.752	0.807	0.863	0.918	0.994
0.9 aq-PVOH	0.811	0.880	0.916	0.981	1.059
5 aq-ethyl acetate	0.894	0.958	1.007	1.076	1.172
Mixed solvent	1.711	1.814	1.931	2.080	2.240

$\sigma \pm 0.001$ - 0.003



It was observed that specific conductance increased with the increase in concentration of aqueous PVOH. In aqueous polyvinyl alcohol, aqueous ethyl acetate, and in mixed solvent systems of aqueous polyvinyl alcohol + borax + ethyl acetate solvent systems, the values of specific conductance were found to be in order  $0.1 \text{ g.dL}^{-1}$  aqueous PVOH <  $0.5 \text{ g.dL}^{-1}$  aqueous-PVOH <  $0.9 \text{ g.dL}^{-1}$  aqueous PVOH <  $5 \text{ g.dL}^{-1}$  aqueous ethyl acetate < mixed solvent system. The specific conductance increased with the increase in temperature. The increment in specific conductance with respect to increase in temperature in mixed solvent system was greater as compared to that in binary

solvent systems. Molar conductance ( $\Lambda_m$ ) was calculated from specific conductance by using relation of equation (1).

$$\Lambda_m = 1000K / C \dots\dots\dots (1)$$

where,  $\Lambda_m$  is the molar conductance,  $K$  is the specific conductance of transition metal salts and  $C$  is the concentration of the transition metal salt in  $\text{mol dm}^{-3}$ . The results of  $\Lambda_m$  are tabulated in table 2.

**Table 2: Molar conductance  $\Lambda_m$  ( $\text{S.cm}^2.\text{mol}^{-1}$ ) of transition metal salts in different solvent systems at different temperatures**

Solvent system ( $\text{g.dL}^{-1}$ )	$T$ (K)				
	298	303	308	313	318
<b>[CoSO<sub>4</sub>.7H<sub>2</sub>O] = 6.0x 10<sup>-3</sup> mol.dm<sup>-3</sup></b>					
0.1 aq-PVOH	126.0	132.8	141.3	148.8	160.2
0.5 aq-PVOH	129.8	138.3	148.3	158.1	169.8
0.9 aq-PVOH	138.8	146.0	156.8	163.5	173.3
5 aq-ethyl acetate	144.0	153.5	163.8	179.5	197.0
Mixed solvent	292.0	309.6	338.3	370.0	391.6
<b>[NiSO<sub>4</sub>.6H<sub>2</sub>O] = 6.0x 10<sup>-3</sup> mol.dm<sup>-3</sup></b>					
0.1 aq-PVOH	121.3	129.3	135.5	142.8	152.5
0.5 aq-PVOH	127.5	136.3	143.3	155.8	164.3
0.9 aq-PVOH	133.0	141.1	150.0	160.8	174.3
5 aq-ethyl acetate	144.5	152.0	159.8	168.6	179.0
Mixed solvent	294.0	303.5	323.6	351.6	376.6
<b>[CuSO<sub>4</sub>.5H<sub>2</sub>O] = 6.0x 10<sup>-3</sup> mol.dm<sup>-3</sup></b>					
0.1 aq-PVOH	118.0	124.5	130.8	140.5	148.6
0.5 aq-PVOH	123.6	130.6	138.5	148.5	160.6
0.9 aq-PVOH	128.1	133.5	142.5	151.0	162.3
5 aq-ethyl acetate	144.5	149.5	155.6	166.3	181.3
Mixed solvent	249.6	265.0	286.3	313.6	341.6
<b>[ZnSO<sub>4</sub>.7H<sub>2</sub>O] = 6.0x 10<sup>-3</sup> mol.dm<sup>-3</sup></b>					
0.1 aq-PVOH	123.3	129.3	138.0	146.6	161.6
0.5 aq-PVOH	125.3	134.5	143.8	153.0	165.6
0.9 aq-PVOH	135.1	146.6	152.6	163.5	176.5
5 aq-ethyl acetate	149.0	159.6	167.8	179.3	195.3
Mixed solvent	285.1	302.3	321.8	346.6	370.6

$\sigma \pm 0.1 - 0.5$

Molar conductance increased with the increase in concentration of aqueous PVOH because at higher concentration of aqueous PVOH, the number of electrolyte ion per unit area of a conductor was greater as compared to that at low concentration of aqueous PVOH. Thus aqueous PVOH acts as a binder for transition metal salts by decreasing the size of solvation shell [26]. The values in  $5 \text{ g.dL}^{-1}$  aqueous ethyl acetate were slightly higher than the values in  $0.1 \text{ g.dL}^{-1}$  aqueous PVOH thus  $5 \text{ g.dL}^{-1}$  aqueous ethyl acetate, makes the solvation shell smaller as compare to  $0.1 \text{ g.dL}^{-1}$  aqueous PVOH. Molar conductance values in mixed solvent system were higher as compared to the values in binary solvent system because of the higher

amphiphicity of the resulting crosslinking complexes of transition metal salts with PVOH borax mixture in aqueous ethyl acetate. It was also due to the fact that the free volume of resulting crosslinking complexes of transition metal with PVOH borax mixture in aqueous ethyl acetate was high [7]. On increasing the temperature, molar conductance increased in binary and tertiary solvent system, that was because the molecules vibrates more energetically results in increasing the free volume of solvent system thus, ion mobility and segmental mobility both were enhanced [27]. The increment in molar conductance in tertiary solvent system was greater as compared to that in binary solvent system. The rapid increase in



conductivity was due to the transition from amorphous to the elastomeric phase [6,11] which was the high conducting phase as it enhances the ion migration.

Molar conductance at infinite dilution or limiting molar conductance ( $\Lambda_m^\circ$ ) was calculated from relation equation (2).

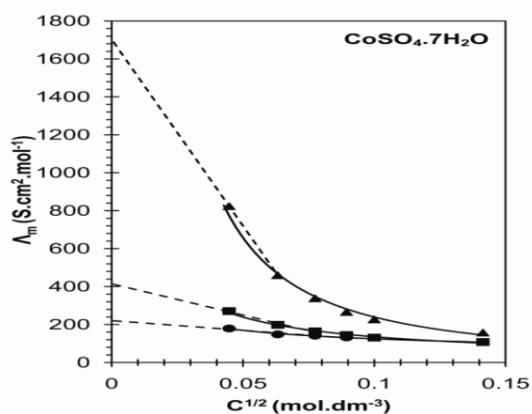
$$\Lambda_m = \Lambda_m^\circ - (A + B\Lambda_m^\circ)C^{1/2} \quad (2)$$

where,  $\Lambda_m^\circ$  was the molar conductance at infinite dilution and  $A$  and  $B$  are constants depend upon the nature of solvent. The results of  $\Lambda_m^\circ$  for transition metal salts are tabulated in table (3),

**Table 3: Molar conductance at infinite dilution  $\Lambda_m^\circ$  ( $S.cm^2.mol^{-1}$ ) of transition metal salts in different solvent system at different temperatures**

Solvent system (g.dL <sup>-1</sup> )	T (K)				
	298	303	308	313	318
[CoSO <sub>4</sub> .7H <sub>2</sub> O] = 6.0x 10 <sup>-3</sup> mol.dm <sup>-3</sup>					
0.1 aq-PVOH	188.0	206.1	220.1	230.9	243.7
0.5 aq-PVOH	231.3	242.8	266.3	288.2	312.6
0.9 aq-PVOH	277.6	299.4	322.7	351.9	377.7
5 aq-ethyl acetate	420.3	424.9	445.5	484.9	533.8
Mixed solvent	1493	1603	1702	1820	1880
[NiSO <sub>4</sub> .6H <sub>2</sub> O] = 6.0x 10 <sup>-3</sup> mol.dm <sup>-3</sup>					
0.1 aq-PVOH	183.1	197.6	207.6	227.8	241.1
0.5 aq-PVOH	219.7	237.2	242.3	254.3	282.4
0.9 aq-PVOH	284.0	304.7	328.0	364.6	392.5
5 aq-ethyl acetate	446.9	463.3	477.1	481.7	512.1
Mixed solvent	1168	1268	1366	1467	1602
[CuSO <sub>4</sub> .5H <sub>2</sub> O] = 6.0x 10 <sup>-3</sup> mol.dm <sup>-3</sup>					
0.1 aq-PVOH	180.2	186.1	192.6	207.7	220.6
0.5 aq-PVOH	211.4	226.1	235.2	250.0	268.1
0.9 aq-PVOH	251.2	271.1	286.3	306.3	334.1
5 aq-ethyl acetate	432.4	459.5	478.6	511.5	552.7
Mixed solvent	1246	1341	1441	1573	1659
[ZnSO <sub>4</sub> .7H <sub>2</sub> O] = 6.0x 10 <sup>-3</sup> mol.dm <sup>-3</sup>					
0.1 aq-PVOH	179.8	195.7	206.5	229.3	238.9
0.5 aq-PVOH	235.8	240.2	254.3	276.5	302.9
0.9 aq-PVOH	277.0	282.3	302.7	322.7	345.3
5 aq-ethyl acetate	445.5	452.6	483.1	504.1	552.4
Mixed solvent	1165	1259	1366	1477	1612
$\sigma \pm 0.3 - 0.7$					

which were calculated by plotting  $\Lambda_m$  versus  $C^{1/2}$  and intercept of graph on extrapolation gives the value of  $\Lambda_m^\circ$ . The representative plot between  $\Lambda_m$  versus  $C^{1/2}$  is shown in Figure (1).



**Figure 1: Plot  $\Lambda_m$  versus  $C^{1/2}$  for molar conductance at infinite dilution of CoSO<sub>4</sub>.7H<sub>2</sub>O in different solvent systems for 0.1 g.dL<sup>-1</sup> aq-PVOH (●), 5 g.dL<sup>-1</sup> aq-ethyl acetate (■) and Tertiary Solvent (▲) at 308 K.**

Results show that, with the increased in concentration of aqueous PVOH  $\Lambda_m^\circ$  for transition metal salts increased in aqueous-PVOH. This was due to decrease in solvation shell, attributed due to hydrophobic nature of aqueous-PVOH or aqueous-ethyl acetate. The  $\Lambda_m^\circ$  values for transition metal salts in mixed solvent system were higher as compared to the values in aqueous polyvinyl alcohol and in aqueous ethyl acetate system because resulting crosslinking complexes of transition metal with PVOH-borax mixture in aqueous-ethyl acetate was highly amorphous. From the values of  $\Lambda_m^\circ$  for transition metal salts in aqueous polyvinyl alcohol, aqueous ethyl acetate, and in mixed solvent systems of aqueous polyvinyl alcohol + borax + ethyl acetate, it can be concluded that ion-solvent interaction decreased with increasing the concentration of PVOH from 0.1 to 0.9 g.dL<sup>-1</sup>. The values of  $\Lambda_m^\circ$  for transition metal salts in 5 g.dL<sup>-1</sup> aqueous-ethyl acetate were higher than the values in aqueous PVOH because of higher concentration of aqueous-ethyl acetate were used. The  $\Lambda_m^\circ$  values for transition metal salts in mixed solvent system



were higher than the binary solvent system because ion-ion interaction increased in the resulting crosslinking complexes of transition metal with PVOH borax mixture in aqueous ethyl acetate resulting decrease in the ion-solvent interactions. On increasing the temperature,  $\Lambda_m^\circ$  for transition metal salts increased in aqueous polyvinyl alcohol and aqueous ethyl acetate, and in mixed solvent systems of aqueous polyvinyl alcohol + borax + ethyl acetate, because at infinite dilution the ionic association was considerably negligible and increment in temperature results in increasing the mobility of ions which was due to the increase in different modes of vibration. The increment for  $\Lambda_m^\circ$  of transition metal salts in mixed solvent systems of aqueous polyvinyl alcohol + borax + ethyl acetate, with respect to increase in temperature was greater as compared to that in aqueous polyvinyl alcohol and aqueous ethyl acetate system because at high temperature the crosslinking complexes

of transition metal with PVOH-borax mixture in aqueous-ethyl acetate were present in elastomeric state which was highly conducting phase.

Walden product ( $W.P$ ) shown in equation (3), describes the solvent properties of an electrolytic system and the effect of solvent on the ionic interactions of an electrolyte.

$$\Lambda_m^\circ \eta^\circ = W.P \quad \text{..... (3)}$$

where,  $\eta^\circ$  is the viscosity of the solvent. The results of Walden product for transition metal salt are tabulated in table (4).

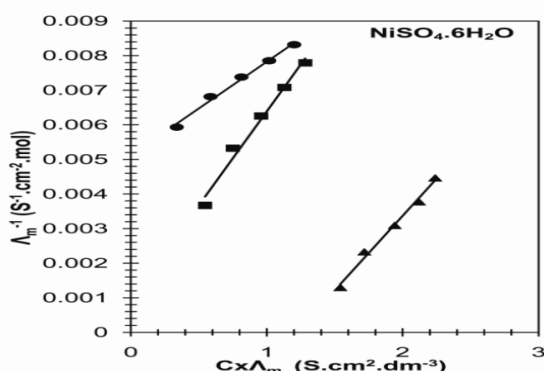
**Table 4: Walden product  $W.P.$  ( $S.cm^3.mol^{-1}.P$ ) of transition metal salts in different solvent systems at different temperatures.**

Solvent system (g.dL <sup>-1</sup> )	T (K)				
	298	303	308	313	318
	[CoSO <sub>4</sub> .7H <sub>2</sub> O] = 6.0x 10 <sup>-3</sup> mol.dm <sup>-3</sup>				
0.1 aq-PVOH	1.854	1.805	1.764	1.742	1.649
0.5 aq-PVOH	3.167	2.938	2.797	2.756	2.646
0.9 aq-PVOH	4.872	4.278	4.270	4.374	4.138
5 aq-ethyl acetate	3.822	3.471	3.266	3.191	3.186
Mixed solvent	14.80	13.74	13.54	13.34	12.28
	[NiSO <sub>4</sub> .6H <sub>2</sub> O] = 6.0x 10 <sup>-3</sup> mol.dm <sup>-3</sup>				
0.1 aq-PVOH	1.805	1.731	1.664	1.719	1.632
0.5 aq-PVOH	3.008	2.870	2.545	2.432	2.391
0.9 aq-PVOH	4.984	4.354	4.340	4.532	4.300
5 aq-ethyl acetate	4.064	3.784	3.498	3.169	3.056
Mixed solvent	11.58	10.87	10.87	10.75	10.47
	[CuSO <sub>4</sub> .5H <sub>2</sub> O] = 6.0x 10 <sup>-3</sup> mol.dm <sup>-3</sup>				
0.1 aq-PVOH	1.777	1.630	1.544	1.567	1.493
0.5 aq-PVOH	2.894	2.736	2.471	2.391	2.269
0.9 aq-PVOH	4.409	3.874	3.788	3.807	3.660
5 aq-ethyl acetate	3.932	3.753	3.509	3.366	3.299
Mixed solvent	12.35	11.50	11.46	11.53	10.84
	[ZnSO <sub>4</sub> .7H <sub>2</sub> O] = 6.0x 10 <sup>-3</sup> mol.dm <sup>-3</sup>				
0.1 aq-PVOH	1.764	1.714	1.655	1.730	1.617
0.5 aq-PVOH	3.228	2.907	2.671	2.644	2.564
0.9 aq-PVOH	4.862	4.034	4.005	4.011	3.783
5 aq-ethyl acetate	4.051	3.697	3.542	3.317	3.297
Mixed solvent	11.55	10.80	10.87	10.82	10.53

$\sigma \pm 0.3 - 0.7$

The representative plot between  $1/\Lambda_m$  versus  $C.\Lambda_m$  for equilibrium constant is shown in Figure (2).





**Figure 2:** Plot  $1/\Lambda_m$  versus  $C\Lambda_m$  for equilibrium constant of  $\text{NiSO}_4 \cdot 6\text{H}_2\text{O}$  in solvent systems for  $0.1 \text{ g.dL}^{-1}$  aq-PVOH (●),  $5 \text{ g.dL}^{-1}$  aq-ethyl acetate (■) and Tertiary Solvent (▲) at 308 K.

Walden product increased with the increase in concentration of aqueous PVOH, this was due to increase in both conductance and viscosity with the increase in solvent concentration. The Walden product in aqueous ethyl acetate and mixed solvent system were greater as compared to that in aqueous PVOH because of higher  $\Lambda_m^\circ$  values in aqueous ethyl acetate and in mixed solvent system. 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 PVOH  $0.1 \text{ g.dL}^{-1}$  and decreased with increase in concentration of aqueous PVOH. In mixed solvent system, significantly higher values of  $\Lambda_m^\circ$  indicating weakest solvation of resulting

crosslinking complexes of transition metal (Co(II), Ni(II), Cu(II), Zn(II)) with PVOH borax mixture in aqueous ethyl acetate.

On increasing the temperature, Walden product decreased in binary and mixed solvent system. This decrement due to decrease in viscosity of solvent with the increase in temperature, which overweigh the effect of increase in  $\Lambda_m^\circ$  values with the rise in temperature.

Degree of dissociation ( $\alpha$ ) is the ratio between molar conductance and molar conductance at infinite dilution, dissociation constant ( $K_d$ ) gave the information about the dissociation of electrolyte ion while from equilibrium constant ( $K_c$ ) association can be estimated. They were formulated as in equations (4-6). The equilibrium constant can be obtained by a plot between  $1/\Lambda_m$  versus  $C\Lambda_m$ , and from the slope of the line  $K_c$  was obtained.

$$\alpha = \Lambda_m / \Lambda_m^\circ \quad \dots\dots\dots (4)$$

$$K_d = \alpha^2 C / 1 - \alpha \quad \dots\dots\dots (5)$$

$$1/\Lambda_m = 1/\Lambda_m^\circ + \Lambda_m^\circ \cdot K_c \cdot C\Lambda_m \quad \dots\dots\dots (6)$$

The results of  $\alpha$ ,  $K_d$ ,  $K_c$  are tabulated in table (5).

**Table 5: Degree of dissociation ( $\alpha$ ), dissociation constant ( $K_d$ ) and equilibrium constant ( $K_c$ ) of transition metal salts in different solvent systems at 308 K.**

Solvent system (g.dL <sup>-1</sup> )	$\alpha$	$K_d \times 10^2$	$K_c$ (mol.dm <sup>-3</sup> )
<b>[CoSO<sub>4</sub>·7H<sub>2</sub>O] = 1.0x 10<sup>-2</sup> mol.dm<sup>-3</sup></b>			
0.1 aq-PVOH	0.570	0.756	0.440
0.5 aq-PVOH	0.476	0.433	0.639
0.9 aq-PVOH	0.408	0.281	0.774
5 aq-ethyl acetate	0.293	0.122	1.336
Mixed solvent	0.133	0.020	5.617
<b>[NiSO<sub>4</sub>·6H<sub>2</sub>O] = 1.0x 10<sup>-2</sup> mol.dm<sup>-3</sup></b>			
0.1 aq-PVOH	0.578	0.796	0.560
0.5 aq-PVOH	0.509	0.529	0.605
0.9 aq-PVOH	0.386	0.243	0.984
5 aq-ethyl acetate	0.269	0.099	1.431
Mixed solvent	0.164	0.032	5.327
<b>[CuSO<sub>4</sub>·5H<sub>2</sub>O] = 1.0x 10<sup>-2</sup> mol.dm<sup>-3</sup></b>			
0.1 aq-PVOH	0.584	0.820	0.404
0.5 aq-PVOH	0.499	0.498	0.588
0.9 aq-PVOH	0.423	0.310	0.715
5 aq-ethyl acetate	0.269	0.099	1.435
Mixed solvent	0.143	0.024	6.340



	[ZnSO <sub>4</sub> .7H <sub>2</sub> O] = 1.0x 10 <sup>-2</sup> mol.dm <sup>-3</sup>		
0.1 aq-PVOH	0.589	0.848	0.413
0.5 aq-PVOH	0.490	0.473	0.610
0.9 aq-PVOH	0.425	0.315	0.726
5 aq-ethyl acetate	0.281	0.109	1.449
Mixed solvent	0.165	0.033	5.054
σ	± 0.001 - 0.003	± 0.01 - 0.06	± 0.005 - 0.009

Degree of dissociation and dissociation constant decreased while equilibrium constant increased with increase in aqueous PVOH concentration because of binding nature of aqueous PVOH. The high solvent-solvent interaction results in association instead of dissociation of transition metal salts [28].

The value of  $\alpha$  and  $K_d$  for transition metal salts in mixed solvent system was found lesser and  $K_c$  was found greater as compared to the values in binary solvent system. This was because of the fact that transition metal ions were more strongly associated in resulting crosslinking complexes with PVOH-borax mixture in aqueous-ethyl acetate. In different solvent systems the inverse relation between dissociation constant  $K_d$  and equilibrium constant  $K_c$  was verified. The  $K_d$  values were found to be in order aqueous PVOH > aqueous ethyl acetate > mixed solvent system, while  $K_c$  was found to be in order aqueous PVOH < aqueous ethyl acetate <

mixed solvent system. This confirmed that with the increase in solvent concentration dissociation decreased and association increased and after crosslinking in mixed solvent system dissociation was significantly decreased and association was significantly increased. In mixed solvent system, from the values of degree of dissociation it was found that the dissociation of transition metal salts was in the order of Co (II) < Cu (II) < Ni (II)  $\approx$  Zn (II), thus association will be in reversed order.

Thermodynamic parameters regarding to the activated states like energy of activation ( $E_a$ ), free energy change of activation ( $\Delta G^*$ ), enthalpy change of activation ( $\Delta H^*$ ) and entropy change of activation ( $\Delta S^*$ ) were obtained in order to confirmed the ion-association in crosslinking complexes. The conductance data of  $E_a$ ,  $\Delta G^*$ ,  $\Delta H^*$ ,  $\Delta S^*$  for transition metal salts are tabulated in table 6.

**Table 6: Thermodynamic parameters of transition metal salts in different solvent systems at 303 K**

Solvent system (g.dL <sup>-1</sup> )	E <sub>a</sub> (kJ.mol <sup>-1</sup> )	ΔG* (kJ.mol <sup>-1</sup> )	ΔH* (kJ.mol <sup>-1</sup> )	ΔS* x 10 <sup>2</sup> (kJ.mol <sup>-1</sup> .K <sup>-1</sup> )
[CoSO <sub>4</sub> .7H <sub>2</sub> O] = 6.0x 10 <sup>-3</sup> mol.dm <sup>-3</sup>				
0.1 aq-PVOH	9.994	12.50	-0.114	-4.162
0.5 aq-PVOH	12.17	13.60	-0.268	-4.576
0.9 aq-PVOH	12.25	14.83	-0.516	-5.063
5 aq-ethyl acetate	9.554	16.89	0.363	-5.454
Mixed solvent	10.15	20.64	0.331	-6.700
[NiSO <sub>4</sub> .6H <sub>2</sub> O] = 6.0x 10 <sup>-3</sup> mol.dm <sup>-3</sup>				
0.1 aq-PVOH	10.91	12.35	-0.421	-4.214
0.5 aq-PVOH	8.98	13.53	0.191	-4.474
0.9 aq-PVOH	13.02	15.20	-0.363	-5.222
5 aq-ethyl acetate	4.901	17.51	0.459	-5.625
Mixed solvent	12.26	19.41	-0.260	-6.490
[CuSO <sub>4</sub> .5H <sub>2</sub> O] = 6.0x 10 <sup>-3</sup> mol.dm <sup>-3</sup>				
0.1 aq-PVOH	8.080	12.13	0.210	-3.933
0.5 aq-PVOH	9.056	13.48	0.210	-4.308
0.9 aq-PVOH	10.91	14.75	-0.229	-4.944
5 aq-ethyl acetate	9.401	17.56	-0.076	-5.819
Mixed solvent	11.56	20.51	0.118	-6.728
[ZnSO <sub>4</sub> .7H <sub>2</sub> O] = 6.0x 10 <sup>-3</sup> mol.dm <sup>-3</sup>				
0.1 aq-PVOH	11.46	12.25	-0.191	-4.107
0.5 aq-PVOH	10.07	13.75	0.114	-4.425
0.9 aq-PVOH	9.037	14.35	0.153	-4.683
5 aq-ethyl acetate	8.443	17.05	0.248	-5.543
Mixed solvent	12.74	19.40	-0.281	-6.492
σ	± 0.02 - 0.04	± 0.02 - 0.03	± 0.01-0.04	± 0.07- 0.09



Energy of activation which shows the effect of temperature on conductance was evaluated using Arrhenius relation equation (7), by a plot  $\log \Lambda_m^\circ$  versus  $1/T$  and the slope of the line gives the value of  $E_a$ .

$$\log \Lambda_m^\circ = \log A - E_a / 2.303RT \quad (7)$$

where,  $E_a$  is the energy of activation,  $R$  is the molar gas constant,  $A$  is the frequency factor and  $T$  is the temperature of the system. The representative plot of  $\log \Lambda_m^\circ$  versus  $1/T$  is shown in Figure (3).

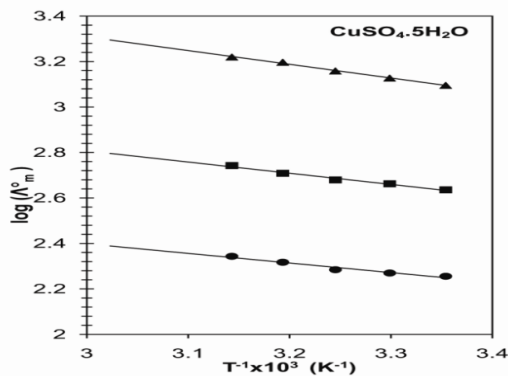


Figure 3: Plot  $\log \Lambda_m^\circ$  versus  $1/T$  for energy of activation of  $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$  in solvent systems for  $0.1 \text{ g.dl}^{-1}$  aq-PVOH ( $\bullet$ ),  $5 \text{ g.dl}^{-1}$  aq-ethyl acetate ( $\blacksquare$ ) and Tertiary Solvent ( $\blacktriangle$ ).

Activation energy increased for  $\text{CoSO}_4 \cdot 7\text{H}_2\text{O}$ ,  $\text{NiSO}_4 \cdot 6\text{H}_2\text{O}$  and  $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$  in aqueous PVOH indicated that at higher concentration of aqueous PVOH, rate of movement of ions was slow and reversed behavior was observed for  $\text{ZnSO}_4 \cdot 7\text{H}_2\text{O}$ . The exception in  $\text{ZnSO}_4 \cdot 7\text{H}_2\text{O}$  was possibly due to its inert configuration. In aqueous ethyl acetate the values are lesser than the rest of the aqueous PVOH solvent, because of having higher  $\Lambda_m^\circ$  value indicating less solvation. The value of  $E_a$  for transition metal salts in mixed solvent system were slightly increased as compared to the value in aqueous  $0.1 \text{ g.dL}^{-1}$  PVOH solvent indicating that the increase in energy of activation was possibly due to enhancement in ion association in PVOH borax mixture in aqueous ethyl acetate system. Free energy change of activation describes the spontaneity of process. Free energy change of activation was calculated by using relation equation (8).

$$\Delta G^* = -2.303RT \cdot \log K_d \quad (8)$$

The increased in  $\Delta G^*$  values with the increase in concentration of aqueous PVOH, confirmed the association of ions with the solvent system at higher concentrations [26]. The values of  $\Delta G^*$  for transition metal salts were comparatively higher in mixed solvent system (PVOH + borax + ethyl acetate)

because of comparatively greater association of transition metal ions in crosslinked complex. The increased in  $\Delta G^*$  values with the increase in temperature in aqueous PVOH, aqueous ethyl acetate and mixed solvent system (PVOH + borax + ethyl acetate) prevailed with the fact that the dissociation process was endothermic in nature.

Enthalpy change of activation is measure of total heat content of a process on the basis of which exothermic and endothermic nature of process can be described. Enthalpy change of activation was graphically obtained by a plot between  $-\log K_d$  versus  $1/T$  from the slope of line value of  $\Delta H^*$  was obtained. The representative plot between  $-\log K_d$  versus  $1/T$  is provided in Figure (4).

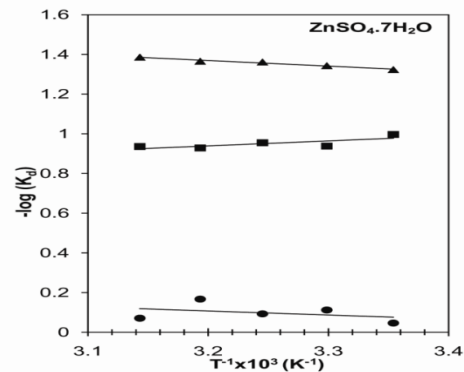


Figure 4: Plot  $-\log K_d$  versus  $1/T$  for enthalpy change of activation of  $\text{ZnSO}_4 \cdot 7\text{H}_2\text{O}$  in solvent systems for  $0.1 \text{ g.dl}^{-1}$  aq-PVOH ( $\bullet$ ),  $5 \text{ g.dl}^{-1}$  aq-ethyl acetate ( $\blacksquare$ ) and Tertiary Solvent ( $\blacktriangle$ ).

There was a variation in the values of  $\Delta H^*$  for transition metal salts with the increase in concentration of aqueous PVOH and in aqueous ethyl acetate and in mixed solvent system (PVOH + borax + ethyl acetate).

Entropy change of activation determines the randomness of process to ensure the order and disorder of system with respect to temperatures. Entropy change of activation was evaluated by using relation equation (9).

$$\Delta S^* = (\Delta H^* - \Delta G^*) / T \quad (9)$$

The decreased in  $\Delta S^*$  with the increase in concentration of aqueous PVOH because association of ions results in less randomness in the system. The values were comparatively lower in mixed solvent system (PVOH + borax + ethyl acetate), show that the system was highly ordered and well associated [27].  $\Delta S^*$  also decreased with the increase in temperature in aqueous PVOH show that the randomness decreased with temperature, thus association was favorable at high temperatures. In case of mixed solvent system (PVOH + borax + ethyl acetate), with the increase in temperature entropy



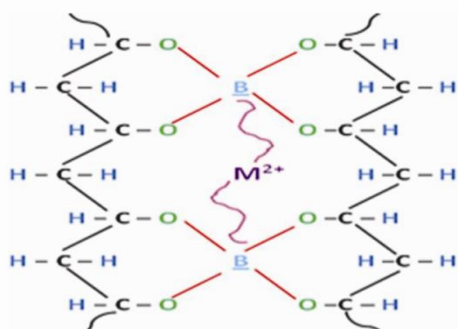
change of activation increased for  $\text{CoSO}_4 \cdot 7\text{H}_2\text{O}$  and  $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$  which shows the dissociation of Co (II) and Cu (II) complexes increased with temperature and there was same pattern for  $\text{NiSO}_4 \cdot 6\text{H}_2\text{O}$  and  $\text{ZnSO}_4 \cdot 7\text{H}_2\text{O}$  with the increase in temperature as in aqueous PVOH.

FTIR spectra of PVOH, PVOH + borax + transition metal salts were obtained by solid sampling using KBr disk technique. The spectra are shown in Figure (5).

In Polymeric complexes the C-O stretching frequency at  $1097.50 \text{ cm}^{-1}$  was shifted to higher stretching frequency  $1140\text{--}1116 \text{ cm}^{-1}$  in resulting polymeric complexes, this attributed to association of complex in the presence of PVOH borax mixture [29,30]. The C-O stretching peak in the presence of Co (II), Ni (II), Cu (II) and Zn (II) appears at  $1139.93 \text{ cm}^{-1}$ ,  $1116.78 \text{ cm}^{-1}$ ,  $1124.50 \text{ cm}^{-1}$  and  $1118.71 \text{ cm}^{-1}$  respectively. Thus the association was in the order of Co (II) > Cu (II) > Ni (II)  $\approx$  Zn (II). This pattern was also observed on studying degree of dissociation from conductivity data. The peak at  $1458 \text{ cm}^{-1}$  was assigned due to  $\text{CH}_2$  bending and  $1074 \text{ cm}^{-1}$  was attributed to B-O-C stretching frequency. The peaks in region  $990\text{--}877 \text{ cm}^{-1}$  was assigned as B-O stretching frequency,  $\text{CH}_2$  rocking frequency was also obtained in region  $794\text{--}670 \text{ cm}^{-1}$  in polymeric complexes.

#### 4. CONCLUSIONS:

The increments in the values of  $\Lambda_m^\circ$  with increasing concentration of aqueous PVOH indicate that ion-solvent interaction decreased with the increase in concentration of solvent. The values of  $\Lambda_m^\circ$  in mixed solvent system (PVOH + borax + ethyl acetate) were found greater as compared to the values in aqueous polyvinyl alcohol and aqueous ethyl acetate solvent system. Thus mixed solvent system has least value of ion-solvent interaction indicates the higher ion-ion interaction of metal crosslinking complexes with PVOH borax mixture in ethyl acetate. The structure of crosslinking complexes of PVOH borax with divalent transition metal is represented as:



Degree of dissociation and dissociation constant value indicated that the strong association of transition metal ions in mixed solvent system. FTIR study also confirmed the ion-association in transition metal complexes with PVOH-borax

mixture. The association was in order Co (II) > Cu (II) > Ni (II)  $\approx$  Zn (II) which correlated with conductance data.

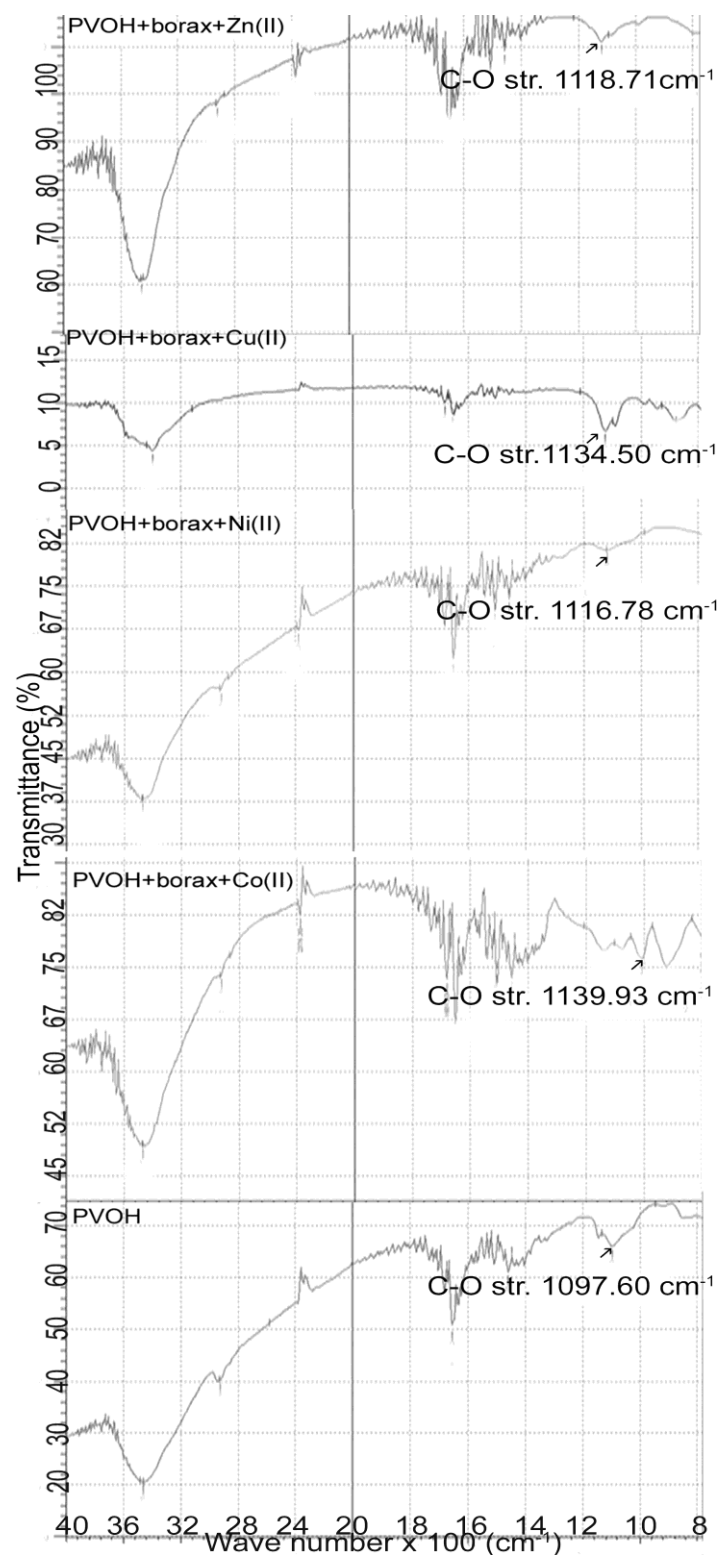


Figure (5): FTIR Spectra of PVOH, PVOH + borax +  $\text{CoSO}_4 \cdot 7\text{H}_2\text{O}$ , PVOH + borax +  $\text{NiSO}_4 \cdot 6\text{H}_2\text{O}$ , PVOH + borax +  $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ , PVOH + borax +  $\text{ZnSO}_4 \cdot 7\text{H}_2\text{O}$



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