

Ionic Interactions of Divalent Transition Metal Sulfate in Aqueous PVOH Systems by Viscosity Method

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Abstract

Viscosities of divalent transition metal sulfate (MnSO_4 , CuSO_4 and ZnSO_4) having concentration ranging from 2×10^{-2} to 10×10^{-2} mol dm^{-3} in aqueous polyvinyl alcohol (PVOH; 0.1 and 0.9 g dL^{-1}) systems were measured at different temperatures from 298 to 318 K with interval of 5 K. The viscosity data were used to evaluate the ion-ion interaction and ion-solvent interactions in terms of A and B coefficients of Jones-Dole equation respectively. The positive value of B coefficient increased with the increase in temperature reveals that salts behave as structure maker in aqueous polyvinyl alcohol systems. With the help of viscosity data the thermodynamic parameters like energy of activation (E_η), free energy change of activation (ΔG^*) and the entropy change of activation (ΔS^*) were also evaluated as a function of salt concentration, solvent composition and temperature.

Keywords:

Viscosity, Divalent transition metal sulfate, Polyvinyl alcohol, Thermodynamic parameters

Introduction

Ionic solutions having solute-solvent interaction has great importance in biological chemistry, physical chemistry, surface chemistry, environmental chemistry, geochemistry and also in solution chemistry. The attraction between solute and solvent depends on ionic size and solvent polarity. Solute-solute and solute-solvent interactions helps in studying the nature of solute and solvent that either added solute modifies (structure maker) or distorts (structure breaker) the structure of the solvent. Viscometric study of aqueous solutions of salts is valuable in understanding the nature of solute-solvent and solvent-solvent interactions [1-4]. Viscosity measurement is a suitable tool for a rapid and reliable characterization of polymer interactions in solvents. The viscosity of polymer for molecular weight determination is important for commercial production and processing of polymers [5-10]. Polyvinyl alcohol is a water-soluble polyhydroxy polymer, employed in practical applications because of its excellent chemical resistance and physical properties and is completely degradable. Polyvinyl alcohol serve as a thickening agent for various emulsions and suspensions and used as wet-strength adhesive. An important use of polyvinyl alcohol is as the plastic inter layer for automotive and aircraft also for coating electrical wire [11,12]. Divalent transition metal sulfates play a vital role in life systems as a vitamins, enzymes and proteins [13].

The thermodynamic data by viscosity method of a binary mixture are important from practical and theoretical points of view to understand liquid theory. The viscometric and thermodynamic properties of

polymers at different temperatures have been studied [14-16]. The effect of electrolyte on the flow process of the solvent can be explained in terms of Jones-Dole [17] coefficients. The B coefficient of the Jones-Dole equation is a better measurement of the interaction of added electrolyte [18-22].

The physicochemical property of water soluble polymers in solutions depends on the dissociated ionic groups, quality of the solvent, concentration of the salt and polymer-substrate interactions. Therefore the purpose of this work is to study the ionic interaction of hydrated divalent transition metal sulphates in aqueous polyvinyl alcohol solution by viscosity method. The viscosity data for the solutions of zinc sulphate, manganese sulphate, copper sulphate is in the concentration ranges from 2×10^{-2} to 10×10^{-2} mol dm^{-3} in aqueous polyvinyl alcohol (0.1 and 0.9 g dL^{-1}) systems will be determined at different temperature ranges from 298 to 318 K. Ion-ion and ion-solvent interactions will be evaluated from the Jones-Dole equation in terms of A and B coefficients respectively. The thermodynamic parameters for viscous flow like energy of activation (E_η), free energy change of activation (ΔG^*) and change in entropy of activation (ΔS^*) will also be evaluated as a function of concentration of electrolyte, concentration of polymer and temperature.



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Materials and Method

Polyvinyl alcohol (PVOH) of E. Merck 99 % pure was used for the experimental work. Average molecular weight of polyvinyl alcohol at 298 K was calculated by Mark-Houwink relation [12].

$$[\eta]_{\text{int}} = kM_v^\alpha \quad (1)$$

where, $[\eta]_{\text{int}}$ is the intrinsic viscosity, the values of k and α are 33.88×10^{-5} and 0.716 respectively for polyvinyl alcohol having average molecular weight 46835 Da is 98 % hydrolyzed .

Zinc sulphate ($\text{ZnSO}_4 \cdot 7\text{H}_2\text{O}$), manganese sulphate ($\text{MnSO}_4 \cdot \text{H}_2\text{O}$), and copper sulphate ($\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$) of E. Merck, 99 % pure were used without further purification. Stock solution of aqueous polyvinyl alcohol (PVOH), 1.0 g dL^{-1} were prepared in a known volume of double distilled water by weighing particular amount of polyvinyl alcohol. The solutions were constantly stirred and heated (353 K) by magnetic stirrer with 78HW-1 (made in Czechoslovakia) to make the solutions homogenized, resultant solutions were then cooled to room temperature and the volume was made up to the mark with double distilled water. Different dilutions from stock solution having compositions 0.1 and 0.9 g dL^{-1} of aqueous polyvinyl alcohol were also prepared by taking particular volume from stock solutions.

Stock solution of divalent transition metal sulfate having concentration of 0.1 mol dm^{-3} was prepared with 0.1 g dL^{-1} aqueous PVOH solution in 250 mL volumetric flask. Different dilutions from stock solution of divalent transition metal sulfate were made in the range of 2×10^{-2} to $8 \times 10^{-2} \text{ mol dm}^{-3}$. Similar procedure for solution preparation as above was repeated with 0.9 g dL^{-1} aqueous solution of polyvinyl alcohol.

A relative density bottle (R.D bottle) having capacity 10.0 mL by volume was used to measure the densities of solvents and solutions at various temperatures (298, 303, 308, 313 and $318 \pm 0.1 \text{ K}$). The uncertainty in the experimental data for density was found to be $\pm 0.0001 \text{ g mL}^{-1}$.

An Ostwald viscometer type Techniconomial constant 0.05 cycle per second (Cs/s) capillary ASTM D 445 was used to measure the viscosity. A definite quantity of solvent (aqueous polyvinyl alcohol) and salt solution respectively was taken into the viscometer kept for 15 to 20 minutes at fixed temperature in a water bath to attain the required temperature. The solution was drawn up into the upper bulb and time required for its meniscus to fall in between the calibration marks was accurately measured by stop watch. Each measurement was taken at least three times to attain reliability in the

results. The uncertainty in the experimental data for viscosity was found to be $\pm 0.01 \text{ mPa s}$.

Results and Discussion

Viscosities of divalent transition metal sulphates in aqueous polyvinyl alcohol systems (0.1 and 0.9 g dL^{-1}) at various temperatures ranging from 298 to 318 K with difference of 5 K temperature were measured. Viscosity data was used for the calculation of relative, specific and reduced viscosity. The values of viscosities and densities of manganese sulphate (MnSO_4), copper sulphate (CuSO_4) and zinc sulphate (ZnSO_4) are tabulated in Tables 1 and 2 which show that viscosity and density increased with the increase in concentration of polyvinyl alcohol and also with the divalent transition metal (II) sulphate salts. The large and rapid increase in viscosity is due to configurational changes in polymeric system [23]. The increased in values of viscosity for MnSO_4 , CuSO_4 and ZnSO_4 solutions in aqueous polyvinyl alcohol systems shows that as the concentration increased the kinetic energy of molecules decreased therefore viscosity increased. The viscosity of solutions increased as the concentration of solvent (aqueous polyvinyl alcohol) increased showing that polymer molecule may associate either by inter or intramolecular forces in aqueous solvent system. Electrostatic, hydrophobic interactions, vander waals forces and hydrogen bonding are the sources responsible for the formation of association in polymer solution led to increase in viscosities as shown in Tables 1 and 2. Representative plot showing the effect of viscosity with the increase in electrolyte concentration is shown in Fig. 1.

While, decrease in viscosity and density observed with the rise in temperature at particular concentration of divalent transition metal (II) sulphates in polyvinyl alcohol solvent systems. This shows that with the rise in temperature, intermolecular forces decreases between solvent molecules resulting increase in molecular motion.

The effect of ionic interactions of divalent transition metal (II) sulphates on the flow process in polyvinyl alcohol systems were studied in terms of Jones-Dole coefficients [17] by using the relation:

$$\eta_r = 1 + AC^{1/2} + BC \quad (2)$$

$$\eta_{sp} / C^{1/2} = A + BC^{1/2} \quad (3)$$

where η_r is the relative viscosity of the solution which is derived by the η/η_0 , η is the viscosity of solution, η_0 is the viscosity of solvent C is the concentration of salt, $\eta_{sp} = \eta_r - 1$, is the specific viscosity of the solution, A coefficient is the ion-ion interaction and coefficient B is ion-solvent interaction. The coefficients A and B of Jones-Dole

equation were obtained from the slope and intercept by plotting $\eta_{sp}/C^{1/2}$ versus $C^{1/2}$ as shown in Fig. 2. A coefficient is related to the long range interionic forces showing an ion-ion interaction while B coefficient is related to the interaction between the ions and the solvent and is interpreted as a measure of the structure making and structure breaking tendency of an electrolyte in solution [24].

The B coefficient of Jones-Dole equation was evaluated from the slope of linear plot of $\eta_{sp}/C^{1/2}$ versus $C^{1/2}$ is shown in Fig. 2. The values of B coefficient at different temperatures ranging from 298 to 318 K for 0.1 and 0.9 g dL⁻¹ aqueous polyvinyl alcohol are tabulated in Table 3. The large positive B coefficient values increased with the rise in temperature were showing structure making behavior of the transition metal salts in PVOH systems. The results show that the ion-solvent interaction values increased with the increase of temperature with few exceptions whereas, irregularity in the values were observed with the increase in composition of solvent (polymer). This indicates that the electrostatic ion-solvent interaction varies with the polymeric solvent system. The B coefficient can be discussed in terms of factors affecting the viscosity at a particular concentration of salt and temperature.

$$\eta = \eta^{\circ} + \eta^{+} + \eta^{A} + \eta^{E} + \eta^{D} \quad (4)$$

where, η° is the viscosity for solvent, η^{+} is the positive increase in viscosity caused by long range electrostatic interaction, η^{A} is the increase due to alignment or orientation of the polar molecules by the ionic field, η^{E} is the positive increase in viscosity due to the shape and size of an ion, η^{D} is the decrease in viscosity arising due to the distortion of solvent structure by the ions. Manganese ion, copper ion and zinc ion, having a high charge density, strongly orients solvent molecules making a sheath of firmly attached layers. The high structure making ability of SO_4^{2-} is due to its electrostatic charge and four oxygen atoms, which enhance the formation of hydrogen bonds in water solution. Thus, the solution is highly viscous in the presence of SO_4^{2-} and the viscosity coefficient B is large. The positive and largest value of B -coefficient may be attributed to the stronger association between salt and aqueous polyvinyl alcohol through, multiple hydrogen bonding and ion-solvent interaction. Thus, the ion-solvent association leads to the larger values of η^{A} and η^{E} . The ionic B -coefficients of the Jones-Dole viscosity equation for electrolytes are positive for structure making ions and negative for structure breaking ions at room temperatures. At high temperature, the surrounding sheath of the solvent molecules around the ion is destroyed and the ion-solvent interactions weaken under such circumstances, ions may get a chance to interact with

each other. The ionic B -coefficients values for MnSO_4 and ZnSO_4 higher than the CuSO_4 because the closed shell cations, such as Zn^{2+} and Mn^{2+} (d^5), construct a significant contribution to ion solvation.

The values of A coefficient at different temperatures ranging from 298 to 318 K for 0.1 and 0.9 g dL⁻¹ aqueous polyvinyl alcohol system are tabulated in Table 4. The A coefficient values represents ion-ion interaction including size, shape effects of solute and to some extent ion-solvent interaction. The irregularity in A coefficients were observed with the increase in composition of aqueous PVOH solvent system. The negative values of A -coefficient at higher concentration of polyvinyl alcohol shows that the polymer association to water is stronger as compared to solvent interaction with ions, while at lower concentration of polyvinyl alcohol there were observed ion-solvent interactions between salt and aqueous polyvinyl alcohol. The values of A coefficient in MnSO_4 , CuSO_4 and ZnSO_4 has been found to decrease as the temperature increases. This may be due to at higher temperature greater thermal agitation causing reduction in attractive forces between the ions. However, the interpenetration effect (cation-cation) and (cation-anion), which also brings ion together, may responsible for decreased in A coefficient. The values of A coefficient are smaller than those of B coefficient, indicating weak ion-ion interaction at higher temperature. This may be attributed to the increase in solvation of ions at higher temperatures.

The thermodynamic parameters of activation for viscous flow such as energy of activation (E_{η}), free energy change of activation (ΔG^*) and entropy change of activation (ΔS^*) of $\text{MnSO}_4 \cdot \text{H}_2\text{O}$, $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ and $\text{ZnSO}_4 \cdot 7\text{H}_2\text{O}$ solutions in aqueous PVOH system investigated at various temperatures are listed in Table 5. The viscometric data is applied on 6×10^{-2} mol.dm⁻³ concentration. The value of energy of activation (E_{η}) is simply calculated from slope of a linear plot between $\log \eta$ versus $1/T$, obtained by Arrhenius relation as shown below:

$$\log \eta = \log A + E_{\eta} / 2.303RT \quad (5)$$

where A is called the pre-exponential factor constant for a given liquid, R is the gas constant and T is the absolute temperature. Results for activation energy for $\text{MnSO}_4 \cdot \text{H}_2\text{O}$, $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ and $\text{ZnSO}_4 \cdot 7\text{H}_2\text{O}$ solutions in 0.1 and 0.9 g dL⁻¹ aqueous polyvinyl alcohol are shown in Table 5. Representative plot of $\log \eta$ versus reciprocal of the absolute temperature is shown in Fig 3. From the results, it was observed that the energy of activation is increased with the increase in polymer composition. The high value of energy of activation is due to strong structure making

molecules. Because, the process of degradation of structure and orientation of macromolecules occur during flow, so the positive values of activation energy are obtained. Whereas with the increase in solvent composition, the increase in activation energy may be due to the fact that at higher concentrations, the greater number of ions will be present cause a decrease in the ionic mobility and make it difficult to produce vacant sites in the solvent matrix resulting in the high energy of activation.

The free energy change of activation for viscous flow is given by the following expression.

$$\Delta G^* = \frac{RT \ln \eta V}{h N_A} \quad (6)$$

where h is a Planck's constant, N_A is Avogadro's number and V is volume of one mole of solution particles calculated by the following expression.

$$V = \frac{1000}{(n_1 + v n_2)} \quad (7)$$

where v is the number of species into which the solute molecules dissociated and n_2 is the number of moles of solute per liter of solution. The number of moles of solvent per liter of solution n_1 is given by:

$$n_1 = \frac{(1000 d_o - n_2 M_2)}{M_1} \quad (8)$$

where M_1 and M_2 are the molecular weights of solvent and solute respectively and d_o is the density of solvent. The values of free energy change of activation of $\text{MnSO}_4 \cdot \text{H}_2\text{O}$, $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ and $\text{ZnSO}_4 \cdot 7\text{H}_2\text{O}$ solutions in aqueous polyvinyl alcohol systems are evaluated using relation (7) and summarized in Table 5. The increased in free energy change of activation is also observed with the increase in temperature as well as PVOH compositions. It shows that in dilute polymer solutions the associations are weaker and they can be easily overcome during flow whereas in concentrated polymer solutions these associations are stronger and are little affected during flow process. Therefore the values of free energy change of activation (ΔG^*) are high. The change in entropy of activation (ΔS^*) for $\text{MnSO}_4 \cdot \text{H}_2\text{O}$, $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ and $\text{ZnSO}_4 \cdot 7\text{H}_2\text{O}$ solutions in aqueous polyvinyl alcohol systems are given by:

$$\Delta S^* = \frac{E_\eta - \Delta G^*}{T} \quad (9)$$

where E_η is the activation energy, ΔG^* is the change in free energy of activation, T is the absolute temperature. The values of change in entropy of activation (ΔS^*) at various concentrations of $\text{MnSO}_4 \cdot \text{H}_2\text{O}$, $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ and $\text{ZnSO}_4 \cdot 7\text{H}_2\text{O}$ solutions in aqueous polyvinyl alcohol are summarized in Tables 5. With the increased in

solvent composition of aqueous polyvinyl alcohol it was observed that values of change in entropy of activation increased this led to the structure making ability of divalent transition metal sulfates in aqueous PVOH systems. This variation in change in entropy of activation is due to may be un-coiling and reorientation of macromolecules in aqueous system. The negative values of entropy change of activation also indicate that the formation of transition state is associated with bond making instead of breaking [25]. The negative data for entropy change of activation (ΔS^*) also show that the viscous flow is an ordered process involving contiguous liquid layers which should maintain their structural configuration even moving in a stationary steady state [26].

Motin [27] have also reported the CuSO_4 in pure water behaves as a structure maker. Ravichandran and Ramanathan [28] investigated the ultrasonic studies of divalent salts in aqueous polyvinyl alcohol solutions at 303 K. Results obtained from ultrasonic studies also indicate that divalent transition metal sulfates act as a structure maker.

Conclusions

Viscosities, densities and thermodynamics of viscous flow of $\text{MnSO}_4 \cdot \text{H}_2\text{O}$, $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ and $\text{ZnSO}_4 \cdot 7\text{H}_2\text{O}$ in aqueous PVOH systems were studied at different temperatures. The data have been used to calculate the values of A and B coefficients of Jones-Dole equation for the determination of ionic interactions of divalent transition metal sulfates in aqueous polyvinyl alcohol systems. It was found that these hydrated salts behave as structure maker in aqueous polyvinyl alcohol systems. The structure making ability of these salts were also confirmed by the values of thermodynamic parameters. The results show that the decreased in ΔS^* with the rise in temperature confirm its structure making.

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Figure captions

Fig. 1. Plot of viscosity versus concentration of salts at 303 K in 0.1 (g.dL⁻¹) aqueous PVOH system.

Fig. 2. Plot of $\eta_{sp}/C^{1/2}$ versus $C^{1/2}$ for MnSO₄.H₂O in 0.1 (g.dL⁻¹) aqueous PVOH system at different temperatures.

Fig. 3. Plot of $\log\eta$ versus T^{-1} of 6×10^{-2} mol. L⁻¹ MnSO₄.H₂O in 0.1 and 0.9 (g.dL⁻¹) aqueous PVOH system.

Table 1. Viscosities of $\text{MnSO}_4 \cdot \text{H}_2\text{O}$, $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ and $\text{ZnSO}_4 \cdot 7\text{H}_2\text{O}$ solutions in aqueous polyvinyl alcohol system at different temperatures.

10^2 [Salt] ($\text{mol} \cdot \text{L}^{-1}$)	Viscosities/ $\text{mPa} \cdot \text{s}$ at different temperatures/ K				
	$\text{MnSO}_4 \cdot \text{H}_2\text{O}$				
	298	303	308	313	318
0.1 /(g dL^{-1}) Aqueous PVOH System					
2.00	9.50	8.14	7.00	6.29	5.51
4.00	9.63	8.25	7.13	6.45	5.58
6.00	9.80	8.40	7.34	6.60	5.69
8.00	10.00	8.51	7.62	6.79	5.85
10.0	10.16	8.68	7.82	7.05	5.98
0.9 /(g dL^{-1}) Aqueous PVOH System					
2.00	17.26	13.84	10.75	9.22	7.79
4.00	18.05	14.19	11.15	9.55	8.05
6.00	18.68	14.63	11.74	10.03	8.60
8.00	19.25	14.98	12.25	10.56	9.13
10.0	19.87	15.27	12.77	10.96	9.70
$\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$					
0.1/ (g dL^{-1}) Aqueous PVOH System					
2.00	9.62	8.66	7.25	6.06	5.31
4.00	9.82	8.97	7.45	6.12	5.52
6.00	9.99	9.25	7.67	6.28	5.75
8.00	10.17	9.61	7.94	6.43	5.94
10.0	10.41	9.94	8.14	6.62	6.11
0.9/ (g dL^{-1}) Aqueous PVOH System					
2.00	17.22	14.06	11.13	9.81	8.15
4.00	17.90	14.75	11.73	10.28	8.49
6.00	18.73	15.44	12.27	10.68	8.79
8.00	19.60	15.98	12.83	11.21	9.12
10.0	20.36	16.46	13.22	11.71	9.41
$\text{ZnSO}_4 \cdot 7\text{H}_2\text{O}$					
0.1/ (g dL^{-1}) Aqueous PVOH System					

2.00	9.39	8.18	6.77	6.00	5.42
4.00	9.49	8.37	6.81	6.02	5.43
6.00	9.63	8.52	6.86	6.08	5.47
8.00	9.79	8.66	6.97	6.08	5.58
10.0	9.94	8.82	7.12	6.19	5.63
0.9/ (g dL⁻¹) Aqueous PVOH System					
2.00	15.70	13.38	10.70	9.43	8.22
4.00	15.76	13.85	11.10	9.67	8.52
6.00	15.90	14.39	11.61	10.04	8.89
8.00	16.20	14.83	12.04	10.49	9.31
10.0	16.35	15.28	12.51	10.97	9.82

Table 2. Densities of MnSO₄.H₂O, CuSO₄.5H₂O and ZnSO₄.7H₂O solutions in aqueous polyvinyl alcohol system at different temperatures.

10² [Salt] /(mol.L⁻¹)	Densities/ g cm⁻³ at different temperatures/ K				
	MnSO₄.H₂O				
	298	303	308	313	318
0.1/ (g dL⁻¹) Aqueous PVOH System					
2.00	1.0484	1.0453	1.0422	1.0384	1.0351
4.00	1.0538	1.0507	1.0476	1.0448	1.0363
6.00	1.0631	1.0584	1.0526	1.0490	1.0407
8.00	1.0708	1.0633	1.0556	1.0532	1.0459
10.0	1.0780	1.0682	1.0586	1.0545	1.0503
0.9/ (g dL⁻¹) Aqueous PVOH System					
2.00	1.0452	1.0445	1.0392	1.0360	1.0311
4.00	1.0481	1.0471	1.0459	1.0376	1.0325
6.00	1.0566	1.0536	1.0488	1.0439	1.0429
8.00	1.0587	1.0548	1.0506	1.0461	1.0436
10.0	1.0601	1.0559	1.0546	1.0486	1.0466
CuSO₄.5H₂O					
0.1/ (g dL⁻¹) Aqueous PVOH System					

2.00	1.0399	1.0388	1.0380	1.0331	1.0320
4.00	1.0455	1.0432	1.0395	1.0379	1.0339
6.00	1.0511	1.0468	1.0443	1.0407	1.0382
8.00	1.0530	1.0495	1.0486	1.0455	1.0421
10.0	1.0559	1.0535	1.0521	1.0508	1.0447

0.9/ (g dL⁻¹) Aqueous PVOH System

2.00	1.0468	1.0419	1.0396	1.0365	1.0348
4.00	1.0511	1.0462	1.0443	1.0425	1.0384
6.00	1.0546	1.0519	1.0506	1.0480	1.0407
8.00	1.0572	1.0558	1.0529	1.0502	1.0454
10.0	1.0602	1.0585	1.0561	1.0514	1.0504

ZnSO₄·7H₂O

0.1/ (g dL⁻¹) Aqueous PVOH System

2.00	1.0153	1.0150	1.0136	1.0111	1.0105
4.00	1.0208	1.0185	1.0162	1.0133	1.0118
6.00	1.0232	1.0204	1.0180	1.0175	1.0146
8.00	1.0259	1.0243	1.0231	1.0192	1.0189
10.0	1.0311	1.0305	1.0271	1.0251	1.0198

0.9/ (g dL⁻¹) Aqueous PVOH System

2.00	1.0435	1.0413	1.0376	1.0370	1.0361
4.00	1.0471	1.0459	1.0385	1.0371	1.0365
6.00	1.0501	1.0482	1.0451	1.0413	1.0378
8.00	1.0531	1.0518	1.0467	1.0461	1.0458
10.0	1.0584	1.0568	1.0542	1.0531	1.0518

Table 3. *B* coefficient of salts in aqueous polyvinyl alcohol systems at different temperatures.

Temperature / K	<i>B</i> coefficient / (mol ⁻¹ .L) ^{1/2} of salts in aqueous polyvinyl alcohol system / (g dL ⁻¹)	
Manganese Sulphate (MnSO₄.H₂O)		
	0.1	0.9
298	1.0774	1.2733
303	1.6206	1.3021
308	2.5584	3.2994
313	2.6960	4.1471
318	2.7616	5.5363
Copper Sulphate (CuSO₄.5H₂O)		
	0.1	0.9
298	0.9536	2.0262
303	1.8439	2.2222
308	1.9348	2.6106
313	2.9863	2.9072
318	3.4892	3.0530
Zinc Sulphate (ZnSO₄.7H₂O)		
	0.1	0.9
298	1.0762	1.3135
303	1.5786	2.6768
308	1.9329	3.0102
313	2.0487	3.1988
318	2.3829	3.6644

Table 4. A coefficient of salts in aqueous polyvinyl alcohol systems at different temperatures.

Temperature / K	A coefficient / $(\text{mol}^{-1} \cdot \text{L})^{1/2}$ of salts in aqueous polyvinyl alcohol system / (g dL^{-1})	
Manganese Sulphate ($\text{MnSO}_4 \cdot \text{H}_2\text{O}$)		
	0.1	0.9
298	-0.0851	0.3437
303	-0.3686	0.0320
308	-0.4952	-0.4102
313	-0.5766	-0.8162
318	-0.7921	-1.1918
Copper Sulphate ($\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$)		
	0.1	0.9
298	0.0290	0.1886
303	0.0250	0.0355
308	-0.1561	-0.0375
313	-0.8684	-0.2044
318	-0.9507	-0.4977
Zinc Sulphate ($\text{ZnSO}_4 \cdot 7\text{H}_2\text{O}$)		
	0.1	0.9
298	-0.1611	-0.3592
303	-0.2978	-0.3906
308	-0.6191	-0.3939
313	-0.7867	-0.5514
318	-0.8519	-0.5685

Table 5. Thermodynamic Parameters for 6×10^{-2} mol.dm⁻³ MnSO₄.H₂O in aqueous polyvinyl alcohol at different temperatures.

Temperature / K	Energy of activation (E _η) /kJ mol ⁻¹	Free energy change of activation (ΔG*) /kJ mol ⁻¹	Entropy change of activation (ΔS*) /J/mol.K
MnSO₄.H₂O			
0.1/ (g dL⁻¹) Aqueous PVOH System			
298		28.156	-24.59
303		28.258	-24.53
308	20.943	28.426	-24.67
313		28.564	-24.72
318		28.682	-24.70
0.9/ (g dL⁻¹) Aqueous PVOH System			
298		33.614	-11.16
303		33.587	-10.88
308	31.572	33.630	-10.85
313		33.786	-11.17
318		33.954	-11.53
CuSO₄.5H₂O			
0.1/ (g dL⁻¹) Aqueous PVOH System			
298		28.404	-16.70
303		28.625	-17.22
308	24.099	28.549	-16.69
313		28.587	-16.55
318		28.850	-17.12
0.9/ (g dL⁻¹) Aqueous PVOH System			
298		33.820	-14.27
303		33.855	-14.15
308	29.615	33.870	-13.97
313		34.182	-14.74
318		34.221	-14.63
ZnSO₄.7H₂O			
0.1/ (g dL⁻¹) Aqueous PVOH System			
298		28.222	-24.59

303		28.417	-24.53
308	22.770	28.321	-24.67
313		28.425	-24.72
318		28.839	-24.70

0.9/ (g dL⁻¹) Aqueous PVOH System

298		33.408	-11.16
303		33.738	-10.88
308	24.949	33.762	-10.85
313		33.892	-11.17
318		34.115	-11.53

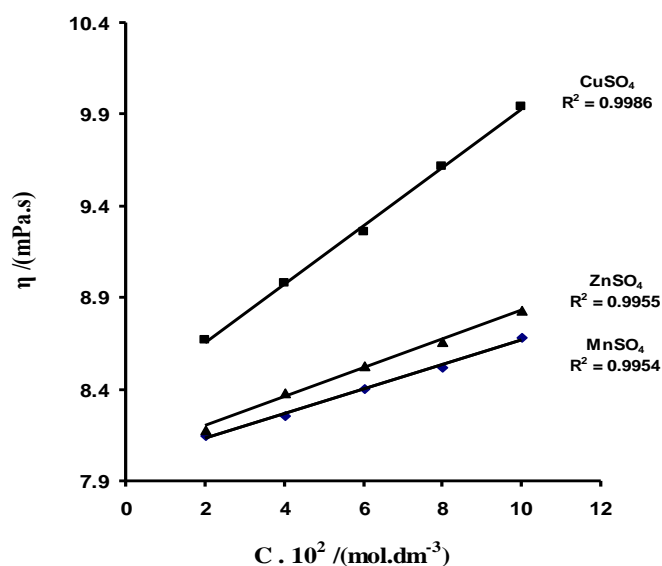


Fig. 1. Plot of viscosity versus concentration of salts at 303 K in 0.1 (g.dL⁻¹) aqueous PVOH system

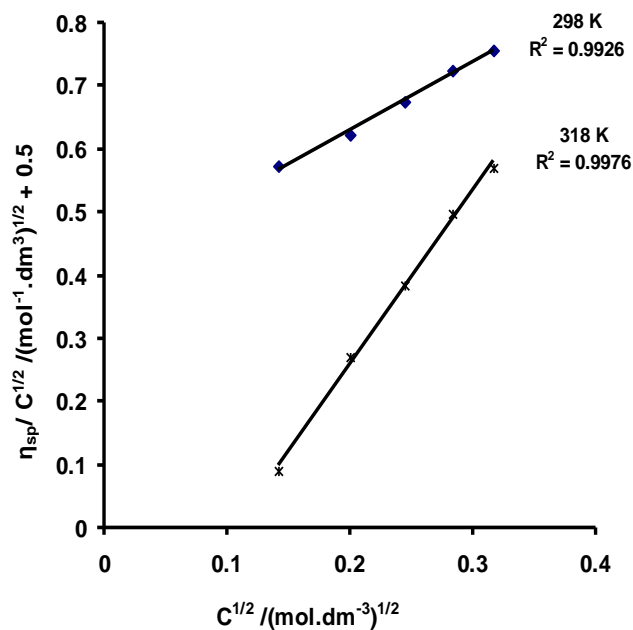


Fig. 2. Plot of $\eta_{sp}/C^{1/2}$ versus $C^{1/2}$ for $MnSO_4$ in $0.1 \text{ (g.dL}^{-1}\text{)}$ aqueous PVOH system at different temperatures

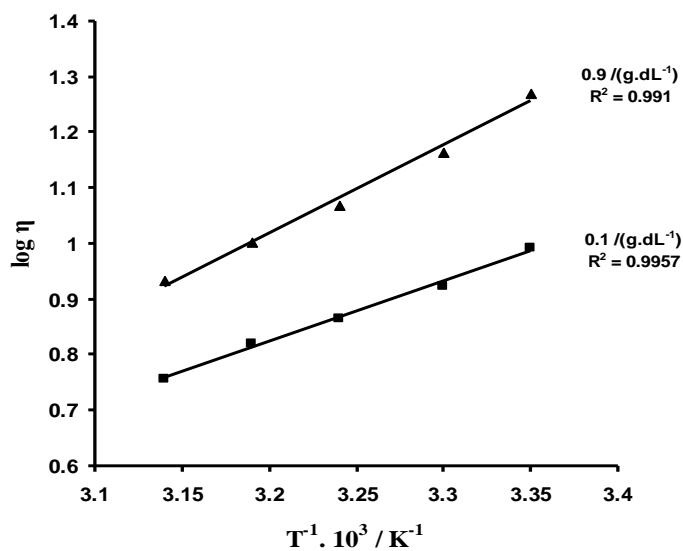


Fig. 3. Plot of $\log \eta$ versus T^{-1} of $6 \times 10^{-2} \text{ mol.dm}^{-3} MnSO_4.H_2O$ in 0.1 and $0.9 \text{ (g.dL}^{-1}\text{)}$ aqueous PVOH system.