Effect of Electrolyte on Ionic Interactions of Dilute Solution of Poly (vinyl alcohol) at Different Temperatures

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A viscometric method was used to determine the effect of sodium chloride on ionic interaction of dilute solutions of poly (vinyl alcohol) at different temperatures. Viscosities of 0.1 to 0.5 g dl^{-1} polyvinyl alcohol solutions were measured under the influence of sodium chloride (1 x 10^{-2} to 6 x 10^{-2} mol. dm^{-3}) at different temperatures (30 to 50 ± 0.1°C). Ion-ion and ion-solvent interactions were evaluated in terms of Jones Dole coefficient A and B respectively. Negative values of B-coefficient at 30 ± 0.1 °C show that sodium chloride behave as structure maker in dilute aqueous poly (vinyl alcohol) solution where as the positive values of B-coefficient reveals the average molecular weight of poly (vinyl alcohol). Activation parameters were also evaluated in terms of energy of activation (Eη*), change in free energy of activation (ΔG*) and change in entropy of activation (ΔS*) as a function of polymer composition, salt concentration and temperature.

Key words: Ion-ion interaction, Ion-solvent interaction, Average molecular weight, Activation parameters.

Introduction

Poly (vinyl alcohol) is an important linear polymer, which has many interesting properties from both physical and biological aspects. The polymer finds utility in dozens of applications across many industrial and consumer markets such as pharmaceutical, agricultural, chemicals, adhesive, fiber, textile, photography, paper manufacture and processing etc. Many researchers (Billmeyer 1962; Staikos and Bokias 1993; Uddin *et al* 2000 a & b) have investigated the characteristics of poly (vinyl alcohol) especially the physiochemical properties. However, little attention was given to the flow properties of this water-soluble polymer under the influence of electrolyte Shoemaker *et al* 1967; Gungor and Dilmac 1997).

Different relation and experimental techniques are used for characterizing the polymer solutions like viscometry, osmometry, and light scattering and IR studies. The viscometric method has been employed extensively due to its simplicity and high sensitivity to agregation. The viscosity behaviour of aqueous polyelectrolyte solutions is one of the most complicated problems of polymer solutions. As the polymers of both types natural and synthetic have generally the molecules, which are not spherical, but either rod-like or flexible chain-like (Ahmed *et al* 1988) and thus specific viscosity increases more rapidly with concentration. In dilute polymer solutions the change of reduced viscosity with concentration is general expressed by Huggins equation (Ahmed and Ahmed 1990).

$$(\eta_{sp}/C = [\eta] + K_H [\eta]^2C \text{--------------------}(1)$$

Where KH is known as Huggins constant, [η] is the intrinsic viscosity and C is the molar concentration. The plot of η_{sp}/C versus concentration when extrapolated to $Conc_{lim\cdots0}$, the

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intercept gives the value of intrinsic viscosity.

The average molecular weight of polymer has been estimated by the Mark-Houwink relation (Billmeyer 1962).

$$[\eta] = KM^a \text{......................................} (2)$$

Where 'M' is the average molecular weight and at a given temperature, 'K' and 'a' are constants for a specific polymer in a specific solvent.

For salt free polyelectrolyte solution, or for salt solution weaker than 1.0 x 10^{-3} M, the empirical Fuoss equation has been proposed (Staikos and Bokias 1993):

$$(\eta_{sp}/C)^{-1}=A^{-1} + (B/A)C^{1/2} \text{...............................} (3)$$

Where 'A' is the intrinsic viscosity [η] of the polyelectrolyte. The validity of this equation has been utilized as its gives extremely high value of [η].

Present study has been undertaken to find out the effect of electrolyte (NaC1) on interactions of dilute poly (vinyl alcohol) solutions temperatures. The ionic interactions of electrolyte with dilute poly (vinyl alcohol) solutions will be determined by the Jones-Dole equation (Jones and Dole 1929).

$$\eta_{as}/\sqrt{C} = A + B \sqrt{C} \text{..}(4)$$

Where η_{as} is the specific viscosity, C is the molar concentration, and A and B is the coefficient representing ion-ion and ion-solvent interactions respectively.

An attempt has also been made to evaluate the molecular weight of polymer and also thermodyanamic study of super molecular order in aqueous solution of poly (vinyl alcohol) under the influence of electrolyte.

Experimental

Poly (vinyl alcohol) (PVOH) used in this study was obtained from Merck. Double distilled water having a conductivity of

Table 1
Viscosities of sodium chloride solution at different temperatures

S.NO	[Salt]10^{-2} mol.dm^{-3}	Viscosites (mp)				
		30°C	35°C	40°C	45°C	50°C
		0.1 (g dl^{-1}) PVOH				
1	1.0	8.726	7.939	6.934	6.347	6.011
2	2.0	8.648	7.967	6.950	6.407	6.733
3	3.0	8.791	7.781	7.087	6.350	5.733
4	4.0	8.590	8.030	6.966	6.481	5.686
5	5.0	8.380	7.981	7.110	6.396	5.686
6	6.0	8.582	8.002	7.037	6.458	5.728
		0.2 (g dl^{-1}) PVOH				
1	1.0	9.017	8.636	7.355	6.692	6.287
2	2.0	9.056	8.783	7.425	6.676	6.287
3	3.0	9.259	8.824	7.516	6.665	6.470
4	4.0	9.126	8.774	7.550	6.840	6.218
5	5.0	9.003	8.945	7.755	6.873	6.231
6	6.0	9.263	8.960	7.765	6.830	6.561
		0.3 (g dl^{-1}) PVOH				
1	1.0	9.345	9.333	7.755	6.762	5.950
2	2.0	9.535	9.827	7.809	7.282	5.968
3	3.0	9.629	9.345	7.910	7.470	6.048
4	4.0	9.803	9.365	7.963	7.492	6.112
5	5.0	9.808	9.394	7.998	7.539	6.174
6	6.0	9.814	9.434	8.068	7.583	6.216
		0.4 (g dl^{-1}) PVOH				
1	1.0	10.334	9.801	7.498	5.658	6.988
2	2.0	10.188	9.618	7.432	5.756	7.028
3	3.0	10.082	9.909	7.454	6.828	7.368
4	4.0	10.073	9.721	7.467	6.844	7.087
5	5.0	10.041	9.517	7.675	6.807	7.095
6	6.0	10.020	9.801	7.686	6.804	7.844
		0.5 (g dl^{-1}) PVOH				
1	1.0	11.53	10.730	9.756	8.999	7.688
2	2.0	11.20	10.814	9.524	8.838	7.580
3	3.0	11.301	10.810	9.634	8.685	7.700
4	4.0	11.355	10.911	9.657	8.543	7.680
5	5.0	11.368	10.895	9.605	8.891	7.578
6	6.0	11.355	10.012	9.601	8.594	7.495

0.01 mS cm^{-1} was used for the preparation of 1 g dl^{-1} stock solution of poly (vinyl alcohol) at 80 °C and for all ranges of polymer solution from 0.1 g dl^{-1} to 0.5 g dl^{-1}. Sodium chloride solutions in the range of concentrations from 1.0×10^{-2} to 6.0×10^{-2} mol. dm^{-3} were prepared in different polymer solutions. All the solutions were prepared and used freshly to prevent the super molecular formation due to long-term storage.

The viscosity of 0.1 to 0.5 g dl^{-1} solution under the influence of constant concentration of electrolyte at different temperatures ranges from 30 to 50 ±0.1°C was determined by Ostwald viscometer (Techniconominal constant 0.1 Cs/s capillary ASTMAD445). The relative densities were measured by using relative density bottle having a capacity of 10 ml at different temperatures. Temperature was kept constant throughout the course of experiment with the help of thermostatic water bath (Haake-13 Germany). All the glassware used were of Pyrex A grade quality.

Table 2
Values of 'A' and 'B' Coefficient of the Jones-Dole equation for sodium chloride solution at 35°C and 50 °C.

[PVOH] (g dl^{-1})	Jones-Dole Coefficient at temperatures	
	A-coefficient (dm^3.mol^{-1})$^{1/2}$	B-coefficient (dm^3. mol^{-1})$^{1/2}$
	35°C	
0.1	0.3932	- 0.976
0.2	0.4972	- 0.737
0.3	-0.2130	0.819
0.4	-0.3640	0.924
0.5	-0.3409	1.476
	50°C	
0.1	0.5075	- 2.472
0.2	-0.1121	- 0.077
0.3	-0.3140	0.137
0.4	-03817	1.916
0.5	-0.0824	0.370

Table 3
Energy of activation (Eη*) free energy change of activation (ΔG*) and entropy change of activation (ΔS*) in different PVOH solutions at 35°C and salt concentrations.

S.NO	[Salt]10^{-2} mol.dm^{-3}	Eη* (K.J.mol^{-1})	ΔG* (K.J.mol^{-1})	ΔS* (J.deg^{-1} mol^{-1})
		0.1(g dl^{-1}) PVOH		
1	1.0	15.981	70.866	-178.49
2	2.0	16.636	70.874	-176.09
3	3.0	17.279	70.813	-173.8
4	4.0	16.485	70.892	-176.64
5	5.0	16.206	70.875	-174.25
6	6.0	16.650	70.881	-176.07
		0.2 (g dl^{-1}) PVOH		
1	1.0	15.967	72.372	-183.3
2	2.0	17.499	72.412	-178.30
3	3.0	6.235	72.421	-182.42
4	4.0	16.673	72.404	-180.94
5	5.0	16.209	72.450	-182.60
6	6.0	15.605	72.452	-184.56
		0.3 (g dl^{-1}) PVOH		
1	1.0	20.047	73.423	-173.30
2	2.0	19.227	73.416	-175.94
3	3.0	18.700	73.417	-177.65
4	4.0	18.930	73.417	-176.90
5	5.0	17.880	73.420	-180.32
6	6.0	18.370	73.427	-178.75
		0.4 (g dl^{-1}) PVOH		
1	1.0	16.830	74.187	-186.22
2	2.0	18.030	74.132	-182.10
3	3.0	16.43	74.202	-187.54
4	4.0	17.270	74.147	-184.66
5	5.0	16.870	74.086	-185.76
6	6.0	16.170	74.154	-188.26
		0.5 (g dl^{-1}) PVOH		
1	1.0	14.625	74.931	-195.81
2	2.0	16.245	74.943	-190.58
3	3.0	16.007	74.934	191.32
4	4.0	17.213	74.949	187.45
5	5.0	17.182	74.937	187.51
6	6.0	17.523	74.956	186.47

Table 4
Values of free energy change of activation (ΔG^*) and entropy change of activation for sodium chloride (6.0 x 10^{-3} mol. dm^{-3}) in poly (vinyl alcohol solutions at different temperatures

Temperature °C	values of free energy change (ΔG^*) (KJ.mol^{-1})		
	0.1 (g dl^{-1})	0.3 (g dl^{-1})	0.5 (g dl^{-1})
30	69.904	72.334	73.813
35	70.881	73.427	74.956
40	71.700	74.214	75.822
45	72.624	75.243	76.742
50	73.450	75.900	77.587
	Values of entropy change (ΔS^*) (J.deg^{-1} mol^{-1})		
30	-175.75	-178.75	-186.47
35	-176.07	-178.75	-186.47
40	-175.88	-178.41	-186.25
45	-176.01	-178.84	-186.22
50	-175.85	-178.11	-185.95

Fig 2. Plot of η_{as}/ C versus concentration for PVOH at 45°C.
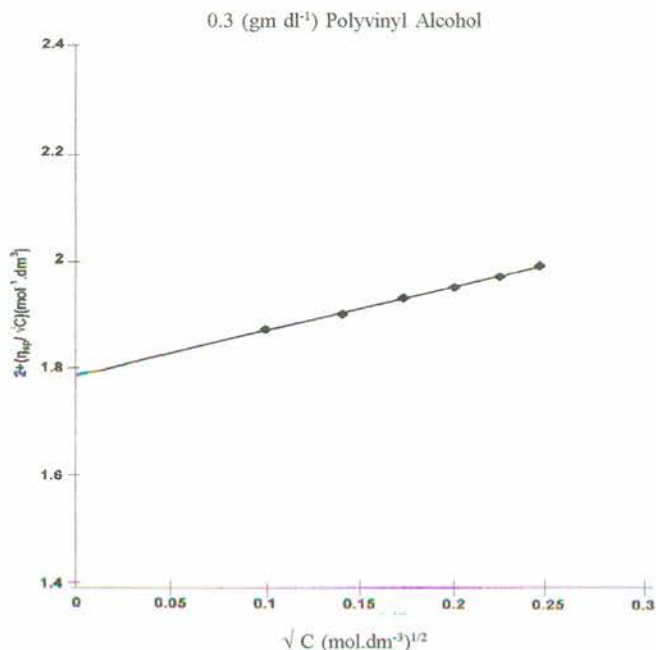
Fig 1. Plot of η_{as}/ $\sqrt{C}$ versus $\sqrt{C}$ for NaCl in 0.3 (g dl^{-1}) PVOH at 35°C.
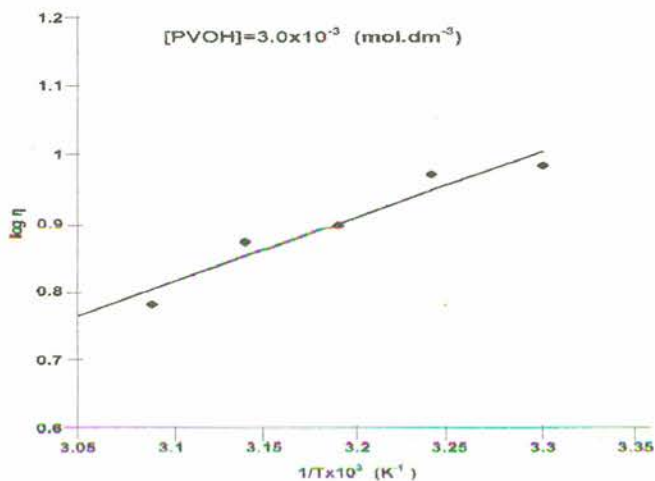
Fig 3. Plot of log η versus 1/T for 0.3 (g dl^{-1}) PVOH at concentration of sodium chlorid $3x10^{-2}$ mol.dm^{-3}).

Results and Discussion

The values of relative viscosities were used to determine the specific viscosities of the sample at different temperatures. The viscometric behaviour of aqueous dilute solution of poly (vinyl alcohol) of varying concentration ranges from 0.1 to 0.5 g^{-1} with electrolyte solutions concentration from $1.0x10^{-2}$ to $6.0x10^{-2}$ mol. dm^{-3} at temperatures 30 to 50±0.1°C has been studied. Results obtained for viscosity data are tabulated in Table 1. Results show that there is a rapid increase in concentration of poly (vinyl alcohol) with the increase in conc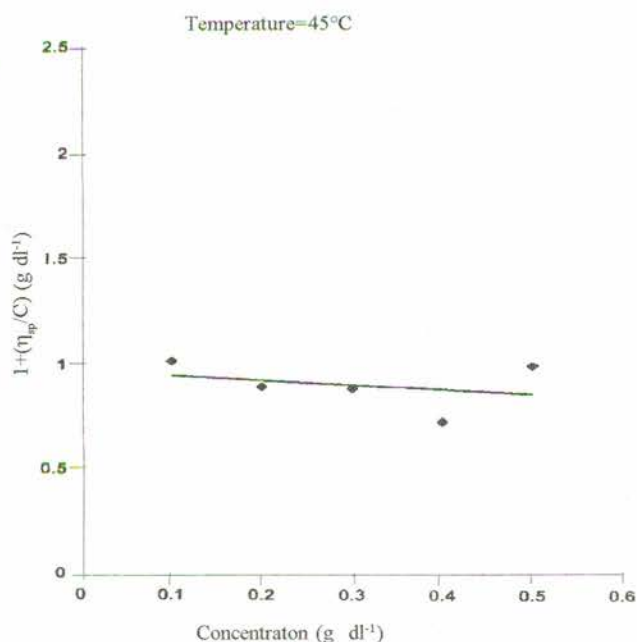entration of poly (vinyl alcohol) at constant concentration of sodium chloride and at fix temperature. The viscosity data decrease with rise of temperature at fix concentration of electrolyte and constant concentration of poly (vinyl alcohol) But an increase in viscosities was observed with some variations at constant poly (vinyl alcohol) concentration and at fix temperature. The increases in viscosity with increase in poly (vinyl alcohol) concentration show that polymer molecules may associate either by inter or intramolecular forces in aqueous polymer solvent. Electrostatic, hydrophobic interactions as well as Van der Waals forces and hydrogen bonding are the sources responsible for the formation of association in polymer solution (Khan *et al* 1996). Mainly the hydrodynamic

properties of molecular weight of poly (vinyl alcohol) led to the conclusion that the experimental value of average molecular weight of polymer is in accordance with the actual value. Ion-ion and ion-solvent interactions of electrolyte in dilute poly (vinyl alcohol) solution were evaluated in terms of A and B-coefficients of Jones Dole equation (Jones and Dole 1992).

The results for A and B coefficients representing ion-ion and ion-solvent interactions for sodium chloride in various composition of poly (vinly alcohol) are tabulated in Table 2. The values of A and B coefficients are determined from the intercept and slope of the linear plot of $\eta_{sp}/\sqrt{C}$ versus square root of concentration by least square method. Representative plot of $\eta_{sp}/\sqrt{C}$ againt square root of concentration for sodium chloride in 0.3 (g dl⁻¹) poly (vinyl alcohol) at 35°C is shown in Fig 1. The lower values of A-coefficients with rise in temperature in dilute poly (vinyl alcohol) show that more violent thermal agitation at higher temperature results in reduction of attraction forces. There is some variations observed in A-coefficients may be attributed to the size of ions which differ in their degree of hydration. B-coefficient in the Jones-Dole equation represents the ion-solvent interaction and is the measure of interaction of the added electrolyte in a particular medium (Jenkins *et al* 1993, Uddin *et al* 2000 a & b). Value of B-coefficient can be obtained by the slope of the plot of $\eta_{sp}/\sqrt{C}$ versus square root of concentration. B-coefficient is a highly specific property of solute concerned with the additivity of ionic concentrations to the viscosity. Thus, it can be determined by adding individual polymer solutions are very sensitive to associations. With the rise of temperature the viscosity of polymer solutions decreases because the super molecules break and due to less bulky particles the rate of flow is large and results in decrease in viscosity. It shows that the temperature dependence of polymer viscosity is determined by the dimensions of not entire macromolecules, but of their small parts segments, which are kinetically independent structure elements of a polymer. These segments shift from one position to another under the action of thermal motion, are responsible for the change in viscosity of polymer.

The plots of $\eta_{sp}/\sqrt{C}$ versus concentration yield intrinsic viscosity [η]value at 30±0.1°C temperature according to equation (1). The values of reduced viscosity for each sample of 0.1 to 0.5 (g dl⁻¹) were studied. The representative plot of $\eta_{sp}/\sqrt{C}$ versus concentration of polymer at 30 ±0.1°C is shown in Fig 2. The Mark-Houwink equation was used for estimation of average molecular weight of poly (vinyl alcohol) in water at 30±0.1°C.

$$[\eta] = 33.88 \times 10^{-5} M^{0.716} \quad \text{.................................. (5)}$$

The average molecular weight was found approximately 34588, where as the actual was 35400. The compression contribution of the solute constituent ion is shown as:

$$B = Z^+ B^- + Z^- B^+ \quad \text{.................................... (6)}$$

where Z is the ionic valence and B is the ionic viscosity. When salt is added to dilute poly (vinyl alcohol) solution, due to the changed nature of the particles, the cluster model and dilation properties are altered and as a result rheological properties is obtained (Khan and Kanwal 1997).

The values of apparent activation energy $E\eta^*$ of viscous flow obtained by plotting logη versus 1/T for different concentration of poly (vinyl alcohol), according to the Arrhenius equation (Baloach *et al* 1986, Ahmed *et al* 1990)

$$\eta = A^{E\eta/RT} \quad \text{... (7)}$$

Where A is pre-exponential factor, R is gas constant and T is absolute temperature. The representative plot of log η against 1/T for 0.3 (g dl⁻¹) poly (vinyl alcohol) at concentration of sodium chloride 3.0×10^{-2} (mol.dm⁻³) is shown in Fig 3. Result for activation energy up to 0.3 (g dl⁻¹) polymer which show that with increase in kinetic energy, the forces of attraction reduce the result decrease in viscosity. At high observed. The high value of energy of activation is due to strong structure molecules. Because the process of degradation of structure and orientation of macromolecules occur during flow, so the positive value of activation energy are obtained.The free energy of activation is calculated form the relation (Khan *et al* 1999, Uddin *et al* 2000 a & b):

$$\Delta G^* = RT \ln \eta \, V/hN \quad \text{....................................... (8)}$$

Where h is Planck's constant, N is Avogadro's number and V is the volume of one molecule of solution particles. Result for free energy change of activation (ΔG^*) are summarized in Table 3 and 4. Results show that the free energy of viscous flow increases regularly with rise in temperature, but the effect with increase in the concentration of electrolyte is irregular, the value of free energy change of activaion increases with some variation. The high value of free energy change at high temperature and high concentration of polymer, with increase in electrolyte concentration show that in dilute solution at lower temperature associations are weaker and are easily come over during flow process. Entropy is a measure of disorderness expressed by the relation:

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

Where ΔS^* is the change in entropy of activation. The results listed in Table 3 an 4 show the negative value of entropy change of activation was observed for viscous flow of poly (vinyl alcohol) solution. High negative value are obtained with the rise of temperature as well as with increase in concentration of polymer and electrolyte. It shows that the uncoiling and reorientation of macromolecules prevails, the system becomes more ordered in the course of flow and the entropy change of activation is negative. It also confirms the structure making nature of electrolyte is more viscous poly (viyl alcohol) solution.

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