Viscometric Study of Interactions of Poly(Vinyl Alcohol) with Different Solvents at Various Temperatures

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Abstract. Viscosities of poly(vinyl alcohol) in aqueous-methanol system (10% to 50%, v/v) and aqueous-butanol system (1% to 5%, v/v) were measured at different temperatures (25 to 45 ± 0.1 °C) with different concentrations of poly(vinyl alcohol) ranging between 3.0 to 9.0 g/l. Solute-solvent interactions were found affected by changes in the compositions of solvents and the temperature. Various thermodynamic parameters were determined by the change in viscosity data as a function of temperature. It was observed that the free energy change of activation *(ΔG*)* increased regularly as the concentration of poly(vinyl alcohol) increased, but the effect with rise in temperature was uncertain. However, the values of ΔG* of poly(vinyl alcohol) in aqueous-butanol were found to be higher than aqueous-methanol, which showed that associations were higher in aqueous-methanol, as compared with aqueous-butanol solutions. The values of entropy change of activation *(ΔS*)* of viscous flow increased with increase in the concentration of the polymer. The high negative values of entropy change of activation *(ΔS*)* showed that the solution of the polymer was more ordered in initial state than the activated one.

Keywords: polymer, viscosity, structural analysis, Mark-Houwink equation, thermodynamic parameters, poly(vinyl alcohol)

Introduction

Poly(vinyl) alcohol is a film-forming and the largest volume synthetic water-soluble resin produced in the world. The resin has wide range of applications in several industries. Viscosity measurement is a suitable tool for a rapid and reliable characterization of the polymer (Rivas *et al.,* 2003; Saeed *et al.,* 2002; Lyoo *et al.,* 2001; Liu *et al*., 1997; Nakamae *et al.,* 1997; Wang *et al.,* 1997). Solute-solvent and solvent-solvent interactions are the measure of interactions between the solute and solvent, and order and disorder (Johansson *et al*., 2003; Pekel and Guven, 2002; Shaikh *et al*., 1998; Ahmed *et al*., 1990). Literature shows different behaviour of polymer viscosity with respect to concentration and molecular weight. In dilute polymer solutions, changes occur in reduced viscosity with the concentration of the solvent (Lewandowska *et al.,* 2001). Viscosity data as the function of concentration have been extrapolated to infinite dilution by means of the Huggin's equation (Lewandowska *et al*., 2001; Ahmed and Ahmed, 1990), which gave the value of intrinsic viscosity [η]:

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

where:

η_{sp} = specific viscosity

C = concentration

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[η] = intrinsic viscosity

K_H = Huggin's constant, showing solute-solvent interactions

Specific viscosity is given by:

$$\eta_{sp} = \eta_{rel} - 1 \quad \text{(dimentionless)} \qquad (2)$$

where:

η_{rel} = relative viscosity, given by:

$$\eta_{rel} = \eta / \eta_o \quad \text{(dimentionless)} \qquad (3)$$

where:

η and η_o = viscosities of solution and solvent, respectively

The thermodynamic properties show that the intrinsic viscosity [η] and the Huggin's constant (K_H) are both influenced by changes of solvent power and temperature (Ahmed and Ahmed, 1990). The effect of temperature is expressed by using the following expression:

$$\eta = A \exp (\Delta E_\eta^* / RT) \qquad (4)$$

where:

A = frequency factor

ΔE_η^* = energy of activation

R = gas constant

T = temperature

The present investigation deals with spectral and thermodynamic study of poly(vinyl alcohol) in aqueous-methanol and aqueous-butanol mixtures at different temperatures. Various thermodynamic parameters, such as energy of activation (E_η*), free energy change of activation (ΔG*), and enthalpy change of activation (ΔS*) for the viscous flow of poly(vinyl alcohol) in aqueous-methanol and aqueous-butanol solutions were studied as the function of temperature. The activation energy of flow gave information about the behaviour of the polymer in different solvents and the structural analysis helped to study the degradation process of poly(vinyl alcohol) (Ahmed *et al.*, 1998; Lu *et al.*, 1993).

Materials and Methods

Poly(vinyl alcohol), 98% (E. Merck) was used without furthur purification. Methanol and butanol (E. Merck) were used for the prepration of stock-solutions. Double distilled water having a conductivity of 0.06 μS/cm was used. All the glassware used was of Pyrex "A" grade quality. Ostwald viscometer with 0.1 (Cs/S) capillary (ASTM-D445) was used to measure the relative viscosities of solutions. The densities were measured by using relative density bottles having the volume capacity of 10 ml. Thermostatic waterbath (Haak W 13, Germany) was used to maintain the temperature of solutions constant throughout the experiment.

Aqueous solution of the polymer was prepared by dissolving 10 g of poly(vinyl alcohol) in known volume of double distilled hot water (80±0.1 °C) with continuous stirring till all the polymer dissolved. The solution was then cooled to room temperature and made-up to the mark. Same process was adopted to prepare solutions of different percentages of aqueous-methanol and aqueous-butanol solvents. The concentrations of poly(vinyl alcohol) prepared in aqueous-methanol and aqueous-butanol solvents ranged from 3.0 to 9.0 g/l. The relative viscosities of all the solutions were measured at various temperatures from 25 to 45±0.1 °C. A known volume of solvent and solution was placed in the viscometer and the temperature was kept constant throughout the course of experiment by placing viscometer in a thermostatic waterbath for about 15 min to attain the required temperature. The time flow was recorded with the help of a stopwatch having least count of 0.25 sec. The densities of solvents and solutions of poly(vinyl alcohol) in aqueous-methanol and aqueous-butanol were measured. The mass of solvent and solutions were determined at different temperatures and the densities were calculated by using mass per unit volume relationship. Reproducibility of the results was checked by taking each measurement thrice. The uncertainty in the experimental data for density and viscosity data was found to be ±0.001 g/l and ±0.002 mPa.s, respectively.

Results and Discussion

The viscosities and densities of poly(vinyl alcohol) in solvents, such as aqueous-methanol (10% to 50%, v/v) and aqueous-butanol (1% to 5%, v/v) solutions were determined in the concentrations ranging from 3.0 to 9.0 g/l at different temperatures (25 to 45±0.1 °C). The results are given in Tables 1 and 2. The viscosity data indicated that there was a regular increment in the viscosity of solution with the increase in concentration of poly(vinyl alcohol) and also with concentration of solvents. The values of viscosities were found to be relatively higher in the aqueous-methanol as compared to the aqueous-butanol. This indicated that poly(vinyl alcohol) showed more interaction with aqueous-methanol, whereas in the bulkier solvent, aqueous-butanol, the polymer showed less interaction, which may be due to a long chain of alkyl groups. The results also show that the viscosity of poly(vinyl alcohol) decreased as the temperature increased, which was due to the breaking-down of molecular structure (Rasheed *et al.,* 2002; Ahmed *et al.,* 1998).

Solute-solvent interactions were evaluated in terms of Huggin's constant (K_H) by using Huggin's equation (Ahmed and Ahmed, 1990). The values of intrinsic viscosity [η] and Huggin's constant (K_H) were determined by the relation (1) and results are given in Tables 3 and 4, respectively. The slope and intercepts of linear plot of η_{sp}/C versus C gave the values of Huggin's constant (K_H) and intrinsic viscosity [η], respectively (Fig.1). Increase in the values of solute-solvent interactions with the rise of temperature, with some variations, indicated that as the temperature rose, the solute-solvent interaction became stronger. Decrease in the solute-solvent interactions with the rise of temperature represented the structure promoting effect due to the ordering and sort of enforcement of hydrogen bonded structure around the solute (Liu *et al.*, 1997). The values of intrinsic viscosity were plotted against the temperature giving a straight line as shown in Fig. 2. The decrease in values of intrinsic viscosity and increase in the Huggin's constant (K_H) with the rise in temperature indicated that as the temperature of solution increased, the size of the individual polymer molecules (monomolecules) decreased and the interaction among polymer molecules increased. It was also observed that with the increase in alcohol content, from 10% to 30% aqueous-methanol and 1% to 3% aqueous-butanol, the Huggin's constant (K_H) decreased and then increased and high values were found in 50% aqueous-methanol and 5% aqueous-butanol. Some negative values of the Huggin's constant (K_H) were obtained in 30% aqueous-methanol, which were meaningless and hence it was concluded that at low concentration of alcohol, the solute-solvent interactions were higher, while at high concentration of alcohol it behaved as poor solvent.

Table 1. Viscosities of various concentrations of poly(vinyl alcohol), ranging between 3.0 to 9.0 g/l in aqueous-methanol, at different temperatures

PVOH conc (g/l)	Viscosity (mPa.s)				
	25 °C	30 °C	35 °C	40 °C	45 °C
(10%, v/v) aqueous-methanol					
3.0	12.254 +0.002	11.518 +0.002	10.453 +0.003	09.101 +0.001	08.379 +0.001
5.0	14.164 +0.002	13.244 +0.004	11.946 +0.002	10.267 +0.003	9.446 +0.001
7.0	17.063 +0.003	15.285 +0.001	13.888 +0.002	12.026 +0.004	11.150 +0.001
9.0	19.794 +0.002	17.745 +0.001	15.978 +0.002	13.909 +0.001	12.728 +0.002
(20%, v/v) aqueous-methanol					
3.0	14.609 +0.001	13.496 +0.001	12.074 +0.001	10.418 +0.002	9.592 +0.002
5.0	17.157 +0.003	15.530 +0.001	14.008 +0.002	12.286 +0.001	11.411 +0.001
7.0	20.168 +0.002	18.301 +0.001	15.689 +0.001	14.429 +0.001	13.094 +0.001
9.0	23.500 +0.001	20.223 +0.003	19.643 +0.003	17.304 +0.001	15.570 +0.001
(30%, v/v) aqueous-methanol					
3.0	15.671 +0.001	13.662 +0.002	12.524 +0.001	11.414 +0.001	10.042 +0.002
5.0	17.552 +0.002	15.841 +0.001	14.503 +0.001	13.554 +0.002	10.703 +0.003
7.0	18.651 +0.002	16.932 +0.002	14.946 +0.001	14.476 +0.001	11.729 +0.001
9.0	21.064 +0.001	19.049 +0.001	18.758 +0.002	17.452 +0.002	12.261 +0.001
(40%, v/v) aqueous-methanol					
3.0	16.305 +0.001	14.381 +0.001	13.166 +0.001	12.173 +0.003	10.083 +0.002
5.0	18.542 +0.002	17.124 +0.001	15.282 +0.002	13.617 +0.003	11.890 +0.001
7.0	22.230 +0.001	20.183 +0.003	17.425 +0.001	15.444 +0.001	13.556 +0.001
9.0	26.582 +0.002	23.132 +0.002	20.233 +0.003	17.682 +0.002	15.618 +0.002
(50%, v/v) aqueous-methanol					
3.0	16.580 +0.002	13.896 +0.001	12.021 +0.001	11.245 +0.001	9.557 +0.003
5.0	20.908 +0.002	16.861 +0.001	13.961 +0.001	13.166 +0.004	11.186 +0.001
7.0	26.852 +0.002	20.643 +0.002	16.374 +0.002	15.341 +0.002	11.175 +0.002
9.0	33.114 +0.001	26.952 +0.002	19.248 +0.002	17.983 +0.003	15.060 +0.001

PVOH: poly(vinyl alcohol); ± standard deviation

Table 2. Viscosities of various concentration of poly(vinyl alcohol), ranging between 3.0 to 9.0 g/l in aqueous-butanol, at different temperatures

PVOH conc (g/l)	Viscosity (mPa.s)				
	25 °C	30 °C	35 °C	40 °C	45 °C
(1%, v/v) aqueous-butanol					
3.0	11.241 +0.001	10.045 +0.001	8.554 +0.002	7.831 +0.001	7.084 +0.001
5.0	12.862 +0.001	11.612 +0.002	9.779 +0.001	9.052 +0.002	8.175 +0.001
7.0	14.806 +0.002	13.506 +0.001	11.898 +0.002	10.470 +0.003	9.401 +0.001
9.0	16.942 +0.002	14.792 +0.002	13.095 +0.001	11.849 +0.001	10.834 +0.002
(2%, v/v) aqueous- butanol					
3.0	10.904 +0.001	10.335 +0.001	8.902 +0.002	8.057 +0.003	7.318 +0.002
5.0	12.391 +0.002	11.923 +0.002	10.215 +0.002	9.356 +0.001	8.461 +0.001
7.0	14.962 +0.002	13.820 +0.001	11.583 +0.002	10.536 +0.001	9.684 +0.001
9.0	17.072 +0.002	15.721 +0.001	13.584 +0.001	12.012 +0.002	10.976 +0.001
(3%, v/v) aqueous- butanol					
3.0	11.891 +0.001	10.802 +0.002	9.445 +0.002	8.747 +0.003	7.473 +0.002
5.0	13.362 +0.002	12.234 +0.001	10.666 +0.001	9.766 +0.001	8.652 +0.001
7.0	15.621 +0.001	14.292 +0.002	12.332 +0.002	11.515 +0.001	9.939 +0.001
9.0	18.043 +0.002	16.491 +0.002	14.423 +0.002	13.292 +0.002	11.372 +0.002
(4%, v/v) aqueous- butanol					
3.0	12.064 +0.001	10.801 +0.001	9.314 +0.001	8.973 +0.003	7.682 +0.002
5.0	13.489 +0.001	12.234 +0.001	10.842 +0.002	9.936 +0.001	8.940 +0.001
7.0	15.483 +0.002	14.292 +0.003	11.604 +0.001	11.564 +0.001	10.365 +0.002
9.0	18.542 +0.003	16.931 +0.001	14.557 +0.003	13.442 +0.002	11.941 +0.001
(5%, v/v) aqueous- butanol					
3.0	12.235 +0.001	10.961 +0.001	9.726 +0.001	9.029 +0.001	8.029 +0.001
5.0	14.263 +0.001	12.853 +0.002	11.383 +0.002	10.203 +0.002	9.229 +0.002
7.0	16.708 +0.002	15.047 +0.003	13.193 +0.002	11.818 +0.002	10.944 +0.001
9.0	19.649 +0.001	17.258 +0.002	15.458 +0.002	13.715 +0.001	12.804 +0.002

PVOH: poly(vinyl alcohol; ± standard deviation

Table 3. Values of intrinsic viscosity [η] of poly(vinyl alcohol) in aqueous alcohols at various concentrations and temperatures

Temp (°C)	Intrinsic viscosity (g/l)				
	Aqueous-methanol (%, v/v)				
	10%	20%	30%	40%	50%
25	0.6881 ±0.001	1.0065 ±0.001	1.2375 ±0.002	0.6842 ±0.002	0.7975 ±0.001
30	0.6636 ±0.004	0.8304 ±0.002	1.0291 ±0.002	0.5881 ±0.001	0.4810 ±0.001
35	0.6261 ±0.001	0.6735 ±0.001	1.0196 ±0.002	0.5622 ±0.001	0.4526 ±0.004
40	0.5845 ±0.002	0.6333 ±0.002	0.6785 ±0.004	0.4612 ±0.002	0.5611 ±0.004
45	0.487 ±0.003	0.5551 ±0.004	0.5745 ±0.001	0.4208 ±0.002	0.5330 ±0.002
	Aqueous-butanol (%, v/v)				
	1%	2%	3%	4%	5%
25	0.5335 ±0.001	0.5474 ±0.001	0.6832 ±0.002	0.6355 ±0.002	0.6073 ±0.001
30	0.5960 ±0.001	0.4731 ±0.001	0.7745 ±0.001	0.7091 ±0.001	0.6712 ±0.001
35	0.5480 ±0.002	0.5152 ±0.002	0.6950 ±0.001	0.6555 ±0.002	0.6641 ±0.002
40	0.5610 ±0.001	0.5925 ±0.003	0.7612 ±0.001	0.6015 ±0.001	0.5985 ±0.001
45	0.4992 ±0.002	0.5305 ±0.001	0.6753 ±0.002	0.4885 ±0.001	0.6095 ±0.001

± standard deviation

Table 4. Values of Huggin's constant (K_H) of poly(vinyl alcohol) in aqueous alcohols at various concentrations and temperatures

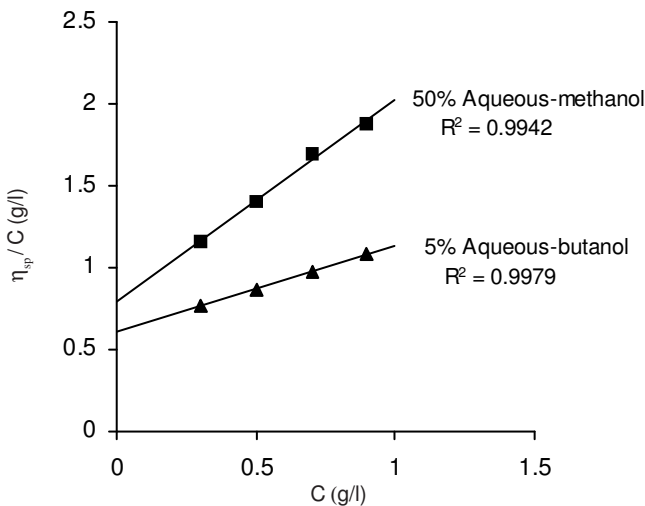| Temp (°C)	Huggin's constant (K_H)				
	Aqueous-methanol (%, v/v)				
	10%	20%	30%	40%	50%
25	0.3391 ±0.001	0.0852 ±0.002	-0.6323 ±0.002	0.3682 ±0.002	1.2251 ±0.001
30	0.3645 ±0.001	0.3560 ±0.002	-0.2910 ±0.001	0.5695 ±0.001	1.1941 ±0.001
35	0.3745 ±0.001	0.5653 ±0.001	0.0536 ±0.002	0.4362 ±0.002	0.5752 ±0.002
40	0.4052 ±0.002	0.5173 ±0.003	0.2156 ±0.001	0.4341 ±0.001	0.5601 ±0.002
45	0.6532 ±0.002	0.6510 ±0.002	0.3554 ±0.001	0.3420 ±0.002	0.5350 ±0.003
	Aqueous-butanol (%, v/v)				
	1%	2%	3%	4%	5%
25	0.4150 ±0.001	0.3754 ±0.001	0.3210 ±0.001	0.3455 ±0.001	0.5360 ±0.002
30	0.3051 ±0.001	0.3431 ±0.002	0.3050 ±0.001	0.3124 ±0.001	0.4417 ±0.003
35	0.4220 ±0.003	0.3551 ±0.002	0.3505 ±0.003	0.3452 ±0.002	0.4613 ±0.002
40	0.3914 ±0.001	0.3412 ±0.002	0.3421 ±0.002	0.3851 ±0.001	0.3652 ±0.002
45	0.4250 ±0.004	0.4053 ±0.003	0.4061 ±0.001	0.4153 ±0.003	0.5054 ±0.001

± standard deviation

Fig. 1. The slope and intercepts of the linear plot of η_{sp}/C against concentration of poly(vinyl alcohol) at 25 °C ; η_{sp}: intrinsic viscosity, C: concentration of poly(vinyl alcohol).

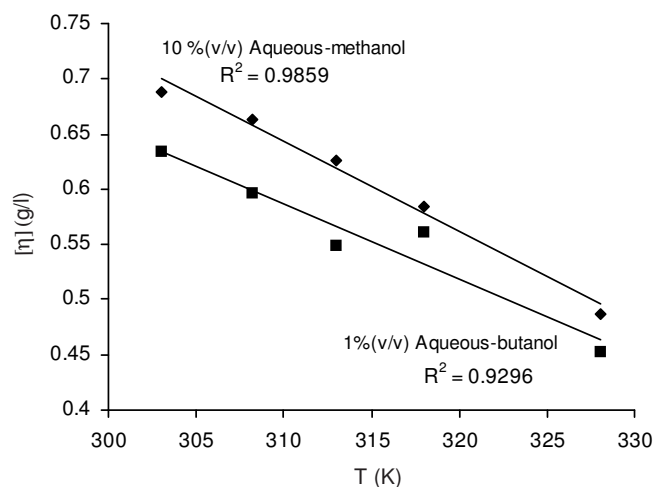**Fig. 2.** The slope of intrinsic viscosity ([η]), against temperature (T).

By using Mark-Houwink equation (Wang *et al*., 1997; Ahmed and Ahmed, 1990), average molecular weight of the polymer can be calculated by the following expression:

$$[\eta] = K M_v^{\alpha} \tag{5}$$

where:

M_v = average molecular weight

K and α = emperical constants characteristic of a polymer pair

The values of K and a for poly(vinyl alcohol) at 30 $^\circ$C are 33.88×10^{-5} and 0.716, respectively (Takada *et al*., 1998; Nagy, 1993). The average molecular weight of poly(vinyl alcohol) was found to be approximately 34588 Da (Saeed *et al.,* 2002).

Various thermodynamic parameters for the poly(vinyl alcohol) solutions were determined as the function of temperature, and concentrations of the polymer and the solvent. The results for activation energy, free energy change of activation and entropy change of activation for aqueous-methanol and aqueous-butanol at 35 $^\circ$C as the function of concentration of poly(vinyl alcohol) and solvent concentrations are given in Tables 5 and 6, respectively. The energy of activation for flow process gave information on the strength of the structure, while the entropy change of activation on its order. High positive values of activation energy showed the process of degradation of structure and orientation of macromolecules occurred during flow. The activation energy in aqueous-methonol and aqueous-butanol at various concentrations of poly(vinyl alcohol) solutions were determined by plotting logarithmic values of kinematic viscosity (log η) against 1/T (Fig. 3). It was found that the energy of activation increased with the increase in pecentage composition of methanol and decreasd with increase in the percentage concentration of butanol. The results show that the energy of activation is also influenced by the nature of solvents as the associations and dipole interactions increased with increase in aliphatic chain of alcohol (Okaya *et al*., 1992). The viscosities of the polymer as a function of temperature can be determined by the dimensions of not the entire macromolcules, but of their small part-segments, which are kinetically independent structural elements of the polymer. It is the segment that shifts from one position to another under the action of thermal motion (Rasheed *et al*., 2002).

Free energy change of activation (ΔG^*) of viscous flow increased with increase in the concentration of poly(vinyl alcohol). The values of free energy change of activation (ΔG^*) were evaluated by using the following formula (Saeed *et al*., 2004):

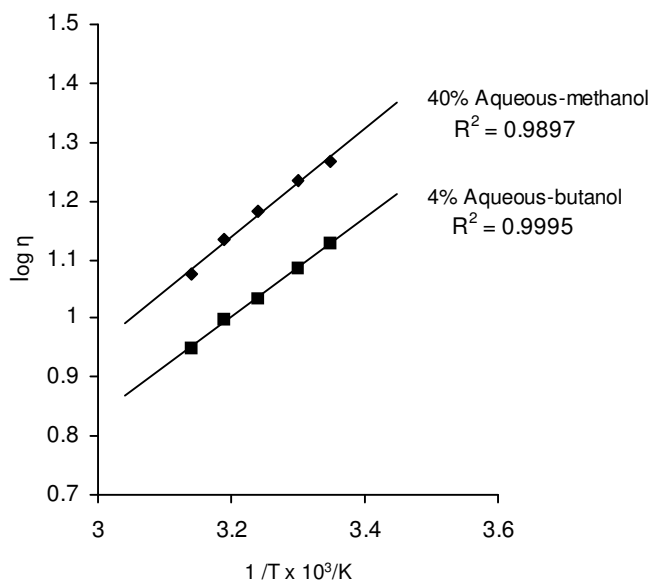$$\Delta G^* = 2.303 \, RT \log (\eta / 10^{-3}) \tag{6}$$

Fig. 3. The graph between the kinematic viscosity (log η) and 1/T for 5 g/l poly(vinyl alcohol) in aqueous alcohol systems.

The values of free energy change (ΔG^*) of viscous flow increased by increasing the concentration of poly(vinyl alcohol) in aqueous-methanol and aqueous-butanol solvents. It showed that in dilute solution the associations were weaker and they were easily overcome during flow (Takada *et al*., 1998; Nagy, 1993), whereas in high concentration of poly(vinyl alcohol) the associations were stronger and showed less effect during the flow process resulting in the high values of free energy change of activation. Increase in the alcohol content did not show much affect on the values of ΔG^*. Moreover, the values of ΔG^* were found a little higher in aqueous-methanol as compared with aqueous-butanol showing that the interactions of poly(vinyl alcohol) and alcohol molecules were determined not only by H-bonding between OH groups but also by hydrophobic interactions between the non-polar basic chain of the polymer and the alkyl chain of alcohol molecules (Okaya *et al*., 1992). This indicated that aqueous-methanol was a better solvent than aqueous-butanol which caused the strong supermolecular structure to collapse. Ahmed *et al.* (1990) made thermodynamic study for viscous flow of poly(vinyl alcohol) in aqueous-propyl alcohol and reported the value of ΔG^* as approximately 17 kJ/mol for 2 kg/m^3 of poly(vinyl alcohol) concentration in 5% aqueous-propyl alcohol, which relatively increased with increase in the concentration of poly(vinyl alcohol), propyl alcohol and also with rise in temperature. They suggested that aqueous-propyl alcohol was a better solvent than water and solute-solvent interactions were greater for poly(vinyl alcohol) in 20% aqueous-propyl alcohol and smaller in other cases.

Table 5. Thermodynamic parameters for viscous flow of different concentrations of poly(vinyl alcohol) in aqueous alcohols at 35 °C

PVOH conc (g/l)	Energy of activation $(E_{\eta*})$ (kJ/mol)	Free-energy change of activation (ΔG^*) (kJ/mol)	Entropy change of activation $(-\Delta S^*)$ (J/mol/K)
Aqueous-methanol (10%, v/v)			
3.0	15.977 ±0.001	23.702 ±0.001	25.080 ±0.002
5.0	17.102 ±0.002	24.044 ±0.001	22.538 ±0.002
7.0	17.481 ±0.001	24.430 ±0.002	22.560 ±0.001
9.0	18.107 ±0.003	24.789 ±0.001	21.696 ±0.001
Aqueous-butanol (3%, v/v)			
3.0	18.273 ±0.002	23.443 ±0.003	16.784 ±0.001
5.0	17.594 ±0.001	23.754 ±0.001	19.998 ±0.002
7.0	17.975 ±0.001	24.126 ±0.001	19.969 ±0.001
9.0	18.242 ±0.002	24.527 ±0.002	20.404 ±0.001

PVOH: poly(vinyl alcohol); ± standard deviation

Table 6. Thermodynamic parameters for viscous flow of 7.0 g/l of poly(vinyl alcohol) in different concentrations of aqueous alcohols at 35 °C

Alcohol conc	Energy of activation $(E_{\eta*})$ (kJ/mol)	Free-energy change of activation (ΔG^*) (kJ/mol)	Entropy change of activation $(-\Delta S^*)$ (J/mol/K)
Aqueous-methanol (%, v/v)			
10	17.481 ±0.001	24.430 ±0.002	22.560 ±0.001
20	18.608 ±0.002	24.742 ±0.002	19.916 ±0.001
30	17.356 ±0.003	24.618 ±0.002	23.578 ±0.002
40	20.180 ±0.002	25.011 ±0.001	15.685 ±0.002
50	32.870 ±0.002	24.852 ±0.002	26.059 ±0.001
Aqueous-butanol (%, v/v)			
1.0	18.704 ±0.001	24.034 ±0.001	17.303 ±0.003
2.0	18.356 ±0.001	23.965 ±0.001	18.211 ±0.001
3.0	17.975 ±0.001	24.126 ±0.001	19.969 ±0.002
4.0	16.299 ±0.001	23.970 ±0.002	24.905 ±0.002
5.0	17.475 ±0.001	24.298 ±0.002	22.155 ±0.001

± standard deviation

Entropy change of activation (ΔS^*) is directly linked with the degree of order in a system and its diemension points to a loss of order. The entropy of viscous flow was evaluated by the following formula (Rasheed *et al.,* 2002; Aggour, 2001):

$$\Delta S^* = \frac{E_{\eta}^* - \Delta G^*}{T} \tag{7}$$

The negative values of ΔS^* of viscous flow increased with the increase in the concentration of poly(vinyl alcohol) in aqueous-butanol and decreased in aqueous-methanol, indicating that the process of fracture of solution structure prevailed and that system became less ordered. The increasing negative values of ΔS^* showed less disorder in aqueous-butanol in comparision with aqueous-methanol. Thus, the ability of poly(vinyl alcohol) to form stronger hydrogen bond with methanol was greater (Liu *et al*., 1997).

Acknowledgement

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