Study of Hydrodynamic and Non-Hydrodynamic Interaction Parameters for Water / PVP / PVA Ternary System by Solution Viscometry

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Summary: Polymer-Polymer interaction parameters from a water soluble polymer-blend solution have been determined by viscometry at 25°C. The ternary system assayed is distilled water poly (N-vinyl-2-pyrrolidone) (PVP)/Poly (vinyl alcohol) (PVA). The intrinsic viscosity and the viscometric interaction parameters have been determined for the water/PVP/PVA ternary system. Experimental results obey the Huggins equation. Degree of miscibility of this ternary system was estimated on the basis of the signs of ΔK_{exp} , κ (kappa) and the value of K_{12} a dimensionless quantity. The positive values of ΔK_{exp} and κ , and the higher values of K_{12} than K_H value of the individual polymers reveals the miscibility of PVP/PVA blends.

Introduction

The systems containing mixtures of two distinguishable kinds of polymer molecules are known as polymer blends or polyblends. These multiphase polymer systems have become a very important subject for scientific investigation in recent years because of their growing commercial acceptance. Studies on polyblends and multi-component polymeric materials have been growing increasingly in the past three decades. Such studies are not only by the ceaseless industrial need for developing new materials but also by the long-standing academic interest in these complex multiphase polymeric systems [1-6]. The growth rate of industrial output of multiphase systems is at least twice as high as that of the polymer industry in general. Environment protection and health legislation has had a side effect of making the introduction of new polymers very expensive and time consuming. There is a strong incentive from the polymer industry to solve technical problems and upgrade the products by working with the existing materials [7]. Blending of two polymers is an alternate method for modification of properties of polymers. Polymers, however are strongly incompatible and non-homogeneous microstructures result upon mixing which lead to poor mechanical properties. Complicated phase separation kinetics with complicated interfaces is observed in simple ternary blends, which only contain chemically homogeneous polymers.

The polymer-polymer miscibility in a polyblend can be detected by a number of techniques including differential scanning calorimetry, inverse gas chromatography, FTIR spectroscopy [8], light scattering, electron microscopy, wide angle X-ray scattering, thermal methods [9] and viscometry. Several works on miscibility studies of poly (vinyl alcohol) (PVA) with poly (N-vinyl-2-pyrrolidone) (PVP) have been carried out in solid state [10-17]. The hydrogen bonding interactions have been confirmed by high-resolution ^{13}C NMR technique and X-ray photoelectron spectroscopy [18]. The dilute solution viscosity method is simple, inexpensive and reliable technique to analyze polymer miscibility in solution and the bulk structure of polyblends [10]. This technique provides information about the polymer-polymer interactions and polymer-solvent interactions in a polyblend solution [8-10]. The mutual interactions of macromolecules in solution have a great influence on the viscosity in a ternary system. The common solvent greatly affects the hydrodynamic volume and configurations of the two dissolved polymers. Various criteria of polymer-polymer miscibility determined by viscometry have been proposed [19-24]. In this study some new hydrodynamic and thermodynamic viscometric parameters proposed by Chee *et. al.*, [19] for polymer-polymer interactions has been estimated for poly (vinyl alcohol) (PVA) and poly (N-vinyl-2-pyrrolidone) (PVP) mixtures in

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aqueous solution. Huggins equation for ternary polymer system has been adopted and extended to derive a constant κ (kappa), based on approach proposed by Cragg *et. al.*, [25]. This new constant contains contributions from attractive or repulsive intermolecular actions between the two polymers.

Theoretical

The equation proposed by Huggins for the polymer solvent system has the form [26].

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

Or $\eta_{sp} = [\eta]c + K_H [\eta]^2 c^2$ (2)

and

$$\eta_{sp1} = [\eta]_1 c + K_1 [\eta]_1^2 c^2 \text{ (For polymer 1)} \qquad (3)$$

$$\eta_{sp2} = [\eta]_2 c + K_2 [\eta]_2^2 c^2 \text{ (For polymer 2)} \qquad (4)$$

K_1 and K_2 are the Huggins coefficients and $[\eta]_1$ and $[\eta]_2$ are the intrinsic viscosities for Polymer 1 and 2 respectively, c is the concentration. The above equation I, formulated for polymer blend solution reads (Cragg *et. al.,)* [25].

$$\eta_{sp,b} = [\eta]_b c_b + K_b [\eta]_b^2 c_b^2 \qquad (5)$$

or

$$\eta_{sp,b} = [\eta]_1 c_1 + [\eta]_2 c_2 + K_1 [\eta]_1^2 c_1^2 + K_2 [\eta]_2^2 c_2^2 + 2K_{12} [\eta]_1 [\eta]_2 c_1 c_2$$
(6)

The ideal value of intrinsic viscosity for polyblend solution from equation (6).

$$[\eta]_{b,id} c_b = [\eta]_1 c_1 + [\eta]_2 c_2 \qquad (7)$$

where $c_b = c_1 + c_2$ (8)

and introducing mass fraction of polymer 1, it is

$$w = \frac{m_1}{m_1 + m_2} = \frac{c_1}{c_b} \qquad (9)$$

Values of K_b can be determined from dilute solution viscosity measurements. Applying equation (7), the quantity K_b reads in terms of individual constituents.

$$K_b [\eta]_{b,id}^2 c_b^2 = K_1 [\eta]_1^2 c_1^2 + K_2 [\eta]_2^2 c_2^2 + 2K_{12} [\eta]_1 [\eta]_2 c_1 c_2 \qquad (10)$$

An ideal polyblend solution is also defined by geometrical mean of the K_1 and K_2, (Huggins Coefficients of polymer 1 and polymer 2 in the polyblend solution).

$$K_{12} = (K_1 K_2)^{1/2} \qquad (11)$$

The above equation (11) permits the separation of experimental value of Huggins coefficient. K_b into two parts.

$$K_b = K_{id} + \Delta K_{exp} \qquad (12)$$

K_{id} = Huggins coefficient of ideal solution.
ΔK_{exp} = Experimental excess quantity
Equation (10) can be written for an ideal solution as

$$K_{id} = \frac{\left(K_1^{1/2} [\eta]_1 c_1 + K_2^{1/2} [\eta]_2 c_2\right)^2}{\left([\eta]_1 c_1 + \eta_2 c_2\right)^2} \qquad (13)$$

The parameter α is introduced to simplify the notations, and it represents the ratio of size of the macromolecules in the polyblend.

$$\alpha = \frac{[\eta]_1}{[\eta]_2} > 1 \qquad (14)$$

The value of K_{id} and theoretical excess quantity ΔK are determined by the method proposed by Chee *et. al.*, [19], using equations (5) – (10) and (13), (14).

$$K_{id} = \left(\frac{\sqrt{K_1}\alpha w + \sqrt{K_2}(1-w)}{1 + w(\alpha - 1)}\right)^2 \qquad (15)$$

$$= \frac{K_1 \alpha^2 w^2 + K_2 (1-w)^2 + 2(K_1 K_2)^{1/2} \alpha w (1-w)}{(1 + w(\alpha - 1))^2} \qquad (16)$$

and $K_b = \dfrac{K_1 \alpha^2 w^2 + K_2 (1-w)^2 + 2K_{12} \alpha w (1-w)}{(1 + w(\alpha - 1))^2}$ (17)

Subtracting equation (16) from equation (17) gives ΔK

$$\Delta K = 2\frac{w(1-w)\alpha}{1 + w(\alpha - 1)^2} [K_{12} - K_1 K_2]^{1/2} \qquad (18)$$

or $\Delta K = 2\dfrac{w(1-w)\alpha}{1 + w(\alpha - 1)^2} \kappa$ with

$$\kappa = [K_{12} - K_1 K_2]^{1/2} \qquad (19)$$

According to equation (19) ΔK is a function of composition and denoting the factor in front of κ by q, this function is given by

$$q_i = 2\frac{w(1-w)\alpha}{(1+w(\alpha-1))^2} \qquad (20)$$

for different blend compositions w_i. The experimental excess quantity $\Delta K_{\exp}$ follows from equation (12) with equation (16). $\Delta K_{\exp}$ reveals deviations from ideal behaviour that are, to a good approximation, chiefly due to specific thermodynamic interactions between structurally different polymer species. At high polyblend concentrations, the attractions between the different polymer molecules cause swelling of the coils leading to an excess increase in viscosity as compared to ideal behaviour. Positive deviations from ideal behavior indicate attraction between the two polymer molecules, whereas negative deviations result from repulsions. The above findings if expressed in terms of κ (kappa) it follows that the polymer mixture is miscible if $\kappa > 0$ and immiscible if $\kappa < 0$. The constant κ (kappa) is determined for a polyblend solution using all the experimental values $\Delta K_{\exp,i}$ for many blend compositions w_i, by a least square procedure

$$\kappa = \frac{\sum_{i=1}^{n} \Delta K_{\exp,i}\, q_i}{\sum_{i=1}^{n} q_i^2} \qquad (21)$$

Equation (21) allows the determination of the best value of κ. Where n denotes the number of data points available over the whole composition range. Many data points are desirable for more precise determination of kappa value.

Results and Discussions

The values of relative viscosities were used to determine the specific viscosities $(\eta_r - 1)$ of the pure polymers and blends of PVP-PVA solutions at

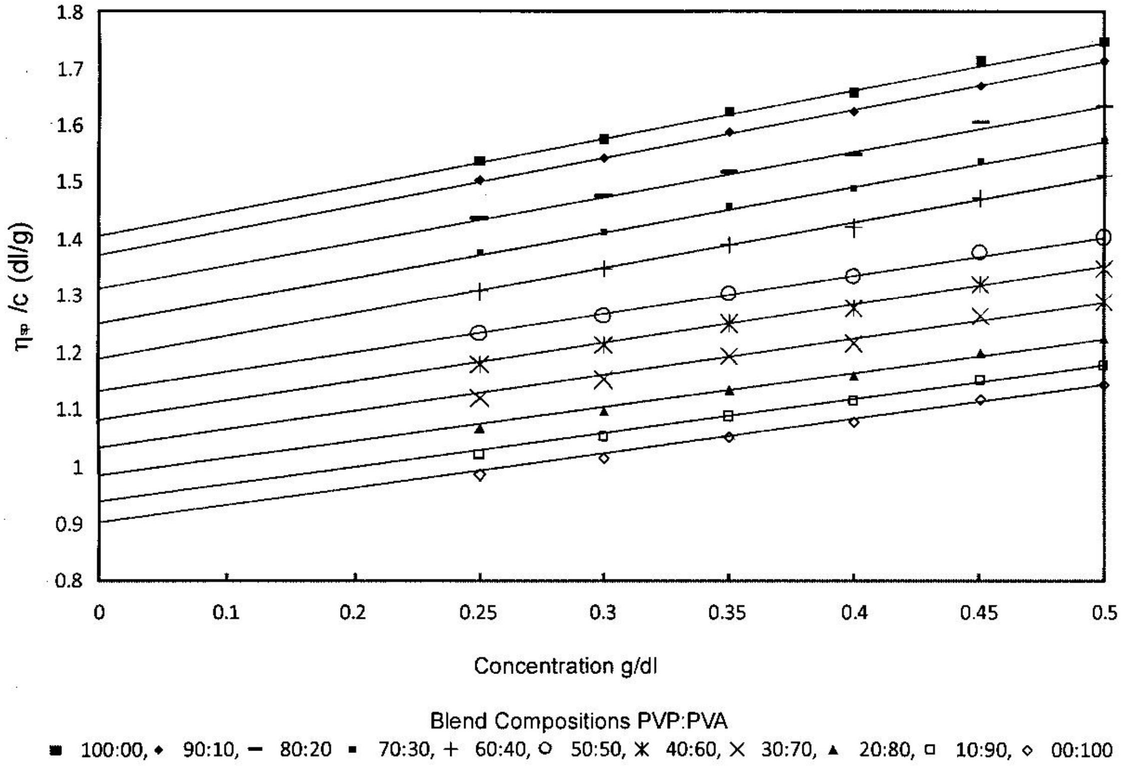

Fig. 1: Plot of reduced viscosity (η_{sp}/c) versus concentration c for aqueous PVP/PVA blend solution at 298 K.

298 K. The values of reduced viscosity η_{sp} / c versus concentration yield intrinsic viscosity $[\eta]$ according to Huggins equations. The representative plots of η_{sp} / c versus c for PVP, PVA and the ternary solutions are shown in Fig. 1 and the data for every system and compositions studied fit to the Huggins equation. The values of intrinsic viscosities, and Huggins coefficients (K_1, K_2, K_b, K_{id}) are listed in Table-1. Intrinsic viscosity of PVP is higher than PVA, so the ternary system exhibit decreasing trend with PVA content. The limiting viscosity number $[\eta]$ is a measure of the shape and size of the individual polymer molecules. The experimental values of intrinsic viscosities versus blend composition of the ternary system plotted in Fig. 2 show a linear relationship. The broken line represents the value of $[\eta]_{b,id}$ obtained from equation (7). $[\eta]_{b,id}$ coincides with the experimental values to an excellent approximation. But a minor negative deviation from the ideal value is observed for the higher PVA content in the ternary system. These observations conclude that when the polymer solutions are sufficiently dilute the polymer molecules in the ternary solution behave independently of one another for the whole composition range i.e. the ternary system (PVP-PVA-water) show an ideal behavior.

The value of Huggins coefficient is a constant for a given polymer-solvent-temperature system and vary between 0.30 – 0.40 for good

Table-1: Intrinsic Viscosities and Huggins coefficients for aqueous PVP/PVA blend solutions at 298k.

	$K_1 = 0.4081$;	$K_2 = 0.6976$;	$\alpha = 1.399/0.905 = 1.5459$		
Blend Composition PVP:PVA	$[\eta]$ dL/g	K_b	K_{id}	ΔK_{exp}	ΔK Theoretical excess quantity
00:10	0.905	0.6976	-		
10:90	0.940	0.7547	0.6503	1.0440	0.0275
20:80	0.980	0.7181	0.6091	0.1090	0.0527
30:70	1.030	0.6732	0.5730	0.1002	0.0746
40:60	1.080	0.6350	0.5410	0.0940	0.9250
50:50	1.130	0.6024	0.5126	0.0898	0.1049
60:40	1.186	0.5468	0.4872	0.0596	0.1099
70:30	1.250	0.5120	0.4644	0.0476	0.1054
80:20	1.310	0.4662	0.4438	0.0224	0.0884
90:10	1.370	0.4439	0.4250	0.0189	0.0550
100:00	1.399	0.4081	-		

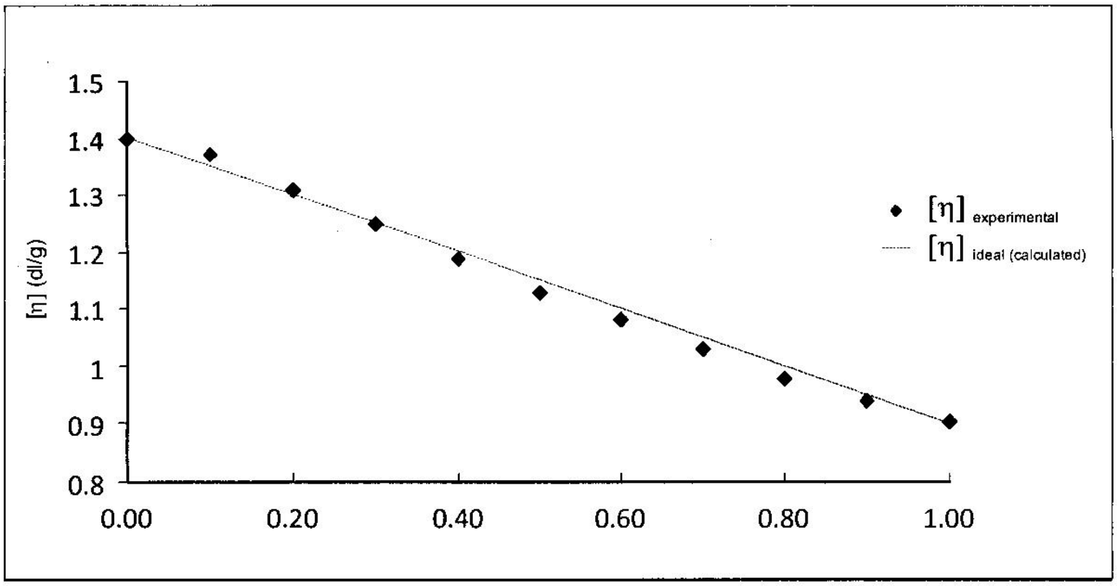

Fig. 2: Intrinsic viscosity as a function of PVA weight fraction in different PVP/PVA blends in water at 298 K.

solvent systems when polymer chains are solvated to highest degree and polymer-solvent interactions are dominant. The values vary between 0.50 – 0.80 in θ solvent. When intermolecular associations exist, the Huggins coefficients increase [27]. Its value is independent of molecular weight for long chains. Experimental values of K_1, K_2 and K_b, the Huggins coefficient for PVP, PVA and the polyblend solutions, respectively were obtained from the slope of the Huggins equation (eq: 22) at 25 °C are

$$K_H = \text{slope} / [\eta]^2 \quad (22)$$

presented in Fig. 1 and the results are listed in Table-1. The value of K_2 for PVA in water is about 0.69, much higher than normal value of polymers in good solvent (0.30 – 0.40). This indicates the existence of additional polymer-polymer interactions between PVA molecules. Values of K_{id} were calculated according to [19]. ΔK_{exp} calculated after equation (12) for the polyblend solutions is listed in Table-1. Its values represent hydrodynamic molecular interactions between structurally different polymer chains. The solution is termed as ideal when according to equation (11) K_{12} is equal to $(K_1K_2)^{½}$. It is observed outside experimental errors that $\Delta K > 0$ for PVP/PVA aqueous solutions indicating miscibility of the two polymers in the blend.

Experimental values of K_b and calculated K_{id} plotted against composition of PVA are presented in Fig. 3. Positive deviations from ideal behavior are evident over the whole range of the composition indicating that the ternary system does not fulfill the criteria of an ideal system according to equation (11). This is an indication of occurrence of non-hydrodynamic interactions, apart from hydrodynamic ones, between the two polymer chains in aqueous solutions. The plot of experimental excess quantity ΔK_{exp} versus composition of PVA is shown in Fig. 4. The theoretical excess quantity ΔK is obtained from equation (19). The solid line represents the value of ΔK. The experimental values fit quite well to the theoretical line. The values of K_{12} exceed significantly K_1 & K_2 for parent polymer indicating miscibility. The coefficient κ (kappa) is determined by a least square procedure using all experimental values $\Delta K_{exp,i}$ for different blend compositions and $\kappa = [K_{12} - (K_1K_2)^{½}]$. This is a constant independent of composition and contains contributions from intermolecular actions, other than hydrodynamic interactions. A positive value of κ (Table-2)

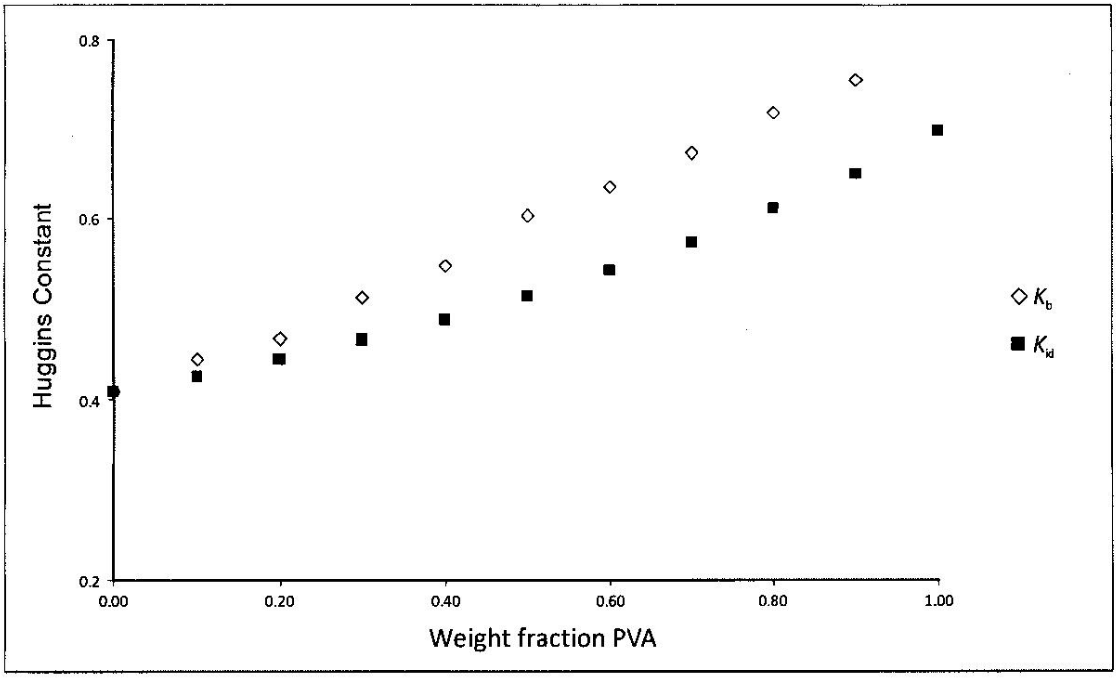

Fig. 3: Variation of Huggins constant with composition of PVP/PVA in aqueous solution.

Table-2: Values of $\kappa_{\text{(Kappa)}}$ and K_{12}.

System	$\sum_{i=1}^{n} \Delta K \exp, i q_i$	$\sum_{i=1}^{n} q_i^2$	K (dimensionless)	K_{12} (dimensionless)
PVP:PVA	0.2229	1.3360	0,1669	0.70

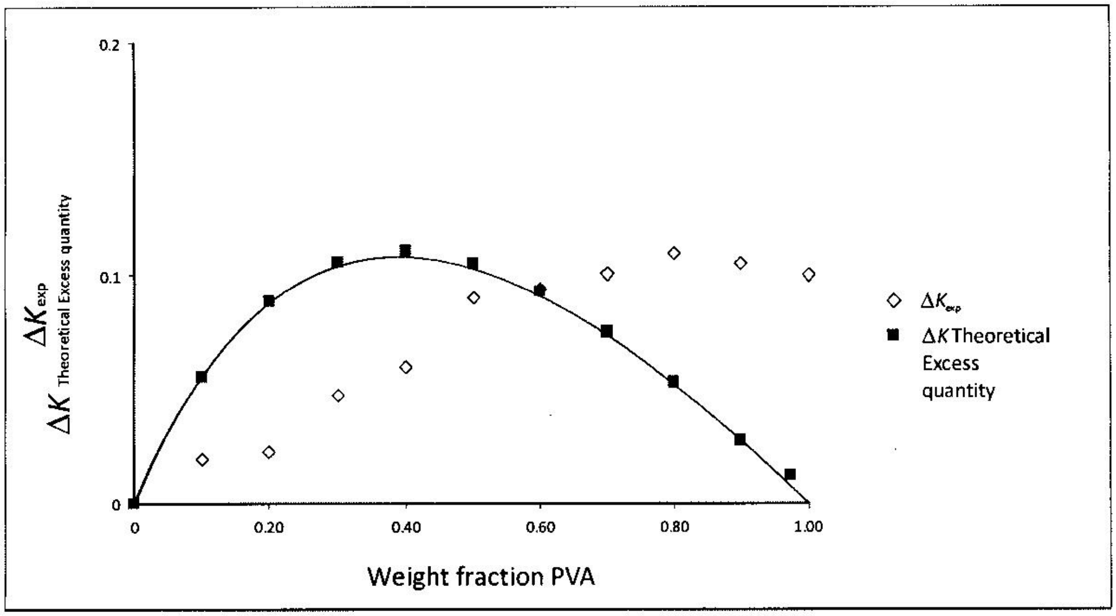

Fig. 4: Variation of ΔK with weight fraction PVA.

indicates an attaractive intermolecular action (or miscibility) between PVP and PVA in aqueous solution.

Experimental

Material

PVA with an average molecular weight of 72000 g/mL was purchased from E Merck (Germany). The PVA has degree of polymerization of 1600 and minimum degree of saponification of 98%. PVP with an average molecular weight of approximately 700000 was obtained from BDH England. Both the polymers were used without further purification. Double distilled water having conductivity near zero was used as solvent.

Sample Preparation

Stock solutions of PVA and PVP were prepared by dissolving the polymers in freshly double distilled water upto a concentration of 1% (w/v). PVA was soluble in hot water (80 ± 1) °C with continuous stirring. The solution of PVP was prepared by shaking the polymer with water at room temperature.

Viscosity Measurements

Ternary solutions of each system having different weight ratios were prepared by mixing the appropriate quantity of freshly prepared polymer solution. Dilutions to yield lower concentrations were made by adding the appropriate aliquots of solvent.

The solutions were filtered through a sintered glass filter before measurements. Viscosity measurements of PVA, PVP and PVA/PVP solution was performed at (25 ± 0.1) °C using dilution Ubbelohde type viscometer immersed in a constant temperature bath (Type LAUDA-D-40-9 Germany) with temperature accuracy of ± 0.1 °C with temperature control device (LAUDA R3 Germany). Efflux time of the pure solvent was always above 200 s, so as to minimize the experimental errors. For each solution a 25 mL sample was loaded into the viscometer and placed in the constant temperature bath. Efflux time measurements were recorded after an equilibration of 15-20 min and were continued until several flow time readings agreed to within ± 0.5%. The elution time of each solution was taken as the average of five concordant readings.

Conclusion

Interactions among polyblend constituents are reflected in the solution viscosity of their aqueous solutions. The η_{sp}/c *vs* c dependence of water solutions of PVP/PVA mixtures is found to be linear and the Huggins equation is valid in the range of intrinsic viscosity *vs* blend composition of the ternary system show a linear relationship. Minor negative deviation from the ideal behavior is observed for the higher PVA content. The value of $\Delta K > 0$ for PVP/PVA aqueous solution indicates miscibility. Positive deviations from ideal behavior of the Huggins coefficient are attributed to miscibility of PVP & PVA. Positive value of κ (kappa) is associated with intermolecular actions other than hydrodynamic ones between PVP & PVA indicating their miscibility in bulk systems. These conclusions are in consistent with results described [10-17] for PVP/PVA blends carried out in solid state.

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