

Miscibility and Interaction Studies on Some Aqueous Polymer Blend Solutions by Ultrasonic and Rheological Techniques

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SYNOPSIS

The aqueous solutions of poly(ethylene oxide)–polyacrylic acid, poly(vinyl pyrrolidone)–poly(vinyl alcohol), and poly(ethylene oxide)–poly(vinyl alcohol) blends have been studied by ultrasonic, rheological, and viscometric techniques. Extensive investigation over a wide range of concentrations, temperatures, compositions, pH, and shear rates indicate the degree of miscibility, extent of interaction between the polymers, and stoichiometry of the polymer complexes formed by the strong interaction between the polymers in solutions. These investigations indicate the miscibility of poly(ethylene oxide)–polyacrylic acid and poly(ethylene oxide)–poly(vinyl pyrrolidone) blends and the immiscibility of poly(ethylene oxide)–poly(vinyl alcohol) blends in conformity with other reported investigations. © 1994 John Wiley & Sons, Inc.

INTRODUCTION

Poly(ethylene oxide) displays a high degree of polymer–solvent interaction in aqueous systems when the polymer structure is relatively nonpolar. The application of the hydrogen-bonding affinity of the ether oxygen in the poly(ethylene oxide) chains has been found in the molecular association complexes formed between this polyether and polymeric acids.¹ The mixing of solutions of interacting polymers produces an immediate precipitation or turbidity or homogeneity, indicating, respectively, stronger, weaker, and no or very small interaction between the polymers. In the blends, the existence of chemically grafted units is of major importance in providing adhesion between the polymers. Interesting products can be formed from the polymers even without the requirement of a chemical graft; in such cases, weaker secondary forces such as hydrogen bonds play a dominant part.

The compatibility or the miscibility of the homopolymers at the molecular level is very important for the blends. Many experimental and theoretical methods^{2–4} have been used to investigate the poly-

mer–polymer miscibility and the interaction between the polymers. A combination of methods is generally used to investigate the polymer–polymer miscibility. In the present investigation, the ultrasonic, rheological, and viscometric methods have been used. A few years back, Singh et al.^{5–8} pointed out that the plots of both absolute viscosity and ultrasonic velocity vs. the composition of the blends deviate from linearity according to the degree of miscibility of polymer blends at all concentrations and temperatures. The curves for miscible systems are linear. Their investigations have been corroborated by a number of research workers.^{9–12}

In the present investigation, the aqueous solutions of poly(ethylene oxide)–poly(acrylic acid) (PEO–PAA), poly(ethylene oxide)–poly(vinyl alcohol) (PEO–PVA), and poly(ethylene oxide)–poly(vinyl pyrrolidone) (PEO–PVP) blends have been studied extensively over a wide range of concentrations, temperatures, compositions, pH, and shear rates.

EXPERIMENTAL

The ultrasonic velocity measurements were carried out by an interferometric technique¹³ employing an ultrasonic interferometer (Mittal Enterprises, New

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Delhi). The ultrasonic experimental cell had a double-wall jacket and thermostated water was circulated from an Ultrathermostat (GDR U10) with a thermal stability of $\pm 0.05^\circ\text{C}$. The experimental frequency used was 2 MHz.

The rheological measurements were performed using a rotary viscometer "Rheotest 2".¹⁴ The specific viscosities of the polymers were measured by a Ubbelohde viscometer using double-distilled water as a solvent.

The grades of the water-soluble polymers used in the present investigation are PEO (BDH, England), PVP (BDH, England), PVA (Thomas Baker), and PAA (BDH, England). The molecular weights (\bar{M}_v) are 1.3×10^5 , 7.0×10^5 , 1.0×10^5 , and 22×10^5 , respectively.

The blends of various polymers with varying compositions were prepared by the solution poly-blending technique. Solutions of both components were prepared in mutual solvent water separately at various concentrations at room temperature. But PVA is not soluble in water at room temperature. The water has therefore been heated to a fairly well-defined dissolution temperature to dissolve the polymer. Then, the required proportions of these solutions have been mixed very thoroughly by stirring for preparation of solutions of the polyblends of various compositions.

RESULTS AND DISCUSSION

The blends of PAA and PEO in aqueous solutions have been studied previously by many workers.^{1,15-18} They observed that the polybase PEO can form polymer complexes with PAA and they also reported that the stabilization of such complexes is due to the cooperative formation of hydrogen bonds between the $-\text{COOH}$ group of acid and the $-\text{O}-$ group of PEO.¹⁵⁻¹⁸ The formation of such complexes is dependent on the pH of the solution. In the present case, the molecular weight of PEO and PAA are 1.3×10^5 and 2.2×10^5 , respectively, and the precipitation occurs at $\text{pH} < 4$. The extensive study of viscosity over a wide range of compositions indicates that at pH 4, a sharp maximum is found at 0.5 wt % of PEO and this essentially corresponds to the stoichiometry found for the precipitate polymer at $\text{pH} < 4$. Bailey et al. also observed the same.¹ The solution studies for the aqueous blend of PEO-PAA have therefore been carried out at pH 4. The desired pH was obtained by adding an acid solution (drop by drop) to the polymer solution under constant stirring.

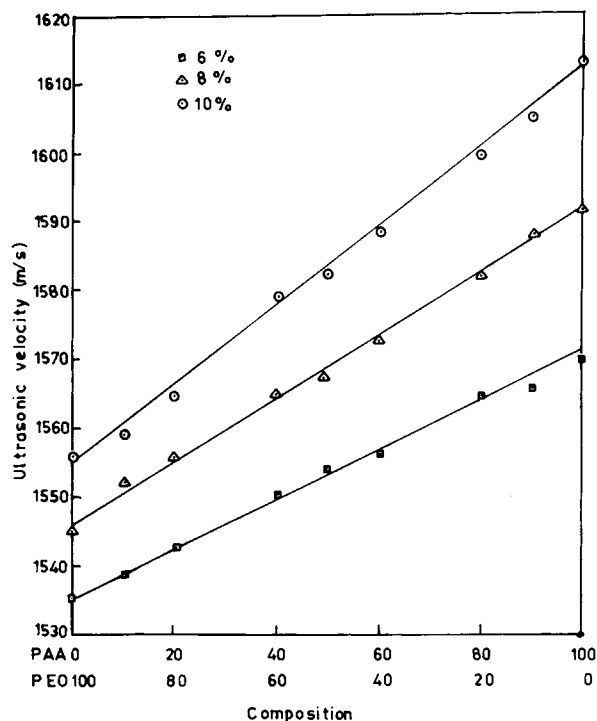


Figure 1 Ultrasonic velocity vs. weight percentage of PAA (Component 1) in PAA-PEO blends of various concentrations at 30°C .

On the other hand, for the blend solutions of PEO-PVP and PEO-PVA, mixing does not produce an immediate precipitation at room temperature.

Ultrasonic Study

Various workers reported the results of extensive studies of PAA and PEO blends but so far no attempt has been undertaken to study the PEO-PAA blends in solution by the ultrasonic technique. The variation of ultrasonic velocity with composition at pH 4 at various concentrations at 30°C for the PEO-PAA blend is plotted in Figure 1. The same has been plotted in Figure 2 for the blends of PEO-PVP and in Figure 3 for the blends of PEO-PVA in water at 30°C . The ultrasonic velocities have also been measured at 40 and 50°C for all these systems.¹⁹

It has been observed that for all these systems over all compositions ultrasonic velocity increases with increase in temperature and concentration. The increase in the ultrasonic velocity with temperature is due to increase in the ultrasonic velocity of water with temperature.²⁰ Increasing concentration increases the polymeric contribution to the ultrasonic velocity of blend solutions and, consequently, increases the ultrasonic velocity. These results support

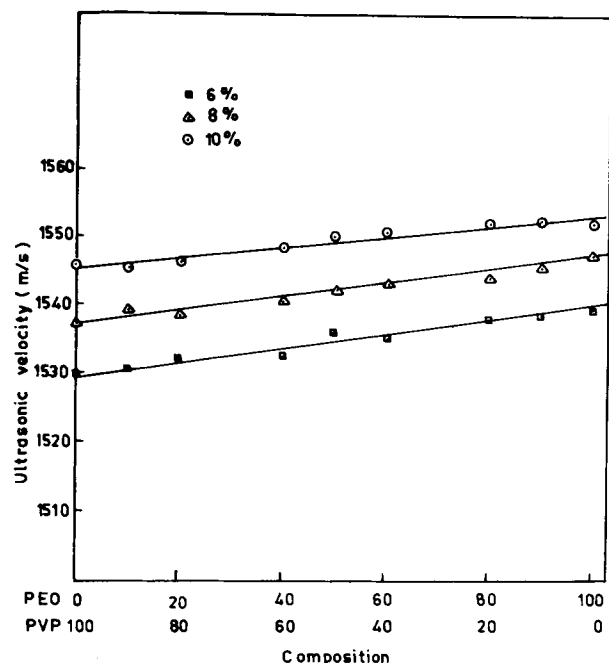


Figure 2 Ultrasonic velocity vs. weight percentage of PEO (Component 1) in PEO-PVP blends of various concentrations at 30°C.

the earlier finding for the blends of PMMA-PVAc in toluene.⁷ It is well established in our laboratory that for a miscible blend ultrasonic velocity varies linearly with composition at all temperatures and concentrations.^{7,21,22} For the blend solutions of PEO-PAA and PEO-PVP, it has also been observed from Figures 1 and 2 that at all concentrations the ultra-

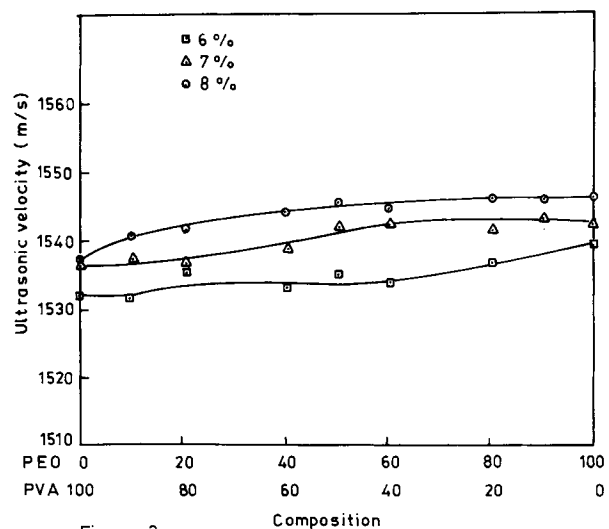


Figure 3

Figure 3 Ultrasonic velocity vs. weight percentage of PEO (Component 1) in PEO-PVA blends of various concentrations at 30°C.

sonic velocity varies linearly with composition at 30°C. Similar behavior¹⁹ has been observed at 40 and 50°C. This behavior, therefore, indicates that in the blend system of PEO-PAA and PEO-PVP complete mixing of the polymers takes place at the molecular level. Consequently, the PEO-PAA and PEO-PVP blends can be considered as a miscible blend in aqueous solution. Smith et al.²³ also observed the miscible nature of PEO-PAA blends on the basis of modulus-temperature data. On the other hand, for the blend solution of PEO-PVA, nonlinear behavior at all compositions and temperatures is found as is evident from the typical results at 30°C depicted in Figure 3. This behavior indicates that the present blend system is a multiphase one at all concentrations and temperatures. Consequently, the PEO-PVA blend can be considered as an immiscible blend in aqueous solution.

Rheological Study

The shear-rate dependence of the apparent viscosity of the solutions of PEO-PAA blends has been studied extensively by Bailey et al.¹ In the present investigation, the same has been studied for PEO-PVP and PEO-PVA blends at various polymer concentrations. Figures 4 and 5 represent the charac-

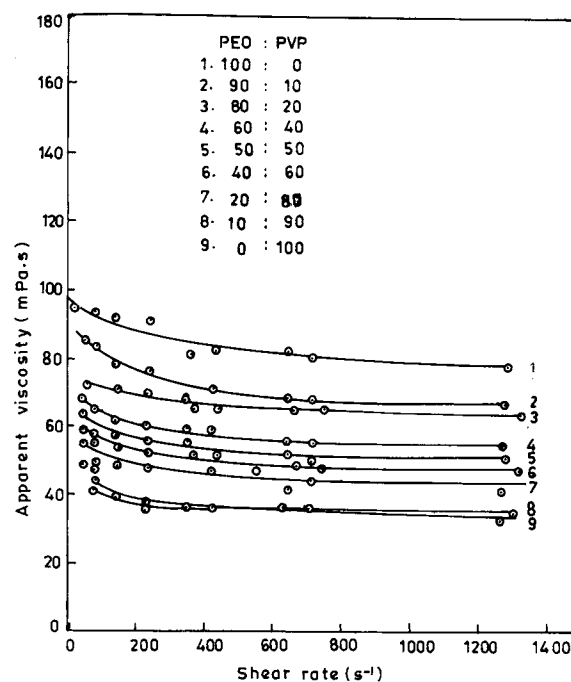


Figure 4 Shear-rate dependency of viscosity for 8% polymer blend (PEO-PVP) solutions with varying proportions of PEO at 30°C.

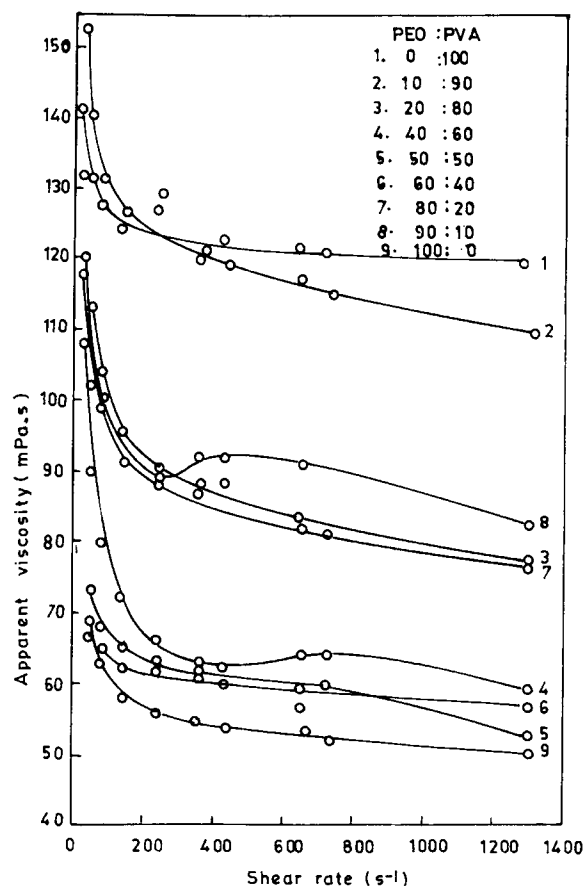


Figure 5 Shear-rate dependency of viscosity for 7% polymer blend (PEO-PVA) solutions with varying proportions of PEO at 30°C.

teristic shear rate behavior for the solutions of PEO-PVP and PEO-PVA, respectively. The shear-rate range used for the present study is 20–1320 S^{-1} . It has been observed from both figures that for all compositions apparent viscosity decreases with increase in shear rate, indicating the pseudoplastic nature of the blends. At higher shear rates, viscosity almost remains constant, indicating limiting Newtonian behavior. It is reported in the literature²⁴ that in the case of PEO the pseudoplasticity decreases with decrease in molecular weight and the solutions of PEO with a molecular weight of 1.0×10^5 are nearly Newtonian. This effect is more pronounced at higher shear rates.²⁴ In the present case, the molecular weight of PEO, PVP, and PVA are 1.3×10^5 , 7.0×10^5 , and 1.0×10^5 , respectively. It is also evident from Figure 4 that viscosity decreases linearly with decrease in the percentage composition of PEO. On the other hand, nonlinear behavior has been observed for the PEO-PVA blend as is evident from Figure 5. This indicates the miscible nature of PEO-

PVP blends in solution and the immiscible nature of PEO-PVA blends in solution, as was reported by Chitrangad and Middleman²⁵ for PPO-PS blends in solution.

The variations of apparent viscosity with composition at various concentrations and at the temperature of 30°C are plotted in Figure 6 for the PEO-PVP blend and in Figure 7 for the PEO-PVA blend. It has been observed from Figure 6 that at all concentrations viscosity varies linearly with composition at the shear rate of 656 S^{-1} . Similar behavior has been found at other shear rates, indicating the miscible nature of the blend as it was described previously by Singh and Singh for the PMMA-PVAc blend in solution.⁷ However, for higher concentrations, viscosity increases sharply with the decrease in proportion of PVP and that may be due to the interacting nature of PVP,²⁴ which is supposed to be higher at higher concentrations. As the weight percentage of PVP decreases, the extent of interaction decreases and it converts from its coiled form to an extended form that may give rise to a sharp increase in viscosity at higher concentration. It is reported that for PEO viscosity increases with concentration.²⁴

It is evident from Figure 7 that viscosity decreases up to 50% of PEO, and then it remains almost constant for lower concentrations. At higher concentrations, the sharp decrease in viscosity has been observed and it again passes through a maximum at about 80% of PEO in the blend solution. PVA is

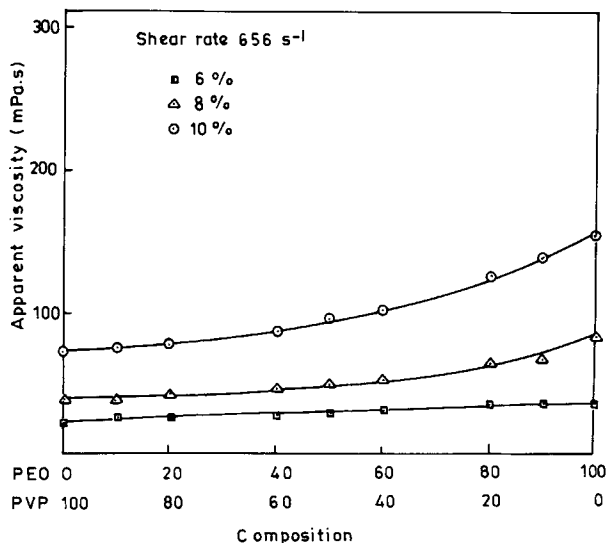


Figure 6 Apparent viscosity vs. weight percentage of PEO (Component 1) in PEO-PVP blends of various concentrations at 30°C.

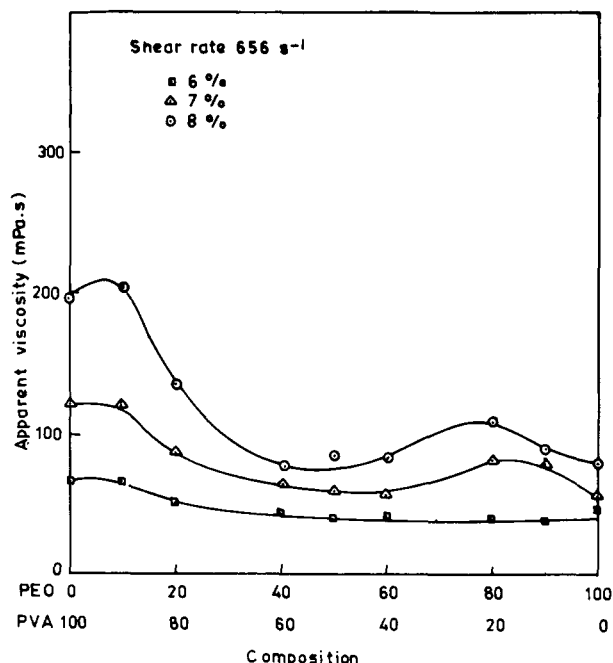


Figure 7 Apparent viscosity vs. weight percentage of PEO (Component 1) in PEO-PVA blends of various concentrations at 30°C.

soluble in hot water and it is reported in the literature²⁶ that the homogeneous solutions of PVA seem to be unstable and that agglomeration as well as crystallization are possible. In the more concentrated solutions, cross-linking or gelation can occur,

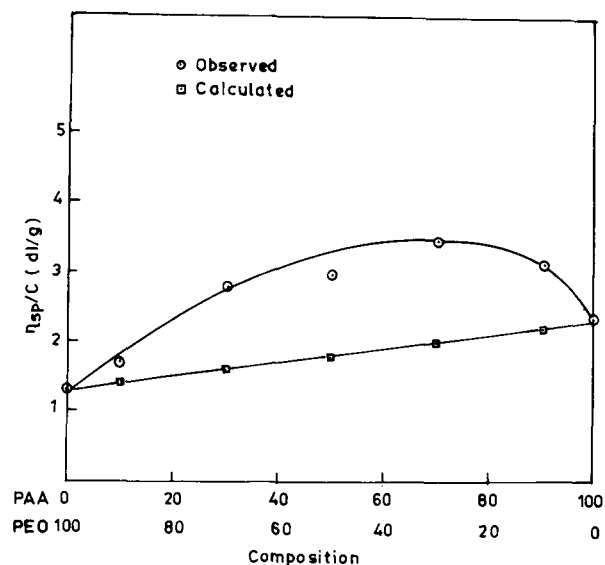


Figure 8 Reduced viscosity vs. weight percentage of PAA (Component 1) in PAA-PEO blends of 0.1% concentrations at 30°C.

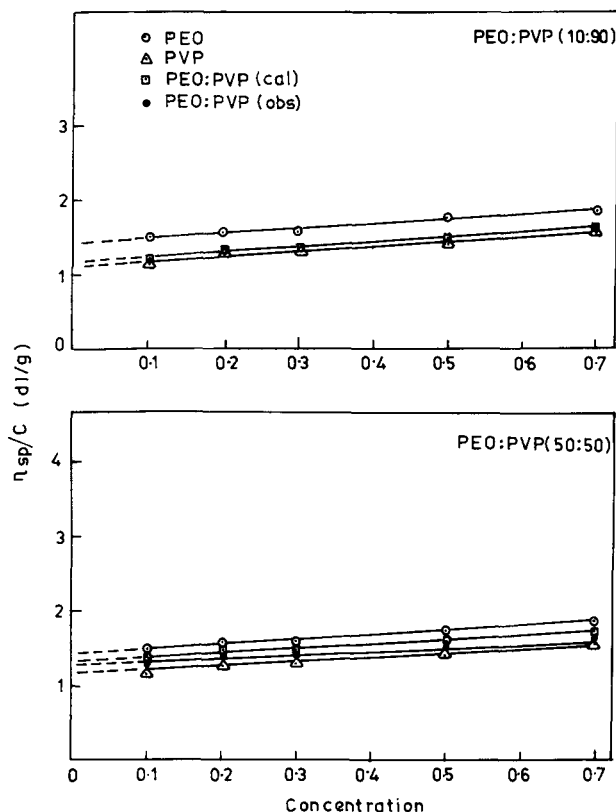


Figure 9 Reduced viscosities of PEO, PVP, and their mixtures (10 : 90, 50 : 50) at 30°C.

resulting in increased viscosity.²⁶ As the percentage of PEO increases in the blend system, because of the paired ether oxygen electrons that have a strong tendency for hydrogen bonding, the cross-linked aggregated gel structure of PVA starts breaking. This may be the cause for the sharp decrease in viscosity. At a higher proportion of PEO, the cross-linked structure of PVA breaks almost completely. However, due to H bonding between the polymers, the viscosity again increases and passes through a maximum at higher concentration, indicating interaction.

Viscometric Study

It is observed in Figure 8 that the reduced viscosity of the blend solution of PEO-PAA deviates from the rule of mixture for all the compositions. In the present cases, positive deviation is observed, which indicates strong interaction between the polymers. Similar behavior had also been observed by Williamson and Wright.²⁷ On the other hand, it is also evident from Figures 9 and 10 that the reduced viscosities of the blend solutions for 10 : 90 and 50 : 50

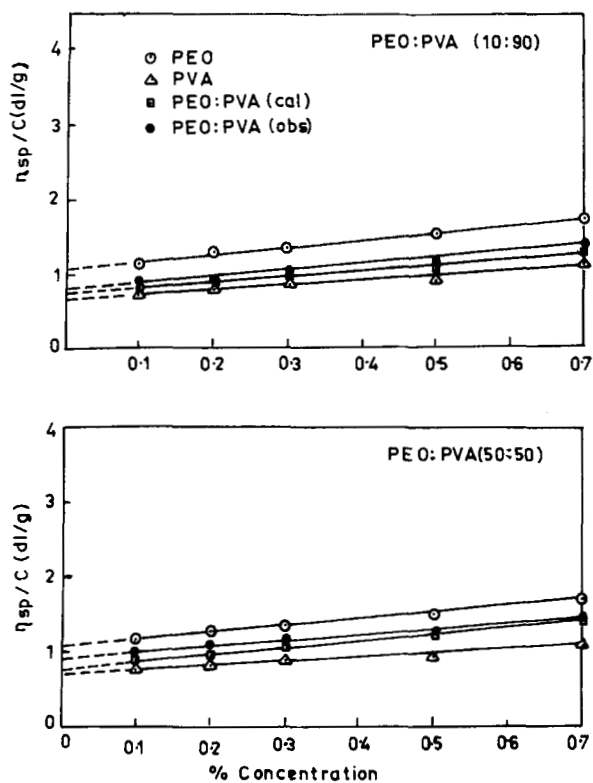


Figure 10 Reduced viscosities of PEO, PVA, and their mixtures (10 : 90, 50 : 50) at 30°C.

compositions of PEO : PVP and PEO : PVA, respectively, exactly follow the additive rule of mixtures. It indicates that the blends behave ideally in solution as described by Williamson and Wright.²⁷ They studied a number of mixed polymer systems

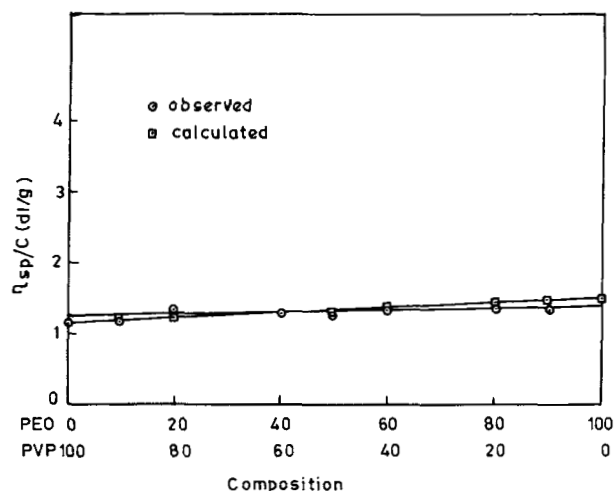


Figure 11 Reduced viscosity vs. weight percentage of PEO (Component 1) in PEO-PVP blends of 0.1% concentrations at 30°C.

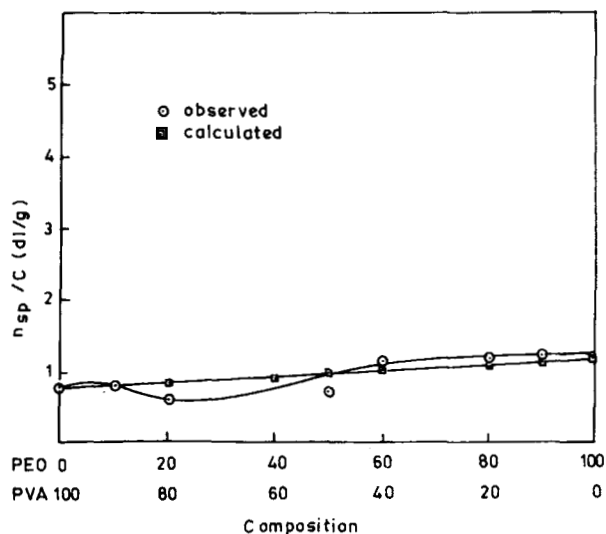


Figure 12 Reduced viscosity vs. weight percentage of PEO (Component 1) in PEO-PVA blends of 0.1% concentrations at 30°C.

and concluded that the deviations of the observed viscosity from the ideal mixing viscosity are larger in the case of strongly interacting polymers. The reduced viscosity follows the simple additive rule of mixtures²⁷ when the polymers are miscible. In the present case, it is evident from Figures 11 and 12, respectively, that the plot of reduced viscosity vs. composition at a fixed concentration of 0.1% of the blend solution and at a temperature of 30°C is exactly coinciding with the calculated reduced viscosity values (using the additive rule of mixture) for the PEO-PVP blend and deviates from the additive rule of mixture for the PEO-PVA blend. The above observations indicate the miscibility of the PEO-PVP blend and a small interaction between PEO and PVA in aqueous solution.²⁷

It has therefore been observed from the above findings and also from the reported results that for the blend solution of PEO-PAA, below pH 4 due to strong H bonding between the —COOH group of PAA and the —O— group of PEO, the polyelectrolyte complex precipitates out. Above pH 4, the two polymers coexist in the solution-forming homogeneous phase. The miscible nature of the PEO-PAA blend in water has thus been confirmed by the ultrasonic technique. It is also evident that the aqueous blends of PEO-PVP are miscible at all concentrations and temperatures and that there is no interaction between the polymers. The aqueous blends of PEO-PVA are immiscible and a small interaction between the polymers is existing between them. This interaction may be due to the presence

of a paired ether oxygen electron in PEO that has a strong tendency for H bonding.

The polymers studied in the present investigation reduce the turbulent drag that is very much dependent on molecular dimensions. The association formed by these interacting polymers may cause a high degree of drag reduction as has been reported in the case of interpolymer associations in organic solvent by Kowalik et al.²⁸

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