

# Viscosimetric Study of Poly(vinyl alcohol)/Poly(styrenesulfonic acid) Miscibility in Dilute Aqueous Solution

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## SYNOPSIS

The miscibility of poly(vinyl alcohol) (PVA) and poly(styrenesulfonic acid) (PSSA) in dilute aqueous solutions was studied by a viscosimetric method. At a constant molecular weight of PSSA, it was found that the miscibility of both polymers increases with the molecular weight and the number of acetate groups of the PVA samples (1 and 12% unhydrolyzed sites). Moreover, this miscibility increases slightly with the total mixture concentration in the interval 1–2 g/dL. By comparison of the results of reduced viscosity of PVA/PSSA and PVA/poly(sodium styrenesulfonate) (PSSNa) mixtures, it has been deduced that the miscibility of two polymers is due mainly to intermolecular interactions between the hydroxyl and sulfonic groups of PVA and PSSA, respectively. These groups act as acceptors and donors of hydrogen bonds which are the responsible for polymers' miscibility.

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## INTRODUCTION

The viscosimetric method presents many advantages due to its simplicity and inexpensive equipment. Moreover, it allows the characterization of macromolecules in the dispersed state.<sup>1</sup> In solution, the establishment of intermolecular interactions has a consequence on the viscosity. In systems dominated by attractive interactions, the viscosity increases and vice versa.<sup>1–4</sup> Therefore, the viscosity variation as a function of the nature of the system component (ionic/ionic, ionic/nonionic, and nonionic/nonionic polymers) is the subject of many research works.<sup>4–7</sup>

Staikos et al.<sup>7,8</sup> proposed a theoretical method useful in characterization of the nonionic/ionic polymers' system in dilute aqueous solution. At constant total concentration  $C$ , they proposed a theoretical relation to calculate the reduced viscosity of a mixture without interactions between the two polymers:

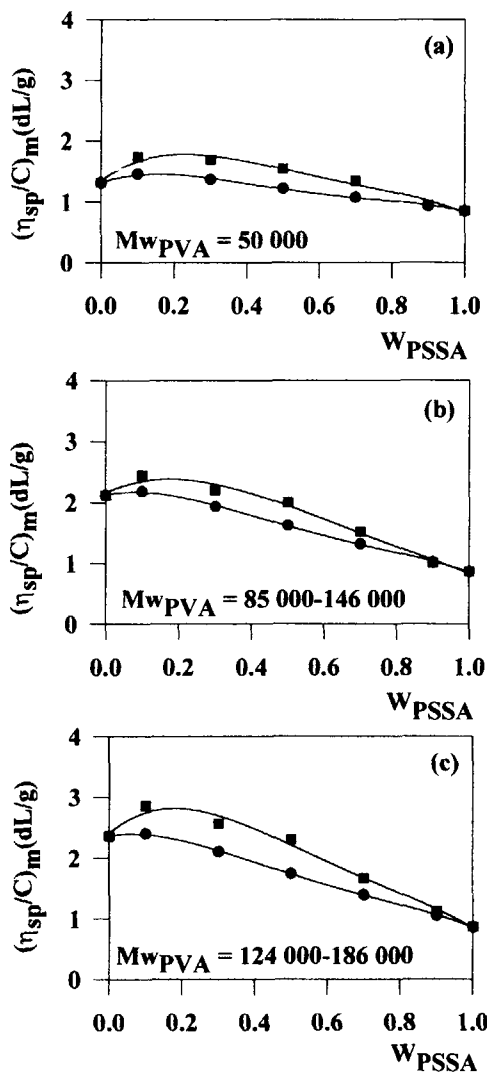
$$(\eta_{sp}/C)_m = W_1(\eta_{sp1}/C_1) + W_2(\eta_{sp2}/C)$$

where  $(\eta_{sp}/C)_m$  is the reduced viscosity of the polymer mixture;  $W_1$  and  $W_2$ , the weight fractions of the ionic and nonionic polymers in the mixture, respectively;  $(\eta_{sp1}/C_1)$ , the reduced viscosity of the ionic polymer at the different concentrations  $C_1$  at which it exists in the different compositions of the mixture; and  $(\eta_{sp2}/C)$ , the reduced viscosity of the nonionic polymer at concentration  $C$ .

The authors considered that the variation of the reduced viscosity of the mixture is due mainly to the reduced viscosity of the polyelectrolyte. This is related to the fact that, in a dilute solution, the decrease of polyelectrolyte concentration induces an increase of its reduced viscosity (polyelectrolyte effect).<sup>9</sup>

In this investigation, we applied the Staikos et al. theoretical relation in order to study the miscibility of the poly(vinyl alcohol) and poly(styrenesulfonic acid) in dilute aqueous solution. Our attention was focused on the dependence of the polymers' miscibility on the molecular weight of poly(vinyl alcohol) and its degree of hydrolysis and

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**Figure 1** Reduced viscosity  $(\eta_{sp}/C)_m$  (dL/g) for PVA/PSSA mixtures vs. PSSA weight fraction ( $W_{PSSA}$ ) at  $C = 2$  g/dL. (■) Experimental curves; (●) theoretical curves.

the total mixture concentration and the nature of the counterion of poly(styrenesulfonic acid) ( $\text{Na}^+$  or  $\text{H}^+$ ).

## EXPERIMENTAL

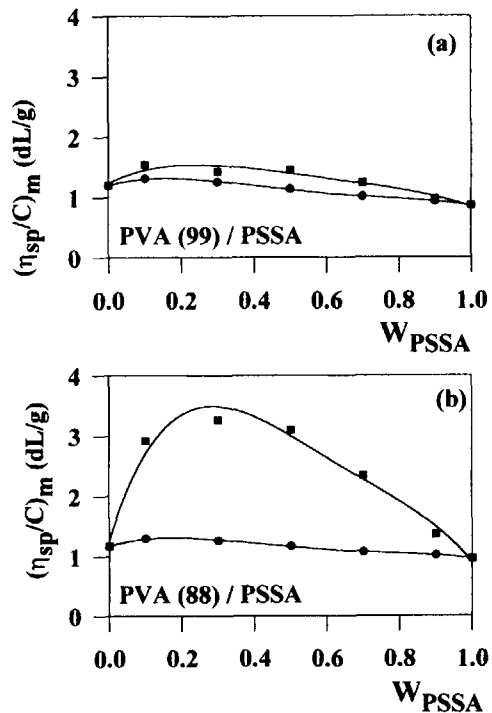
The samples of poly(vinyl alcohol) (PVA) were supplied by Aldrich Chemicals and that of poly(sodium styrenesulfonate (PSSNa) and poly(styrenesulfonic acid) (PSSA) by Scientific Polymer. The molecular weights, as given by the suppliers, were 50,000, 85,000–146,000, and 124,000–186,000 for PVA samples and 70,000 for both PSSNa and PSSA. The samples were used without any further purification. Fourier transform infrared (FTIR)

spectroscopy was used to identify the nature of unhydrolyzed percentage of hydroxyl sites, which was acetate groups.

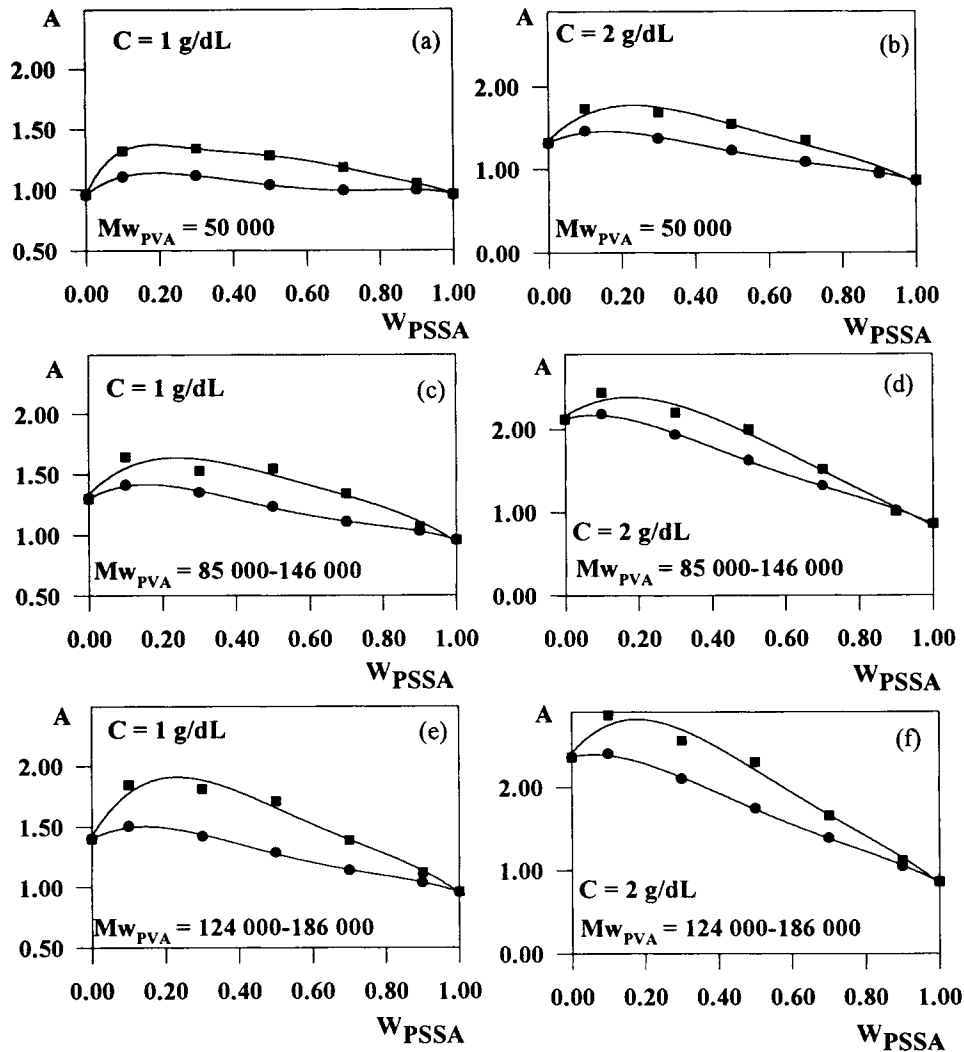
PVA, PSSA, and PSSNa solutions were prepared, separately, by dissolving 1 or 2 g of polymer in 100 mL of deionized water and heating under reflux at  $90^\circ\text{C}$  for 1 h with stirring. Afterward, the solutions were cooled at room temperature and clarified, respectively, through  $1.2\ \mu\text{m}$  (PVA) and  $0.45\ \mu\text{m}$  (PSSA and PSSNa) Millipore filters R.H. type. The two solutions were mixed in a defined proportion to obtain 1 or 2 g/dL as the total concentration. For the viscosimetric measurements of PVA and PSSNa (or PSSA) mixtures, we used a Couette-type viscosimeter ("low shear rheometer 30" from Contraves) at  $25^\circ\text{C}$ .

## RESULTS AND DISCUSSION

The variation of the experimental and theoretical reduced viscosities are represented as a function of polyelectrolyte fraction ( $W_{\text{polyelectrolyte}}$ ). Moreover, it was studied as a function of the molecular weight of PVA and its degree of hydrolysis and the total mixture concentration and the nature of the coun-



**Figure 2** Reduced viscosity  $(\eta_{sp}/C)_m$  (dL/g) for PVA/PSSA mixtures at  $C = 1$  g/dL vs. PSSA weight fraction ( $W_{PSSA}$ ). (■) Experimental curves; (●) theoretical curves.



**Figure 3** Reduced viscosity [ $A = (\eta_{sp}/C)_m$  (dL/g)] for PVA/PSSA mixtures vs. PSSA weight fraction ( $W_{PSSA}$ ). (■) Experimental curves; (●) theoretical curves.

terion ( $\text{Na}^+$  or  $\text{H}^+$ ) of PSSA. The molecular weight of the PSSA sample was the same ( $\text{MW} = 70,000$ ) in all experiments. As with Staikos et al., we admit that the deviation of the experimental curve from the theoretical one is positive when the experimental reduced viscosity is higher than the theoretical one and negative in the opposite case. These two cases characterize the good and poor miscibility of both polymers, respectively.

#### Influence of the Molecular Weight of PVA Sample

At constant total concentration  $C = 2 \text{ g/dL}$  of PVA and PSSA mixtures, three samples of PVA of different molecular weights and the same degree of hydrolysis (99%) were investigated. As represented in Figure 1, the deviation of the experimental curve

from the theoretical one is always positive whatever the molecular fraction of PSSA ( $W_{PSSA}$ ). Moreover, the reduced viscosity of the mixtures increases with the rising PVA molecular weight. This behavior can be assigned to the miscibility of these two polymers which increases with the PVA molecular weight. It is well known that the contribution of polymer in the mixture entropy tends to zero with the increase of its molecular weight and that, in these conditions, the miscibility of PVA and PSSA, in an aqueous dilute solution, can be explained as the result of intermolecular interactions.<sup>8,11</sup>

#### Influence of Hydrolysis Degree (DH) of PVA Sample

Two samples of PVA having the same molecular weight ( $\text{MW} = 85,000\text{--}146,000$ ) but with different

degrees of hydrolysis (99 and 88%) were mixed, separately, with the PSSA sample to obtain a constant total mixture concentration  $C = 1$  g/dL.

Figure 2(a) and (b) represent the variation of the reduced viscosity of the mixture of PVA (88%)/PSSA and PVA (99%)/PSSA, respectively. It is evident that the two mixtures present one region corresponding to a positive deviation of the experimental curve from the theoretical one. But this region is more important in the PVA (88)/PSSA than in the PVA (99)/PSSA mixture. Therefore, in both cases, it can be considered that these two polymers are well miscible, but the PVA (88)/PSSA mixture presents the higher miscibility. Thus, the miscibility of PVA and PSSA, in dilute aqueous solution, is enhanced by the decrease of the hydrolysis degree. This behavior was explained in literature<sup>12</sup> as the consequence of the decrease of the potential for intramolecular hydrogen bonds of the PVA sample because the acetate groups decrease with the intermolecular interactions and improve the expansion of the PVA chains. The hydroxyl groups are considered as acceptors and donors of hydrogen bonds. So, their presence appears necessary to obtain PVA/PSSA miscibility.

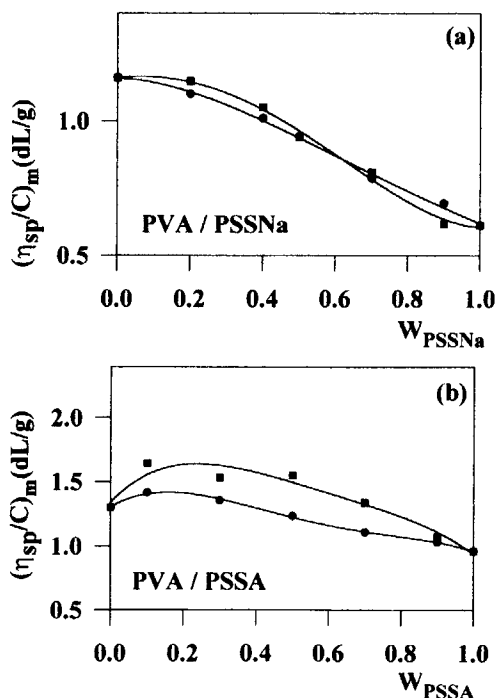
#### Influence of the Total Mixture Concentration $C$

With a known molecular weight of the PVA samples, we studied two total concentrations  $C = 1$  and 2 g/dL (Fig. 3). The results show that whatever the molecular weight and the concentration these two polymers are well miscible and their miscibility increases with molecular weight and concentration. Thus, it can be deduced from these results that at a constant molecular weight of the PVA sample, the PVA and PSSA miscibility increases with the total mixture concentration in the interval 1–2 g/dL. This result cannot be generalized toward higher concentrations.

In dilute solution, the increase of concentration provokes the enhancement of intermolecular interactions because the amount of participating groups increases. Furthermore, it can consider that the increase of polymers' concentration in the mixture implicates the approach of the polymers' chains and the increase of the molecular contacts probability (intermolecular interactions).<sup>11</sup>

#### Origin of PVA/PSSA Miscibility

Two samples of PSSA and PSSNa, having the same molecular weight ( $MW = 70,000$ ), were mixed with PVA ( $MW = 85,000$ – $146,000$  and  $DH = 99\%$ ) to



**Figure 4** Reduced viscosity  $(\eta_{sp}/C)_m$  (dL/g) for (a) PVA/PSSNa and (b) PVA/PSSA mixtures at  $C = 1$  g/dL and  $DH = 99\%$  vs. PSSNa or PSSA weight fractions ( $W_{PSSNa}$  or  $W_{PSSA}$ ). (■) Experimental curves; (●) theoretical curves.

prepare two mixtures of 1 g/dL each. From the comparison of Figure 4 (a) and (b) which represent, respectively, the reduced viscosities of PVA/PSSNa and PVA/PSSA, it appears that PVA and PSSA is miscible whatever the molecular fraction of the polyion, whereas PVA and PSSNa are slightly miscible in the range  $0.00 < W_{PSSNa} < 0.60$  and are theoretically nonmiscible out of this interval. This behavior is due, of course, to the presence of the counterions. They participate in the formation of hydrogen bonds which are at the origin of PVA and PSSA total miscibility or PVA and PSSNa partial miscibility.<sup>13</sup>

We used Fourier transform infrared (FTIR) spectroscopy to identify the groups which are at the origin of the intermolecular interactions and the miscibility of PVA/PSSNa films ( $C = 2$  g/dL and  $MW_{PVA} = 124,000$ – $146,000$ ). The results of this study display that hydroxyl and unsymmetric sulfonate groups take part in these interactions. Moreover, whatever the proportions of two polymers in the mixture, the films were very transparent.

#### CONCLUSION

In this study, which was limited to dilute aqueous solutions ( $C = 1$  or 2 g/dL), we found that the mis-

cibility of PVA and PSSA is dependent mainly on the nature of the counterion of the polyelectrolyte and the degree of hydrolysis of PVA. Moreover, this miscibility improves with the increase of PVA molecular weight and the total mixture concentration. The miscibility of the two polymers is assigned to the formation of hydrogen bonds between the hydroxyl groups of PVA and the sulfonic groups of PSSA.

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## REFERENCES

1. A. K. Kulshershta, B. P. Singh, and Y. N. Sharma, *Eur. Polym. J.*, **24**, 29 (1988).
2. Maria J. Parets, R. Garcia, V. Soria, and A. Campos, *Eur. Polym. J.*, **26**, 767 (1990).
3. V. Soria, J. E. Figueruelo, and A. Campos, *Eur. Polym. J.*, **17**, 137 (1981).
4. B. Bohmer, D. Berek, and S. Florian, *Eur. Polym. J.*, **6**, 471 (1970).
5. K. K. Chee, *Eur. Polym. J.*, **26**, 423 (1990).
6. D. Staszewska and M. Bohdanecky, *Eur. Polym. J.*, **17**, 245 (1981).
7. G. Staikos and C. Tsitsilianis, *J. Appl. Polym. Sci.*, **42**, 867 (1991).
8. G. Staikos and G. Bokias, *Makromol. Chem.*, **192**, 2649 (1991).
9. R. M. Fuoss, *J. Polym. Sci.*, **3**, 603 (1948).
10. O. Olabisi and L. M. Robeson, *Polymer-Polymer Miscibility*, Academic Press, New York, 1979, p. 108.
11. I. Iliopoulos, J. L. Halary, and R. Audebert, *J. Polym. Sci. Part A Polym. Chem.*, **26**, 275 (1988).
12. T. Q. Nguyen, A. Essamri, R. Clément, and J. Néel, *Makromol. Chem.*, **188**, 1973 (1987).
13. M. O. David and T. Q. Nguyen, *Eur. Polym. J.*, **30**, 1013 (1994).

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