

Interpolymer Associations Between Poly(vinyl alcohol) and Poly(diallyldimethylammonium chloride) in Aqueous Dilute Solution

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ABSTRACT: This article studied the compatibility of poly(vinyl alcohol) (PVA) with poly(diallyldimethylammonium chloride) (PDADMACl) in a dilute aqueous solution. At a total mixture concentration and a constant molecular weight of PDADMACl, it was found that interpolymer associations increase with the molecular weight and decrease with the degree of hydrolysis of the PVA sample (87–89 and 98–99%). From these results, it can be deduced that the compatibility of PVA and PDADMACl is due to specific inter-

molecular interactions that could be assigned mainly to electrostatic interactions between hydroxyl groups within PVA chains and ion atoms within PDADMACl. © 2002 Wiley Periodicals, Inc. *J Appl Polym Sci* 86: 433–435, 2002

Key words: poly(vinyl alcohol); poly(diallyldimethyl ammonium chloride); dipole–ion interactions; compatibility; viscosity

INTRODUCTION

One of the main advantages of the viscosimetric method is the characterization of macromolecules in a dispersed state (solution). Normally, the ability of two polymers to develop attractive or repulsive interactions is associated, respectively, to an increase or decrease of mixture viscosity.^{1–8}

Many theoretical models were proposed to characterize the behavior of two polymers in an aqueous solution.^{6–11} Here, we applied the Staikos et al.^{7,8} model. It was proposed to study the interactions between nonionic and ionic polymers (polyelectrolytes) in a dilute aqueous solution.

Two polymers are considered compatible when their experimental reduced viscosity is higher than is their theoretical one. The latter is calculated from the following equation:

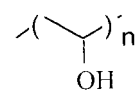
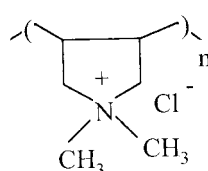
$$(\eta_{sp}/C)_{\text{theo}} = W_1(\eta_{sp1}/C_1) + W_2(\eta_{sp2}/C)$$

where $(\eta_{sp}/C)_{\text{theo}}$ is the theoretical reduced viscosity of a polymer mixture; W_1 and W_2 , respectively, the weight fractions of an ionic and a nonionic polymer in a mixture; (η_{sp1}/C_1) , the reduced viscosity of an ionic polymer at different concentrations C_1 at which it

exists in the different compositions of the mixture; and (η_{sp2}/C) , the reduced viscosity of the nonionic polymer at concentration C .

To make the examination of polymer–polymer compatibility easy, we use the ratio of the experimental to theoretical reduced viscosity $\tau = (\eta_{sp}/C)_{\text{exp}}/(\eta_{sp}/C)_{\text{theo}}$. Two polymers will be considered compatible when the value of this ratio is higher than 1 and of poor compatibility in the opposite case.

In this investigation, we studied the compatibility of poly(vinyl alcohol) (PVA) and poly(diallyldimethylammonium chloride) (PDADMACl) polymers in a dilute aqueous solution. This system is used to prepare an ion-exchange membrane of a semi-interpenetrating polymer network structure, where it is expected that the compatibility of polymers enhances the ion-exchange capacity of the membranes.¹² We focused our attention on the dependence of polymer compatibility on the molecular weight (M_w) of PVA and its degree of hydrolysis (DH) and total mixture concentration. The polymers chemical structures are



Poly(vinyl alcohol)
PVA

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TABLE I
Characteristics of the Used Polymers

Symbol sample	Hydroxyl (%)	Acetate (%)	Supplied M_w
PVA87/13	87–89%	13–11%	13,000–23,000
PVA87/31	87–89%	13–11%	31,000–50,000
PVA87/85	87–89%	13–11%	85,000–146,000
PVA87/124	87–89%	13–11%	124,000–186,000
PVA87/124	98–99%	02–01%	124,000–186,000
PDADMACl	—	—	400,000–500,000

EXPERIMENTAL

Aldrich (Milwaukee, WI) supplied the PVA and PDADMACl polymers, which were used without any further purification. Their properties are summarized in Table I.

PVA and PDADMACl solutions were prepared separately by dissolving 2 g of the polymer in 98 mL of deionized water and heating under reflux, with stirring, at 90°C for 1 h. Afterward, the solutions were cooled at room temperature. The two solutions were mixed in defined proportions (volume/volume) to obtain 1, 1.5, or 2 g/dL as the total mixture concentration.

For the viscosity measurements of the PVA and PDADMACl mixtures, we used a Couette-type viscosimeter ("low shear rheometer 30" from Contraves) at shear rates ranging from 3.23–5.96 s⁻¹. To assure the establishment of interpolymer association, the viscosity measurements were done at 25°C and at least after 14 h of polymer mixing.

RESULTS AND DISCUSSION

The main parameters that we took into account are the effect of the hydroxyl content (DH), the molecular weight (M_w) of the PVA sample, and the total mixture concentration.

Influence of the molecular weight of PVA sample

In this study, many PVA samples having different molecular weights were used to determine the influence of this parameter on polymer compatibility. At a constant total mixture concentration, $C = 2$ g/dL. We examined four PVA samples having the same DH (87–89%) but different molecular weights ($M_w = 13,000$ – $23,000$, $31,000$ – $50,000$, $85,000$ – $146,000$, and $124,000$ – $186,000$).

Figure 1 shows that, whatever the molecular fraction of PDADMACl ($W_{PDADMACl}$), the ratio values of the experimentally reduced viscosity to the theoretical one are always higher than is the limit of compatibility (–) criterion. In any case, this behavior proves that PVA and PDADMACl are totally compatible in these conditions. But polymer compatibility increases slightly with the molecular weight of the PVA sample.

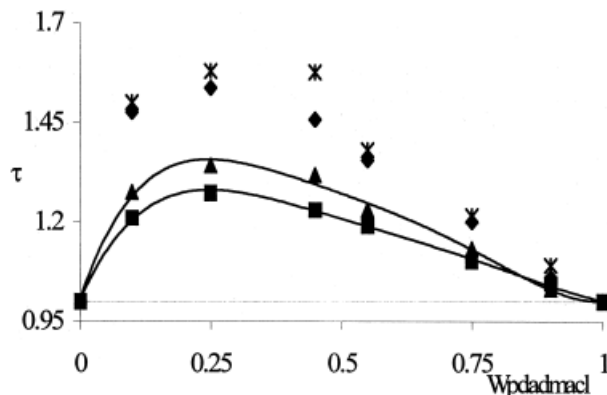


Figure 1 Ratio of experimental reduced viscosity on theoretical one [$\tau = (\eta_{sp}/C)_{exp}/(\eta_{sp}/C)_{theo}$] via PDADMACl fraction ($W_{PDADMACl}$) of (■) PVA87/13/PDADMACl mixture, (▲) PVA87/31/PDADMACl mixture, (◆) PVA87/85/PDADMACl mixture, and (*) PVA87/124/PDADMACl mixture.

It is well known that, with an increase of molecular weight, in absence of specific interactions like hydrogen bonds or strong attractive electrostatic interactions, the mixture entropy tends to zero and the chance of polymer compatibility is reduced.¹³

Here, contrary to our expectations, the results show that with increase of the molecular weight the PVA and PDADMACl compatibility increases. Therefore, both polymers develop specific interactions that are capable of offsetting the reduction of the mixture entropy and provoking polymer compatibility.^{14,15}

Thus, the compatibility of PVA with PDADMACl, in a dilute aqueous solution, is due to specific intermolecular interactions. These interpolymer interactions could be assigned to attractive electrostatic forces that associate hydroxyl groups within PVA chains and ions atoms as nitrogen within PDADMACl chains.

Influence of DH of PVA sample

For this case, we examined two PVA samples having the same molecular weight ($M_w = 124,000$ – $186,000$)

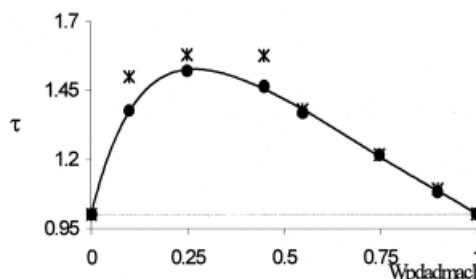


Figure 2 $\tau = (\eta_{sp}/C)_{exp}/(\eta_{sp}/C)_{theo}$ via $W_{PDADMACl}$ for (*) PVA87/124/PDADMACl mixture and (●) PVA98/124/PDADMACl mixture.

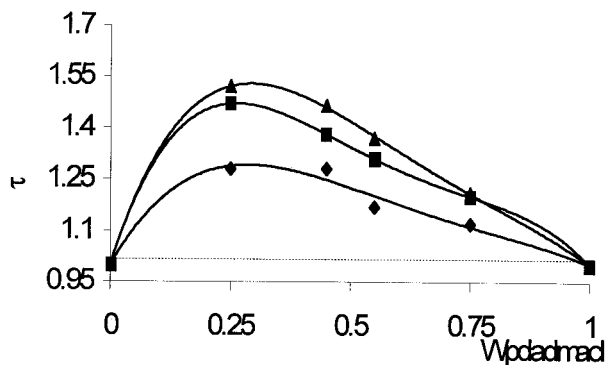


Figure 3 $\tau = (\eta_{sp}/C)_{exp}/(\eta_{sp}/C)_{theo}$ via $W_{PDADMACI}$ for (▲) PVA87124/PDADMACI mixture, $C = 2$ g/dL, (■) PVA87124/PDADMACI mixture, $C = 1.5$ g/dL, and (◆) PVA87124/PDADMACI mixture, $C = 1$ g/dL.

but different DHs (87–89 and 98–99%). The total mixture concentration was $C = 2$ g/dL. Figure 2 indicates that PVA and PDADMACI are compatible whatever the fraction of PVA or PDADMACI. But this compatibility increases inversely with the DH. Here, the slight increase of polymer compatibility with the reduction of the DH could be attributed to the increase of acetate groups, which reduce the intramolecular interactions among hydroxyl groups within the PVA chains and favor the interpolymer association between PVA and PDADMACI segments.¹⁶

Influence of mixture concentration

Three mixtures of different total concentrations of 1, 1.5, and 2 g/dL were examined to verify the influence of the total mixture concentration. As represented in Figure 3, it can be deduced that interpolymer associations increase with the total mixture concentration. It can be supposed that increase of the total concentration enhances the probability of polymer contact^{17,18} and intermolecular interactions. But these results cannot be generalized.

CONCLUSIONS

Owing to the high limpidity of the PVA and PDADMACI mixtures, viscosity was considered as a sufficient technique to investigate the compatibility of these polymers in a dilute aqueous solution. The results of this investigation prove that, in a dilute aqueous solution, PVA and PDADMACI develop interpolymer associations that are responsible for their compatibility. Contrary to thermodynamic waiting, the compatibility improves slightly with increase of the molecular weight of the PVA sample. Furthermore, this compatibility was enhanced by the augmentation of the percentage of acetate groups. These associations could be ascribed to dipole-ion interactions between hydroxyl groups within the PVA chains and ion atoms in the polyelectrolyte chains.

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