Hydrogen Bonding in Poly(4-vinylpyridine)/Poly(vinyl acetate-*co*-vinyl alcohol) Blends. An Infrared Study

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Received June 3, 1993; Revised Manuscript Received September 14, 1993®

ABSTRACT: In this paper the specific interactions between poly(vinylpyridine) and copolymers of vinyl alcohol/vinyl acetate of different compositions have been studied by Fourier transform infrared spectroscopy (FTIR). Hydrogen bonding between both polymer components leads to significant spectral modification in hydroxyl, carbonyl, and pyridine rings spectral bands. Minor modifications in other spectral modes have also been detected. The spectral results indicate at least three competing equilibrium processes in the blends: copolymer slef-association (hydroxyl–hydroxyl and hydroxyl–carbonyl) and hydroxyl–pyridine interassociation. The Painter–Coleman association model for three interacting units was successfully applied. Finally, quantitative results show that hydroxyl–hydroxyl association is the predominant one.

Introduction

Polymer blends are one of most studied topics in polymer science in the last decade. Although a number of problems remain unresolved in this area, some fundamental bases are well established. For instance, the relevance of specific interactions (hydrogen bonding, dipole–dipole interactions, charge transfer, etc.) between components on polymer–polymer miscibility is well stated. For macromolecules, the Gibbs free energy of mixing is controlled by its enthalpic contribution because the entropic term is usually favorable but very small. In this way, polymer pairs with complementary chemical structures favoring specific interactions (and, thus, a negative enthalpy of mixing) usually lead to miscible systems. On the contrary, when only dispersive forces can be expected between components, the result is a positive (unfavorable) contribution of the enthalpic term and as a consequence these systems are usually immiscible.

Recently, we have reported several polymer blends[1] having components with complementary chemical structures favorable for specific interactions by hydrogen bonding, but with a miscibility behavior also controlled by other complementary factors. These systems are blends of random copolymers of poly(vinyl alcohol) (PVA) and poly(vinyl acetate) (PVAc) with poly(vinylpyridines) in their 2 and 4 isomer forms; the former act as proton donors and the latter as proton acceptors. Experimental results show that poly(4-vinylpyridine) (P4VP) is miscible with poly(vinyl acetate-*co*-vinyl alcohol) (ACA) copolymers in a wide range of copolymer compositions but immiscible with both homopolymers. Nevertheless, poly(2-vinylpyridine) (P2VP) is found to be immiscible with ACA copolymers (or homopolymers) independent of the copolymer or blend composition. Taking into account the strong proton acceptor character of pyridine groups, the immiscibility of both poly(vinylpyridines) with pure PVA (strong proton donor) and that of P2VP with all ACA copolymer compositions is remarkable. Immiscibility in P2VP/ACA systems can be attributed to steric hindrance effects that limit the contribution of hydrogen bonding for these blends. In P2VP, the nitrogen atom of the pyridine ring is very close to the backbone, which seriously limits the scope of hydrogen bonding with hydroxyl groups in vinyl alcohol units of ACA copolymers or PVA. On the contrary, the nitrogen atom of the pyridine ring in P4VP is placed far from the backbone and we can expect a minor steric hindrance. Recent results for other blends[2,3] seem to confirm a smaller ability for hydrogen bonding in P2VP than in P4VP.

A second point to solve is the miscibility behavior of P4VP with poly(vinyl alcohol). According to previous results,[1] there are spectral evidences of hydrogen bonding in ACA/P4VP blends. Hydrogen bonding takes place not only between pyridine and vinyl alcohol units but also between vinyl alcohol and vinyl acetate ones. In other words, competition between ACA copolymer self-association (depending upon its chemical composition) and interassociation with P4VP takes place. Consequently, the final phase behavior in the blend is the result of the balance of all these factors. According to these ideas, immiscibility in P4VP/PVA blends has been attributed to the predominance of hydroxyl self-association processes in PVA.

P4VP/ACA blends are an interesting type of system to study the relevance of specific interactions on polymer–polymer miscibility. The aim of this paper is to elucidate the type and number of specific interactions in P4VP/ACA copolymer blends, using Fourier transform infrared spectroscopy (FTIR) as the experimental tool.

Experimental Part

Samples. Poly(4-vinylpyridine) (P4VP) was a commercial sample kindly supplied by Reilly Chemicals (sample 450). Its weight-average molar mass was 50 000 g/mol, as indicated by the manufacturer. The sample was purified by precipitation from alcohol into ether.

Different poly(vinyl acetate-*co*-vinyl alcohol) (ACA) random copolymers were obtained by hydrolysis–alcoholysis of PVAc. Reaction and purification methods have previously been described.[1]

The obtained copolymers have been titrated according to standard procedures. The hydrolysis degrees of the copolymers employed in this paper are 15.5% (ACA15), 21.5% (ACA21), 31.6% (ACA32), 54.6% (ACA55), 88.0% (ACA88), 97.0% (ACA97), and 99.7% (PVA).

FTIR Analysis. IR spectra for polymer blends were recorded on a Nicolet 520 Fourier transform infrared (FTIR) spectrometer with a resolution of 2 cm^{-1} and were averaged from 100 scans. Films for FTIR measurements were cast from solutions (0.02 g/mL), vacuum dried, and finally annealed at 403 K (temperature above T_g of the samples[1]) to eliminate residual solvent and assure

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® Abstract published in *Advance ACS Abstracts,* November 15, 1993.

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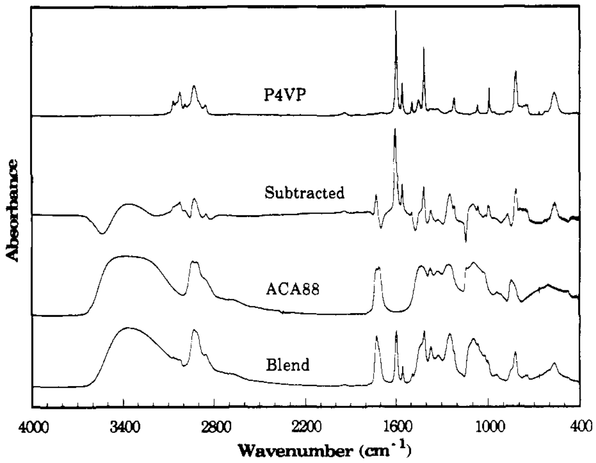

Figure 1. Infrared spectra of a blend of P4VP and ACA88 (40 wt % of P4VP), an ACA88 copolymer, difference, and pure P4VP for comparison.

thermal equilibrium in samples. Samples dissolved in methanol were cast directly on KBr pellets or on Teflon (for samples dissolved in water/methanol mixtures). All films were sufficiently thin to be within the absorbance range where the Beer–Lambert law is obeyed.

Least-squares curve fittings of the spectra were performed using curve analysis software Nicolet FOCAS installed in a Nicolet 620 station. This software enables one to obtain a preliminary determination of the number of peaks to be analyzed and their position by a Fourier self-deconvolution method. After selection of the number of peaks and their tentative location, curve analysis simulates the location, peak width, and peak shape of each individual peak which forms the pattern of overlapping bands found in the sample spectrum.

Results and Discussion

As we have pointed out, a variety of competitive hydrogen-bonding processes in ACA/P4VP blends can be expected. We will start from a qualitative point of view, characterizing by infrared spectroscopy the different types of specific interactions present in these systems. Then a quantitative evaluation of specific interactions will be performed.

Spectral subtraction is a very useful tool for the identification of modifications in infrared spectra originating by specific interactions. When this method is employed in our systems, relevant modifications have been found in the infrared spectra of both components in the blends. Figure 1 shows the infrared spectra of pure P4VP, pure ACA88 copolymer, and a 40/60 wt % P4VP/ACA88 blend. In the same figure is also displayed the difference spectrum resulting from digital subtraction of the pure ACA88 spectrum from the blend. A vibrational mode of the copolymer placed at 1376 cm^{-1} has been employed for digital subtraction. Several S-shaped band profiles can be observed in the difference spectrum. This kind of profile is characteristic of a band shift in the blend for the pure component employed in the subtraction. Also the rising of a new band in the difference spectrum attributable to P4VP can be detected. For ACA copolymers the bands involved in these modifications are those corresponding to stretching modes of hydroxyl and carbonyl groups and bending of acetate ones and in the case of P4VP the twisting modes of the pyridine ring.

Hydroxyl Stretching Region (3100–3650 cm^{-1}). In ACA copolymers the most relevant fact in this spectral region is the presence of a wide band overlapped with C–H stretching modes (see Figure 2a). This wide band can be attributed to the summation of several contributions corresponding to hydroxyl groups in different situations.

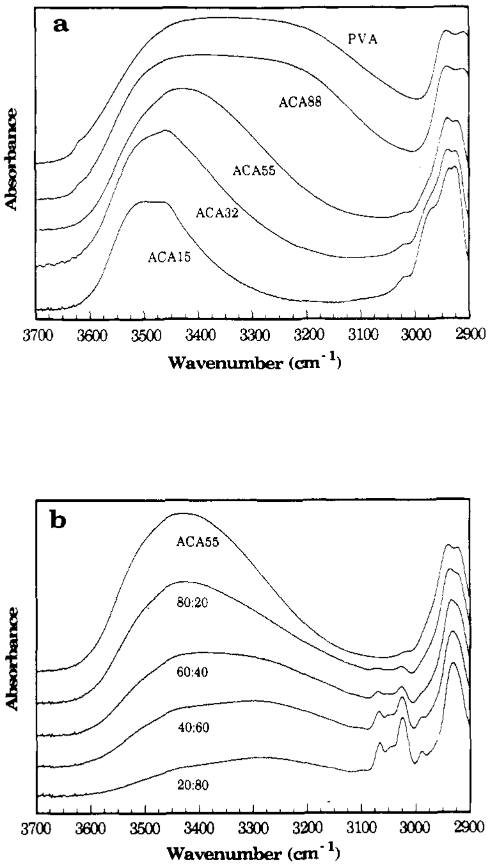

Figure 2. Infrared spectra in the 2900–3700-cm^{-1} region for (a) different ACA copolymers and pure PVA and (b) blends ACA55/P4VP (wt %) as a function of composition.

We can consider at least the following (from lower to higher wavenumbers): hydroxyl groups hydrogen bonded with other hydroxyl groups in the same or vicinal chains, forming dimers, trimers, etc.; hydroxyl groups hydrogen bonded with carbonyl groups in the same or vicinal chains; and finally non-hydrogen-bonded hydroxyl groups. Thus, we can have a wide distribution of hydroxyl groups with force constants differing in an almost continuous range. In fact, the hydroxyl stretching band is almost symmetrical in ACA copolymers with a high content of vinyl alcohol units. It is not possible to find remarkable shoulders indicating a preferred class of association in the copolymer. On the other hand, the maximum of the band is shifted toward high wavenumbers as the content of hydroxyl units in the copolymer is lowered. In this case the contributions corresponding to the stronger associated hydroxyl groups (intramolecular dimers and polymers) are unfavorable by steric reasons. Finally, when the hydroxyl content is very low, a narrowing of the band is observed and two shoulders are evident. These shoulders can be attributed to non-associated hydroxyl groups (at high wavenumber) and to hydroxyl groups associated to carbonyl ones (at low wavenumber).

As can be seen in Figure 2b, the spectra of the blends show significant changes in this region, suggesting a redistribution in the arrangement of the hydroxyl group associations. If we compare the spectra corresponding to the same blend as a function of the P4VP composition, a progressive shift of this band toward low wavenumbers as the P4VP content increases is observed. We must point out that P4VP does not present appreciable absorbance above 3150 cm^{-1}. Consequently, the observed modifications in the hydroxyl stretching band only can be attributed to changes in the association processes of these groups. On the other hand, if we compare the location of the

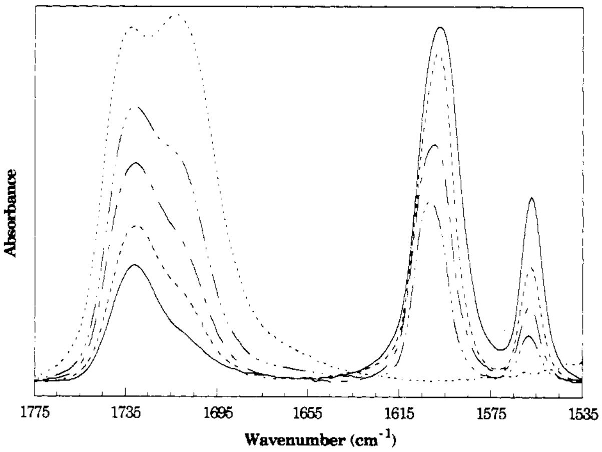

Figure 3. Infrared spectra in the 1535–1775-cm^{-1} region for (· · ·) ACA88, (– . . . –) a ACA88/P4VP (80:20) blend, (– . –) a ACA88/P4VP (60:40) blend, (- - -) a ACA88/P4VP (40:60) blend, and (—) a ACA88/P4VP (20:80) blend.

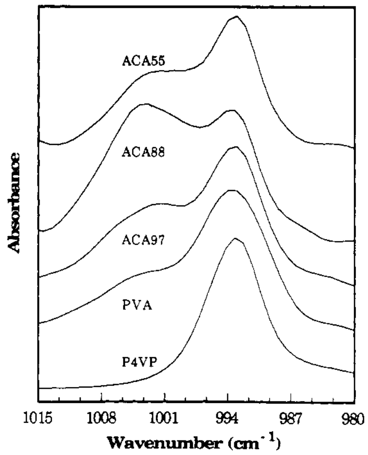

Figure 4. Scale-expanded infrared spectra in the range 980–1015 cm^{-1}; P4VP and blends of PVA, ACA97, ACA88, and ACA55 containing 40 wt % of P4VP. The last four spectra have been digitally subtracted.

maxima of the bands for blends of P4VP with different ACA copolymers, we find that for compositions with a high content of P4VP they are placed around 3290 cm^{-1}. This behavior suggests that a significant part of the hydroxyl groups involved in the association processes previously described for pure ACA copolymers are now hydrogen bonded to pyridine groups in P4VP. According to our results, the location of this spectral contriubtion is placed around 3290 cm^{-1}. The shift in wavenumber of this band is a measure of the average strength of the intermolecular interactions. Taking 3525 cm^{-1} as a typical location for nonassociated hydroxyl groups for vinyl alcohol units,[4] $\Delta\nu$ in these systems is 235 cm^{-1}, close to that reported for poly(hydroxylated methacrylates)/P4VP blends[3] but lower than that for poly(hydroxy ether of Bisphenol A)/P4VP blends[5] ($\approx$370 cm^{-1}).

Carbonyl Stretching Region (1650–1790 cm^{-1}). In PVAc the carbonyl stretching band is placed at 1738 cm^{-1}. For ACA copolymers this band shows relevant modifications depending on its molecular composition. Thus, at low wavenumbers a shoulder can be observed even for copolymers with a low content of vinyl alcohol units (see Figure 3). The relative contribution of this band becomes more important as the content of vinyl alcohol units for the copolymer increases. This fact suggests that such a shoulder can be attributed to inter- or intramolecular hydrogen bonding between carbonyl groups in acetate units and hydroxyl groups in vinyl alcohol units. Accordingly, in ACA copolymers we have two types of carbonyl groups: those associated by hydrogen bonding and the free ones. Obviously, the relative contribution of these two types of carbonyl groups must be dependent on copolymer composition. As has been observed in infrared spectra, we can expect a higher degree of hydrogen-bonded carbonyl groups for copolymers rich in vinyl alcohol units where carbonyl groups are surrounded by a donor medium.

The presence of pyridine rings in the blend leads to a competition with carbonyl groups for hydrogen bonding with hydroxyl groups. As can be seen in Figure 3, this competition is evident in the evolution of the carbonyl band in the blend. Thus, for a particular ACA copolymer a decrease in the contribution corresponding to hydrogen-bonded carbonyl groups (progressive disappearance of the shoulder at low wavenumber) is observed as the content of P4VP in the blend increases. In other words, hydroxyl–pyridine association prevails over hydroxyl–carbonyl association. This result agrees with the evolution previously reported for the hydroxyl stretching region.

Pyridine Ring Modes (1540–1630 cm^{-1}). The most intense bands corresponding to pyridine ring modes in P4VP are those located at 1597 and 1557 cm^{-1}. These bands show a different behavior when pyridine rings are hydrogen bonded. The 1557-cm^{-1} mode is not affected in position or intensity by hydrogen bonding. Nevertheless, 1597-cm^{-1} band shifts toward high wavenumbers by hydrogen bonding[3,6] that has been attributed to an increase of the stiffness in the pyridine ring. Fortunately, ACA copolymers do not show a significant absorbance in this region and, in this way, we can observe without interferences the evolution of pyridine ring modes in the blend.

All the miscible blends show the same trend for 1597-cm^{-1} band: as the ACA content increases in the blend, the band shifts toward high wavenumbers (see Figure 3). Besides, this band is broader in the blends (22–16 cm^{-1} bandwidth at half-height) than in pure P4VP (12 cm^{-1}). In other words, we have two classes of pyridine rings, those hydrogen bonded to hydroxyl groups (with a corresponding effect over the hydroxyl stretching band) and those non-hydrogen-bonded. The addition of their spectral contributions results in a broadening and shifting of the band. From a qualitative point of view this is a logical behavior because, as the content in the ACA copolymer increases in the blend, a larger number of hydroxyl groups are available to the hydrogen bonding with pyridine rings.

Another pyridine ring band affected by hydrogen bonding in the blends is the spectral mode placed at 993 cm^{-1}. This band shifts toward high wavenumbers in a larger magnitude than the previously described pyridine ring modes and results in a new peak that is well resolved in the subtracted spectrum shown in Figure 1. Unfortunately, the 993-cm^{-1} band overlaps with the more intense C–O stretching band of the hydroxyl groups. This fact complicates its quantitative analysis, but a qualitative discussion is even possible by subtracting the ACA spectrum from the blend. Spectral subtraction has been performed using ACA bands nonaffected by blending as the mode placed at 1376 cm^{-1} and also a small group placed at 910 cm^{-1}. The subtracted spectra clearly show that this band splits in two modes (Figure 4) that exhibit a blend composition dependence similar to that previously described for the other pyridine bands: the band placed at high wavenumbers (hydrogen-bonded pyridine rings) becomes more intense as the content of the ACA copolymer increases in the blend. On the other hand, if we compare the subtracted spectra corresponding to the same blend composition (40 wt % of P4VP) for different ACA

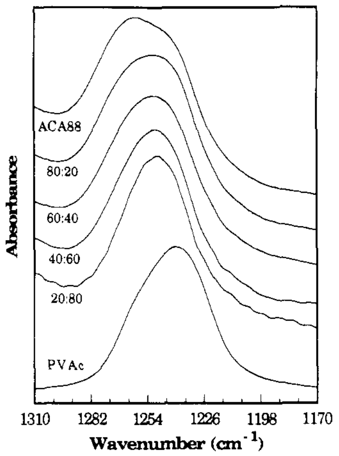

Figure 5. Scale-expanded infrared spectra in the range of 1170–1310 cm^{-1}: PVAc, ACA88, and blends of ACA88/P4VP (80:20; 60:40; 40:60, and 20:80 wt %). The last four spectra have been digitally subtracted.

copolymers, significant differences can be observed (see Figure 4). For miscible blends the contribution of associated pyridine groups becomes more relevant for higher hydroxyl contents in the ACA copolymer. Nevertheless, when the ACA copolymer has a high content in vinyl alcohol units, this contribution decreases again. Now we are close to the miscibility limit, in fact ACA97 is only partially miscible with P4VP. Finally, for a PVA/P4VP blend only a weak shoulder is present. Taking into account that PVA is immiscible with P4VP, the weak contribution of pyridine-associated groups can be attributed to interfacial interactions.

Some other bands are also affected by the presence of P4VP in the blend. The shift toward high wavenumbers in the band corresponding to C–O stretching in vinyl alchol units as the P4VP content increases in the blend is remarkable. For instance, this band is placed at 1094 cm^{-1} for ACA88 and at 1099 cm^{-1} for a 20:80 (w/w) ACA88/P4VP blend. This shift in the C–O band can be attributed to hydrogen bonding. In fact this band must contain at least two contributions: that corresponding to C–O groups where the oxygen atom is hydrogen bonded and that corresponding to nonbonded oxygen atoms. It can be expected that the first contribution will be placed at lower wavenumbers than the second one, because hydrogen bonding must weaken the C–O bond. In this way, the observed shifts can be attributed to the progressive loss of self-association in hydroxyl groups by the presence of P4VP. A similar effect has been previously reported for PVA/poly(vinylpyrrolidone) blends.[7]

The band corresponding to the C–O–C stretching mode in the acetate groups is located at 1250 cm^{-1} in PVAc. For ACA copolymers this spectral mode is more complex, and a new band placed at higher wavenumbers ($\approx$10 cm^{-1}) is present. As can be seen in Figure 5, this band becomes more relevant the higher the content of vinyl alcohol units of the copolymer. In the blends, this band overlaps with some P4VP modes. For this reason, a spectral subtraction has been performed using the P4VP ring mode placed at 1557 cm^{-1}. One more time, the location of the band is a function of the blend composition: it shifts toward low wavenumbers as the content in P4VP increases (see Figure 5). These two facts suggest that this band is the result of hydrogen bonding in ACA copolymers and shows a behavior in the blend according to competitive hydrogen-bonding processes previoulsy described for these systems.

Finally, the last band also affected by the presence of P4VP in the blend is a mode located at 1144 cm^{-1}, corresponding to C–C–C stretching in the crystalline regions of PVA.[8] In ACA copolymers the absorbance of this band decreases as the content of vinyl acetate units increases. Its absorbance is very low for ACA88, and the band is not present for copolymers richer in vinyl acetate units, according to the loss of ordered vinyl alcohol sequences. Blends composed of ACA copolymers with a high degree of crystallinity show a drop in the absorbance of this band as the P4VP content rises. For instance, in ACA88 only blends with a 20% content of P4VP show evidences of this band, in agreement with our calorimetric results.[1] Crystallinity reduction is a typical effect in miscible crystalline–amorphous blends.

Quantitative Analysis. Application of the Painter–Coleman Association Model. The spectral results presented here point out at least three competing processes for hydrogen bonding in the blends: hydroxyl–hydroxyl inter- or intramolecular self-association in ACA copolymers, hydroxyl–carbonyl inter- or intramolecular association in ACA copolymers, and finally hydroxyl–pyridine interassociation between P4VP and ACA copolymers. Infrared spectral analysis not only allows a qualitative description of the specific interactions in the blend but also can be employed as a quantitative tool. Recently, Painter and Coleman[9] have developed a theoretical model that starting from infrared spectral data allows a quantitative characterization of the specific interactions in the blend and also the prediction of its phase behavior. This model was first developed for blends with a self-associated polymer B and a nonassociated polymer A, but with the ability to interact with B. This model has been recently modified[10] to take into account not only one self-association equilibrium in B but several self-associaton equilibria, just as in the blends studied in this work. According to this model, we call B, C, and A the vinyl alcohol, vinyl acetate, and vinylpyridine units, respectively, and K_2, K_B, K_C, and K_A the association equilibrium constants corresponding to:

$$B_1 + B_1 \overset{K_2}{\rightleftharpoons} B_2 \tag{1}$$

$$B_h + B_1 \overset{K_B}{\rightleftharpoons} B_{h+1}\ (h \geq 2) \tag{2}$$

$$B_h + C_1 \overset{K_C}{\rightleftharpoons} B_hC \tag{3}$$

$$B_h + A_1 \overset{K_A}{\rightleftharpoons} B_hA \tag{4}$$

Then, the volume fraction of the components can be expressed as a funtion of the equilibrium constants:

$$\Phi_B = \Phi_{B_1}\left[1 + \frac{K_A\Phi_{A_1}}{r} + \frac{K_C\Phi_{C_1}}{s}\right]\left[\left(1 - \frac{K_2}{K_B}\right) + \frac{K_2}{K_B}\left[\frac{1}{(1 - K_B\Phi_{B_1})^2}\right]\right] \tag{5}$$

$$\Phi_A = \Phi_{A_1} + K_A\Phi_{A_1}\Phi_{B_1}\left[\left(1 - \frac{K_2}{K_B}\right) + \frac{K_2}{K_B}\left(\frac{1}{1 - K_B\Phi_{B_1}}\right)\right] \tag{6}$$

$$\Phi_C = \Phi_{C_1} + K_C\Phi_{C_1}\Phi_{B_1}\left[\left(1 - \frac{K_2}{K_B}\right) + \frac{K_2}{K_B}\left(\frac{1}{1 - K_B\Phi_{B_1}}\right)\right] \tag{7}$$

where Φ_B, Φ_A, and Φ_C are the volume fractions of repeat units in the blend; Φ_{B_1}, Φ_{A_1}, and Φ_{C_1} are the fraction of those units non-hydrogen-bonded in the blend; r and s are

Table I. Curve-Fitting Results for Carbonyl Stretching Bands in ACA88/P4VP Blends

	free carbonyl band			associated carbonyl band			
ACA88/P4VP (wt %)	wavenumber (cm^{-1})	width (cm^{-1})	rel area (%)	wavenumber (cm^{-1})	width (cm^{-1})	rel area (%)	f_F
100/0	1735	19	33.4	1712	28	66.6	0.43
90/10	1734	22	37.9	1711	28	62.1	0.48
80/20	1734	23	43.6	1711	28	56.4	0.54
70/30	1732	24	47.0	1710	27	53.0	0.57
60/40	1734	22	51.1	1713	27	48.9	0.61
50/50	1732	22	55.2	1712	26	44.8	0.65
40/60	1732	22	61.9	1711	25	38.2	0.71
30/70	1732	22	66.6	1710	24	33.4	0.75
20/80	1732	21	73.9	1709	25	26.1	0.81

the ratios of molar volumes of the repeat units: $r = V_A/V_E$ and $s = V_C/V_E$, 3.613 and 2.970 for our systems, respectively.

To calculate the distribution of associated and free groups in the blend, Φ_{B_1}, Φ_{A_1}, and Φ_{C_1} and the equilibrium constants K_2, K_B, K_C, and K_A must be known. The first three equilibrium constants are related to the self-associating component (ACA copolymer) and can be calculated from low molecular weight analogs. An admissible molecular analog for vinyl alcohol units in ACA copolymers is a secondary alcohol as 2-propanol. Recently, Coleman et al.[10] have studied the association equilibria of this molecule by infrared spectroscopy. The reported values for K_2 and K_B equilibrium constants are 2.56 and 4.64 L/mol, respectively. Equations 5–7 require dimensionless equilibrium constants that can be calculated from the following relationship:

$$K_i = K_i^{\text{model}}/V_m \qquad (8)$$

where K_i^{model} is the dimensional constant corresponding to i equilibrium for the model molecule and V_m is the molar volume of repeat units in the polymer (23.50 cm^3/mol for vinyl alcohol). In this way our values for K_2 and K_B are 109 and 197, respectively.

The evaluation of K_C must be directly performed from infrared spectra of the blends. As has been previously pointed out, the carbonyl stretching band in our blends shows two different contributions corresponding to associated and nonassociated carbonyl groups. Thus we have employed a spectral band fit procedure to calculate the relative contribution of these two types of carbonyl groups in the blend. From such values it is possible to determine the fraction of nonassociated acetate groups f_F^{CO}. The procedure requires the ratio of molar absorption coefficients of both spectral contributions. Again we can benefit from the work of The Pennsylvania State University group that has reported a value of 1.5 for this ratio in poly(vinylphenol)/poly(vinyl acetate) blends.[11] The position of both spectral contributions in our systems is similar to that reported in this work and also in other blends with hydrogen-bonded vinyl acetate units.

With the volume fraction values of nonassociated acetate groups, and with use of eq 5 (where Φ_A is zero now) and eq 7, we can calculate K_C by fitting to the experimental data obtained for f_F^{CO}. For the sake of simplicity, we will describe only blends with ACA88 that shows a similar amount of associated (57%) and nonassociated (43%) acetate groups. The obtained K_C value for this copolymer is 51.8.

Finally, the evaluation of K_A is performed from infrared spectra of ACA88/P4VP blends at different compositions. Our systems allow work over two different spectral bands, because, as has been previously pointed out, both carbonyl stretching bands and pyridine ring modes are affected by hydrogen bonding. In order to evaluate the running of the model, these two options will be tested to evaluate K_A.

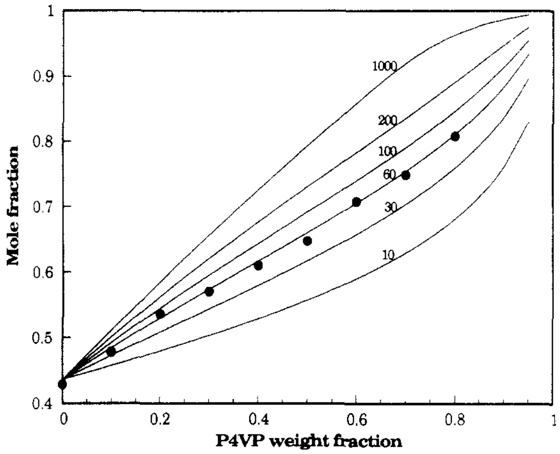

Figure 6. Experimental values (●) of nonassociated carbonyl group mole fractions in the blend, and theoretical curves obtained by using different values of K_A, as a function of the blend composition.

First, we have calculated the theoretical fractions of nonassociated carbonyl groups in the blend from eqs 5–7, by using different values of K_A. Then, we have plotted such values as a function of the blend composition and compared them with the experimental ones obtained from infrared spectra (see Table I). As can be observed in Figure 6, the experimental data fit the theoretical curve obtained for $K_A = 60$.

On the other hand, a similar analysis has been performed on the pyridine bands. Now the error associated with the spectral curve fit procedure is larger because there is a worse resolution in both associated and nonassociated pyridine ring contributions (see Figure 3). In order to minimize errors, we have fixed the position of these two bands in the fitting, at 1596.7 cm^{-1} for the nonassociated contribution and at 1604.4 cm^{-1} for the associated one. These are the average positions obtained for different ACA/P4VP blends when the computer has a complete liberty of action for the spectral curve fitting. The standard deviations in the obtained position were 0.98 for nonassociated pyridine groups, and 0.88 for associated ones. As has been pointed out previously, in order to evaluate the fraction of associated pyridine groups in the blend, the ratio of molar sorption coefficients for both contributions must be known. For this pyridine spectra mode such a ratio is unity, as has been reported for other blends where P4VP is mixed with hydrogen donor polymers.[3,6] The obtained results in the curve-fitting procedure for the pyridine ring band are displayed in Table II. Again, the evaluation of K_A has been performed according to the protocol previously described. In Figure 7 the fit to experimental results for different theoretical values of K_A is displayed. Now, the quality in the fit is worse, but a value between 60 and 80 can be assigned from this plot. The values of K_A obtained from two bands corresponding to distinct association equilibria in the blend are very closed

Table II. Curve-Fitting Results for Pyridine Ring Bands in ACA88/P4VP Blends

	free pyridine ring band			associated pyridine ring band			
ACA88/P4VP (wt %)	wavenumber (cm^{-1})	width (cm^{-1})	rel area (%)	wavenumber (cm^{-1})	width (cm^{-1})	rel area (%)	f_F
90/10	1596.7	11	28.0	1604.4	12	72.0	0.28
80/20	1596.7	12	41.7	1604.4	12	58.3	0.42
70/30	1596.7	14	48.7	1604.4	14	51.3	0.49
60/40	1596.7	14	51.4	1604.4	14	48.6	0.51
50/50	1596.7	14	54.1	1604.4	14	45.9	0.54
40/60	1596.7	17	60.9	1604.4	16	39.1	0.61
30/70	1596.7	18	71.7	1604.4	15	28.3	0.72
20/80	1596.7	19	79.1	1604.4	17	20.9	0.79
10/90	1596.7	21	95.1	1604.4	7	4.9	0.95

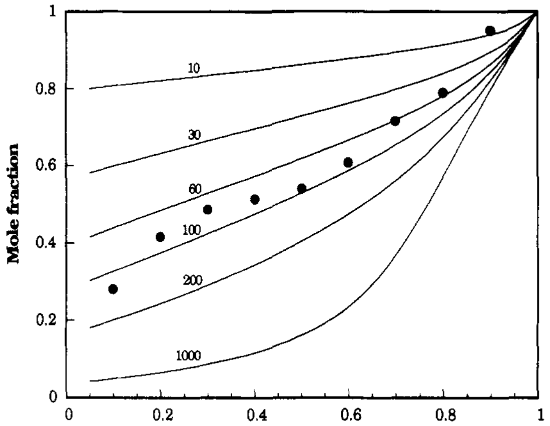

Figure 7. Experimental values (●) of nonassociated pyridine group mole fractions in the blend, and theoretical curves obtained by using different values of K_A, as a function of the blend composition.

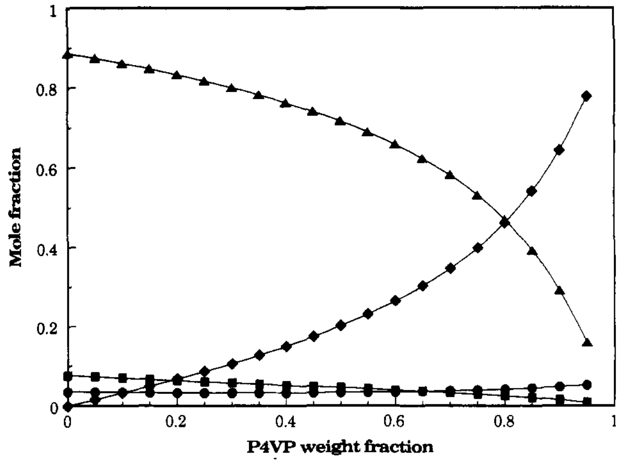

Figure 8. Calculated fractions of associated and nonassociated hydroxyl groups as a function of blend composition: (▲) hydroxyl–hydroxyl; (◆) hydroxyl–pyridine; (■) hydroxyl–carbonyl; (●) free hydroxyl.

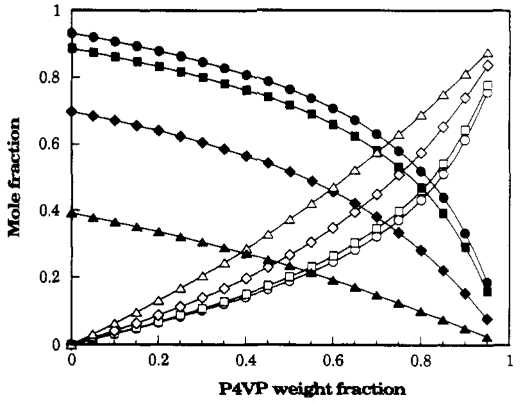

Figure 9. Plot of the variation of hydroxyl–hydroxyl self-association (filled symbols) and hydroxy–pyridine association (empty symbols) for the blends of P4VP with (●) ACA97, (■) ACA88, (◆) ACA55, and (▲) ACA21 as a function of blend composition.

and confirm the validity of the association model of Painter and Coleman for this system.

In this way, we have employed this association model to analyze the quantitative distribution of hydrogen bonding between the chemical groups included in the blend. It is remarkable that this distribution is not accessible in an experimental way for hydroxyl groups. The fraction of associated and nonassociated hydroxyl groups as a function of blend composition according to this model is shown in Figure 8.

Although it is possible to apply the calculated value of K_C to ACA97/P4VP, ACA55/P4VP, and ACA21/P4VP blends, we have preferred to evaluate for each particular system this equilibrium constant. The K_C values calculated with the same protocol as for ACA97, ACA88, ACA55, and ACA21 copolymers are 48.5, 51.8, 41.0, and 52.5, respectively. This is an encouraging result, taking into account the errors associated with the method (little changes in the spectral fitting lead to important modifications in K_C values). Taking 50 as the K_C average value, we have graphically calculated K_A for the ACA55/P4VP blend, and its value is on the order previously reported for the ACA88/P4VP blend. Thus, the results obtained with this model are congruent and must be employed in the analysis of the evolution of association processes in ACA/P4VP blends. In Figure 9 the variation of hydroxyl–hydroxyl self-association and hydroxyl–pyridine association in these systems is shown. The most relevant fact is a progressive increase in hydroxyl–hydroxyl self-association as the content of vinyl alcohol units increases in ACA copolymers; on the contrary, hydroxyl–pyridine association decreases in the same way. In other words, hydroxyl self-association is preferred over hydroxyl–pyridine association; in fact, the equilibrium constant corresponding to the first equilibrium is higher than the second one. Evidently this situation must reach its limit for PVA/P4VP blends, with a predominant hydroxyl–hydroxyl self-association. In conclusion, the model of Painter and Coleman corroborates our hypothesis that immiscibility in a PVA/P4VP blend arises from PVA self-association.

Finally, ACA/P2VP and PVA/P2VP blend immiscibilities can also be regarded in terms of relative values of equilibrium constants for pyridine–hydroxyl and hydroxyl–hydroxyl association. According to the results previously described, the K_A value allows miscibility of P4VP with ACA copolymers depending on the degree of hydrolysis. These systems are close to the miscibility limit,[1] so immiscibility can be expected for lower K_A values. Steric hindrance in P2VP blends can lead to an effective K_A value lower than that in P4VP ones. In fact, Martínez de Ilarduya et al.[5] report a lower value for this association constant in phenoxy/P2VP blends (16.0) than in phenoxy/P4VP (25.0) blends that confirms our hypothesis.

Acknowledgment. The authors thank the CICYT (Project MAT 464/92-C02), CYTED, and Vicerrectorado de Investigación de la Universidad del País Vasco (UPV 39.310-ECC099/92) for financial support. J.R.I. thanks the Departamento de Educación, Universidades e Investigación del Gobierno Vasco, for a grant.

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