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Thermodynamics of hydrogen bonding in polycomplexes of poly(4-vinylpyridine) with maleic acid-*alt*-ethylene copolymer

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Abstract

Hydrogen bonding formation in a polymer complex between poly(4-vinylpyridine) (P4VPy) and maleic acid-*alt*-ethylene (MA-*alt*-E) copolymer has been studied. Fourier transform infrared spectroscopic (FT-IR) studies have evidenced that the carboxylic groups of MA-*alt*-E interact with the pyridine ring of P4VPy. The existence of hydrogen bonding interactions in these systems is shown by the appearance of new bands at 1640 and 1503 cm^{-1} and a broadening of the –C=C– band of the pyridinic ring. The thermodynamic analysis of the hydrogen bonding was performed through the estimation of the enthalpy of mixing in the polycomplex formation process. ΔH_M was determined by means of an association model developed by Painter and co-workers and by flow calorimetric direct measurements. These results showed a high negative value for the enthalpy of mixing, which is consistent with the blend miscibility given that ΔH_M is the main contribution to the change of the free energy of mixing, ΔG_M.

Keywords: Polymer complex; Hydrogen bonding; Flow calorimetry

1. Introduction

Interpolymer complex formation is a matter of current interest from basic and technological point of view and has been the subject of many recent papers [1–11]. These systems have attracted much attention due to the formation of compatible polymer blends [12–14]. The general method of enhancing miscibility in polymer blends is to introduce specific interactions between polymers. When these interactions are stronger than polymer–solvent interactions, the two polymers form precipitates (interpolymer complexes). Polycomplexes can be formed by intermolecular secondary binding forces, such as Coulombic interactions, electron transfer, ion–ion, and hydrogen bonding [13–19]. It is known that basic polymers such as poly(vinylpyridine)s are miscible with proton-donating polymers through hydrogen bonding interactions. Poly(4-vinylpyridine) (P4VPy), a weakly self-associated basic polymer, is miscible with several self-associated polyacids, such as poly(4-vinylphenol) (P4VPh) [20,21], poly(acrylic acid) (PAA) [22,23],

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poly(methacrylic acid) (PMAA) [12], poly(monoalkyl itaconates) [9] and with the strongly self-associated random copolymer ethylene-co-methacrylic acid (E-co-MAA) [12]. In a previous work it was reported the formation of interpolymer complex between P4VPy and maleic acid-*alt*-ethylene (MA-*alt*-E) copolymer, characterized by viscometry, infrared spectroscopy and thermogravimetric analysis [4]. The driving force for polycomplex formation in this system seems to be the specific acid–base interaction between "free" carboxylic groups of the copolymer and the pyridine nitrogen of P4VPy. However, the interactions involved in the interpolymer complex formation have not been quantitatively characterized. The determination of the thermodynamic properties of the complexation process should be a way to better understand this phenomenon. Most of the miscible mixtures where strong interactions occur belong to a special class of polymer mixtures with intriguing phase behaviors and not well understood [24]. This class is formed by miscible mixtures in which specific interactions, mainly hydrogen bonding, are responsible for the intime miscibility level attained. Painter and co-workers [12,19] have developed an association model using infrared spectroscopy for determining parameters that allow to describe the stoichiometry of hydrogen bonding. It is well known that for high molecular weight systems, such as polymer blends, the entropic contribution ΔS_M to the free energy of mixing is very low, so the enthalpic term (ΔH_M) will be therefore dominant. Furthermore, the knowledge of the enthalpy of mixing ΔH_M in the complexation process should be a complementary and important tool to describe, in a quantitative way, the thermodynamics of the process. ΔH_M allows to know the nature of the interactions and its role in the miscibility of polymer blends.

The aim of this work is the thermodynamic analysis and characterization of the hydrogen bonding in the interpolymer complex formation between P4VPy and MA-*alt*-E copolymer. Using the association model of Painter and co-workers [12,19] the temperature-composition phase diagram and the enthalpy of mixing ΔH_M can be calculated. The determination of the enthalpy of mixing by flow calorimetry is another way to get information about the complexation process. Given that the complexation takes place when two solutions, each of them containing one of the polymers, are mixed, it is not possible to measure directly ΔH associated to the complexation. A possible alternative is the use of the Hess law. The main disadvantage of this method is the limited precision of the measurements, but this problem can be solved using an adequate flow calorimeter such as that used in this work.

2. Experimental

2.1. Polymers

Linear P4VPy, with a weight average molecular weight $M_w = 50\,000$ from Polysciences Inc., USA, was used. Maleic anhydride-*alt*-ethylene (MAH-*alt*-E) copolymer, with weight average molecular weight $M_w = 50\,000$ was purchased from Aldrich Chemicals Co., USA. MAH-*alt*-E was hydrolyzed in distilled water by refluxing their aqueous dispersion during 48 h. Then a pale yellow aqueous solution was obtained which was lyophylized to obtain a white hygroscopic solid of MA-*alt*-E copolymer.

2.2. Preparation of the mixtures

Mixtures of P4VPy and MA-*alt*-E were prepared by dissolving both polymers in a water/methanol mixture 1:1 at different equivalent fractions (τ), where τ is defined as

$$\tau = \frac{[\text{P4VPy}]}{[\text{MA-}alt\text{-E}]} \tag{1}$$

2.3. FT-IR measurements

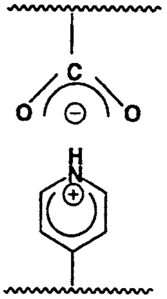
IR spectra were recorded in a Nicolet Magna 560 spectrometer at a resolution of $2\,\text{cm}^{-1}$, and a minimum of 64 scans were signal averaged. For measurements at high temperatures a SPECAC device was used with a uncertainty of ±1 K, and the spectra were obtained at every 10 K from 298 to 363 K. The spectra were obtained from solid blends obtained from casting the solutions on KBr.

2.4. Enthalpy of mixing

A SETARAM C80-D calorimeter was used to determine solution heats of pure polymers, solution heat of the polycomplex and the heat involved in the mixing of both polymer solutions. The special cells designed to measure heats of mixing are named reversal mixing vessels. The two chambers of this kind of vessels are separated by a tilting lid. The samples are separately introduced into the vessel outside of the calorimeter. In order to obtain a complete separation of the chambers, a mercury seal on the lid is used. After the introduction of the vessels into the calorimeter, the thermal equilibrium is to be achieved in order to have the two separated components at the same temperature. The calorimeter must be fitted with two vessels: one will be the reference and the other one will contain the sample. In our measurements the reference vessel was set up "pre-mixed" in order to get a reference vessel as identical as possible to the experimental one, except, obviously, with regard to the reaction to be studied. After that, the apparatus is obliged to turn over several times and the signal is recorded until the base line is recuperated. As little as 0.5 mW of heat flow is detectable, and the calorimetric sensitivity is 50 mJ. The reproducibility of the measurements was <1%.

3. Results and discussion

MA-*alt*-E copolymer is a strongly associated dicarboxylic poly(acid) and P4VPy is a poly(base) weakly self-associated. Both polymers interact by intermolecular hydrogen bonding giving rise to poly(complex) formation [4]. Fig. 1a shows the FT-IR spectrum of MA-*alt*-E copolymer, where characteristic self-association bands attributed to the intermolecular dimer of the carboxylic groups are observed. Thus, a very complex band at about 3000 cm^{-1} (stretching OH) including "satellite" bands and the carbonyl band (>C=O) at 1719 cm^{-1} are present. Fig. 1b corresponds to the FT-IR spectrum of pure P4VPy which shows the most important bands at 1599 and 1416 cm^{-1}. These bands can be assigned to the stretching vibration of the pyridinic ring. Fig. 1c shows the FT-IR spectrum of the blend corresponding to the polycomplex for an equivalent ratio $\tau = 1$. The most evident feature is the appearance of a new band at 1640 cm^{-1} which can be assigned to a ring-stretching vibration of the pyridinium cation interacting with the acid group (Scheme 1). When ionization occurs, the characteristic carbonyl stretching absorption vanishes and the anti-symmetric vibration band of the carboxylate group appears in the region of 1600–1550 cm^{-1}. In this case, this band is not observed due to a possible overlapping with the pyridine ring band. Furthermore, a broadening of the band attributed to the stretching of the pyridinic ring (1607 cm^{-1}) is also observed (see also Fig. 3). This broadening reflects two contributions, one corresponding to the "free" ring and the other to the perturbed ring as a consequence of the hydrogen bonding interaction of the pyridinic nitrogen with the hydrogen of the polyacid.



Scheme 1.

In order to get confidence about the complexation process, the thermodynamic analysis through the application of the Association Model [19,25–27] was performed. The authors of this model have developed equations and methodology to predict phase diagrams, miscibility windows and maps of polymer blend systems involving specific interactions. These interactions are defined by equilibrium constants, describing both self-association (K_B) and interassociation (K_A) between the components of the blend.

The interassociation constant (K_A) for the blend MA-*alt*-E/P4VPy can be determined by FT-IR measurements through the analysis of one of the vibration bands of the pyridinic (C=C) double bond. This band shows three spectral contributions: one due to the stretching vibration of the "free" pyridinic ring at 1597 cm^{-1}, the second one at 1607 cm^{-1} and the last one at about 1640 cm^{-1}, corresponding to pyridinium cation. The first two contributions are overlapped and, therefore, in order to know the relative contribution of the "free" and "associated" pyridinic groups is necessary to split the whole curve in two contributions. Fig. 2 shows, as an example, the resolution of the total stretching vibration band of the pyridinic ring in

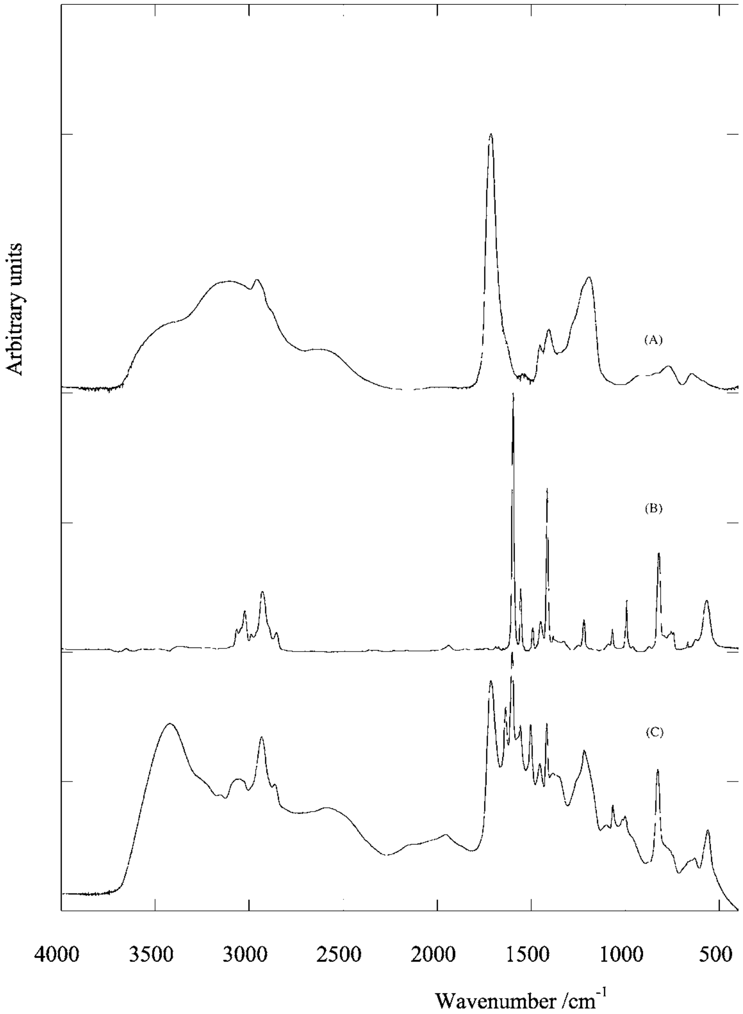


Fig. 1. FT-IR of pure polymers and polycomplex: (a) pure MA-*alt*-E copolymer; (b) pure P4VPy; (c) polycomplex at molar ratio $\tau = 1$.

two bands using the program Spectra Fit [19], which includes a least square fitting procedure.

Fig. 3 shows the FT-IR spectra at 343 K for blends of P4VPy/MA-*alt*-E at five blends ratios: $\tau = 0.33$, 0.5, 1.0, 2.0 and 3.0, respectively. As can be seen, the contribution of the bands at about 1635 and 1607 cm^{-1} increases as the blend gets richer in MA-*alt*-E, what means that there is a higher amount of associated pyridine groups, both due to the hydrogen bonding with the hydroxyl groups of MA-*alt*-E and the formation of ionic species.

Table 1 summarizes the area values of these three bands for $\tau = 0.33$ as a function of temperature. As

Table 1
Evolution of the FT-IR band areas for sample with $\tau = 0.33$ with temperature

Temperature (K)	A_{1633}	A_{1607}	A_{1598}	A_{total}
313	4.21	0.77	0.66	5.64
333	4.07	1.10	1.15	6.32
343	3.38	1.19	1.33	5.90
353	3.31	1.18	1.45	5.94
363	2.94	1.18	1.64	5.76

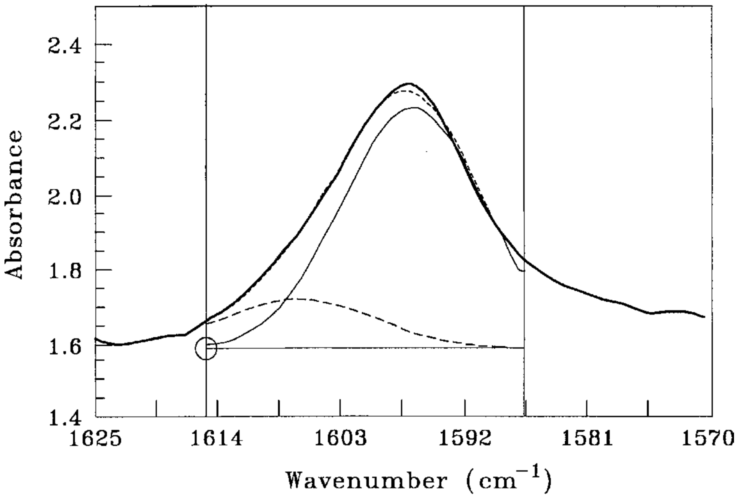


Fig. 2. Resolution of the total stretching band of the pyridinic ring using the program Spectra Fit.

can be seen the area of the "free" band increases with temperature and the area corresponding to the ionic band decreases. This fact responds to a K_A dependence with temperature. However, the total area remains constant with temperature, reflecting that the absorption coefficients of these vibrations are similar. According to this, we can calculate the fraction of the "free" pyridine group at each temperature and equivalent fraction as

$$f_f = \frac{A_{1598}}{A_{1598} + A_{1633} + A_{1607}} \quad (2)$$

Table 2 summarizes the values of "free" pyridine fractions obtained at different compositions and temperatures. It can be observed that the fraction of "free" pyridine at each temperature decreases as the composition of MA-*alt*-E increases. This result is indicative of the interaction between the carboxyl group of the copolymer and the pyridinic nitrogen of P4VPy. Furthermore, for a constant composition, the fraction of "free" pyridine increases as the temperature increases. From the data of Table 2 it is possible to calculate the interassociation constant K_A, taking into account that the stoichiometry of the system can be expressed by

$$\phi_B = \frac{\phi_{B1}}{(1 - K_B\phi_{B1})^2}\left(1 + \frac{K_A\phi_{0A}}{r}\right) \quad (3)$$

$$\phi_A = \phi_{0A}\left[1 + \frac{K_A\phi_{B1}}{(1 - K_B\phi_{B1})}\right] \quad (4)$$

where ϕ_A and ϕ_B are the volume fractions of the carboxylic acid (B) and pyridine (A) species, ϕ_{0A} and ϕ_{B1} are the volume fractions of the "free" A and B groups, and r is the molar volume ratio of A and B. In order to apply Eqs. (3) and (4) to calculate the interassociation constant (K_A), the self-association constant K_B of MA-*alt*-E copolymer must be known. In this case, however, it was not possible to determine the self-association constant due to the incapacity to resolve the "free" and "associated" contributions to the carbonyl vibration band. Therefore, this constant was estimated taken into account that the constant for a couple of polymers can, in principle, be transferred from other mixtures containing the same interacting units. Using the self-association constant of E-co-MAA copolymer reported by Painter and

Table 2
"Free" pyridine fraction for different τ and temperatures

Temperature (K)	τ = P4VPy/MA-*alt*-E				
	3	2.5	2	1	0.33
313	0.55	0.49	0.50	–	0.12
323	0.60	0.61	0.49	0.46	–
333	0.64	0.66	0.51	0.48	0.18
343	0.66	0.66	0.55	0.50	0.23
353	–	0.77	0.55	0.51	0.24
363	–	–	0.56	0.53	0.28

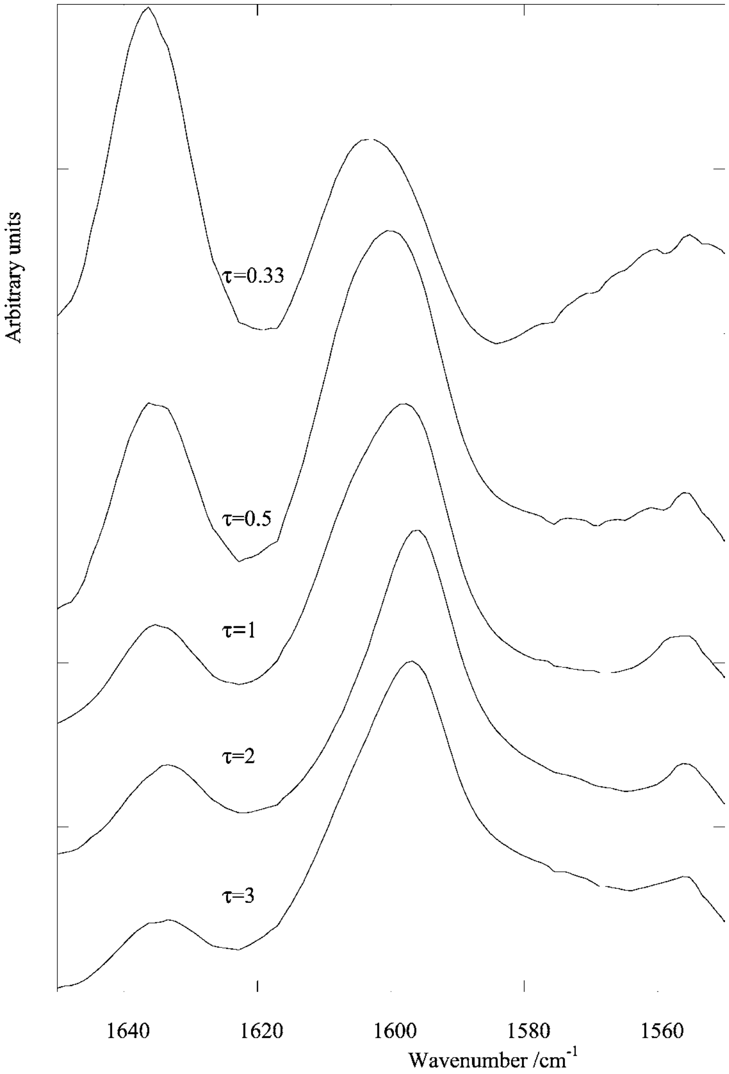


Fig. 3. FT-IR spectra for blends of P4VPy/MA-*alt*-E copolymer at five blend ratios.

co-workers [12] which has similar interacting units as MA-*alt*-E copolymer, the constant is estimated by the equation

$$K_{B1}V_1 = K_{B2}V_2 \quad (5)$$

where K_{B1} and K_{B2} are the self-association constants and V_1 and V_2 are the molar volumes of polymers 1 and 2 that have the same functional groups, respectively. Taking the molar volumes of MA-*alt*-E and E-co-MAA as 38 and 86 cm^3 mol^{-1}, respectively, obtained using group contributions [19], K_B for MA-*alt*-E is 9×10^4 at 298 K. From the Arrhenius equation and the estimated value of the formation enthalpy for the dimer of E-co-MAA by hydrogen bonding as -28.96 kJ mol^{-1}, it is possible to estimate K_B for MA-*alt*-E at different temperatures. Therefore, at one temperature and using the estimated value of K_B, we select one starting value for K_A to calculate ϕ_{B1} for the corresponding ϕ_B values. The fraction of "free" carboxylic groups of the polyacid as a function of the volume fractions of the polyacid units can be determined by fitting simultaneously

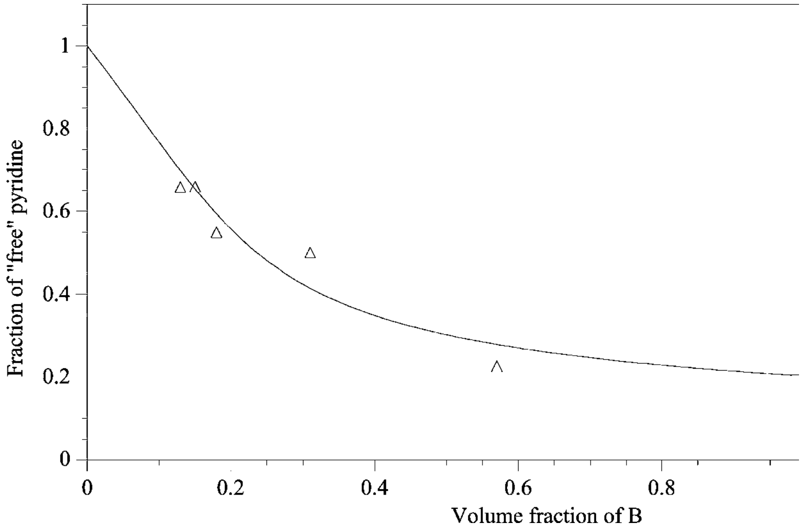


Fig. 4. Fraction of “free” pyridine vs. volume fraction of MA-*alt*-E copolymer.

Eqs. (6) and (7):

$$f_1 = 1 - K_B\phi_{B1} \quad (6)$$

$$\phi_B = \frac{\phi_B}{1 - K_B\phi_{B1}} \quad (7)$$

K_A is sistematically varied and the value that gives the best fit of the experimental data is selected. This fitting is performed using the software developed by the authors of the Association Model, Fit K [19]. Fig. 4 shows an example of the fitting of K_A. The values of the association constants obtained for each temperature are the followings: $K_A = 5064$ at 313 K, 1156 at 323 K, 1091 at 333 K, 790 at 343 K, 625 at 353 K and 477 at 363 K.

From the Arrhenius equation that relates K_A with temperature it is possible to obtain the enthalpy of the complexation process. Fig. 5 shows the Arrhenius plot from which the enthalpy of the hydrogen bonding formation is obtained ($\Delta H_A = -22\,625\,\mathrm{J\,mol^{-1}}$), and

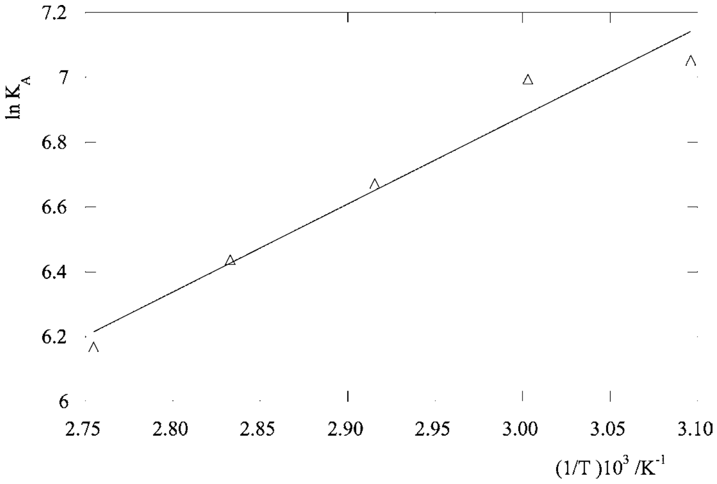


Fig. 5. Arrhenius plot for the variation of K_A with temperature.

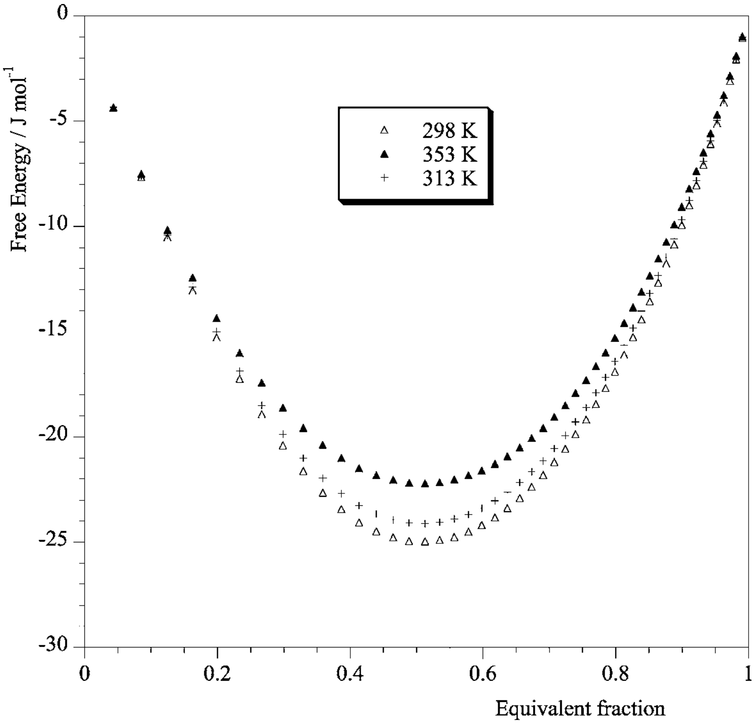


Fig. 6. Variation of the free energy of mixing ΔG_M vs. composition at 298, 313 and 353 K.

extrapolating the constant K_A data at 298 K, the value is 2557 in dimensionless units.

Using polymer data such as molar volumes (V_i), molecular weight (M_i), solubility parameters (δ_i), degree of polymerization X_i, and those related to the interactions as self-association constant (K_B) and interassociation constant (K_A) the temperature-composition phase diagrams were calculated using the software of the Association Model.

Fig. 6 represents the variation of the free energy of mixture (ΔG_M) as a function of the composition at 298, 313 and 353 K, respectively. In all the calculations the same behavior is observed, i.e. ΔG_M is negative along the composition range, showing a unique minimum at about 0.5 for MA-*alt*-E. This behavior is characteristic of completely miscible systems over the whole range of composition.

From the values of ΔG_M at different temperatures, Fig. 6, and the Gibbs–Helmholtz equation

$$\Delta H_M = \frac{\partial(\Delta G_M/T)}{\partial(1/T)} \qquad (8)$$

the enthalpy of mixing was estimated at a 50/50 composition, resulting a negative value of $-28\,\mathrm{J\,g^{-1}}$.

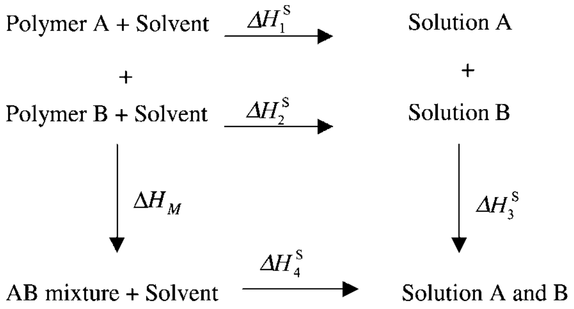
In the other hand, the enthalpy of mixing was experimentally determined by flow calorimetry at 298 K. Comparison of ΔH_M obtained by the association model and by flow calorimetry should be of interest in order to gain confidence about the association model. For the determination of ΔH_M by flow calorimetry, we had to use the Hess [24] cycle, that can be well understood taking into account Scheme 2.

According to that, ΔH_M can be calculated by the following equation:

$$\Delta H_M = w_1\,\Delta H_1^S + w_2\,\Delta H_2^S + \Delta H_3^S - \Delta H_4^S \qquad (9)$$

being ΔH_i the heats measured by flow calorimetry and w_1 and w_2 the weight fractions of the polymers in the mixture.

Table 3 compiles the values of the heats of solution and the heat of mixing for the polymer solutions here studied. The data shown in Table 3 are those corresponding to a mixture with $\tau = 1$ (molar ratio 1:1). It



Scheme 2.

was not possible to analyze the variation of ΔH_M as a function of the composition because the values of the variation of the heats of mixing are very small and lie inside the experimental error.

The enthalpy corresponding to the formation of the polycomplex ($-39.6\,\mathrm{J\,g^{-1}}$) is a very high exothermic value. This high value is in agreement with the strong interactions which are supposed to occur between the components to form the polycomplex and more negative than ΔH values measured in other systems, i.e. poly(methyl acrylate/poly(vinyl acetate) ($-17.8\,\mathrm{J\,g^{-1}}$) [28], poly(styrene)/poly(α-methyl styrene) ($-3.1\,\mathrm{J\,g^{-1}}$) [29], poly(methyl methacrylate)/poly(ethylene oxide)($-1.4\,\mathrm{J\,g^{-1}}$) [30]. It is clear that the possibility of strong interactions are clearly reduced in these systems.

Taking into account the drastic simplification we have been obliged to introduce in the calculation of ΔH_M using the association model, we consider that the value of ΔH_M obtained by flow calorimetry ($-39.60\,\mathrm{J\,g^{-1}}$) is in very good agreement with the value obtained using the association model ($-28\,\mathrm{J\,g^{-1}}$). Furthermore, this agreement confirms that the high negative value obtained for ΔH_M indicates that the polycomplex formation must be the result of strong specific interactions between the components of the blend.

Table 3
Enthalpy of mixing for the polycomplex P4VPy/MA-*alt*-E copolymer 1:1 molar at 298 K and the components of the Hess cycle allowing its determination

	ΔH ($\mathrm{J\,g^{-1}}$)
$w_1\,\Delta H_1$	−9.93
$w_2\,\Delta H_2$	−11.60
ΔH_3	−21.74
ΔH_4	3.69
ΔH_M	−39.60

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