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Application of an association model to the PVC/EVA system

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ABSTRACT

A thermodynamic association model was applied to the PVC/EVA system. In this model the enthalpy component is related quantitatively to intermolecular interaction forces. Molecular modeling was applied to obtain the parameters related with interaction forces. The phase diagrams showed lower critical solution temperature (LCST) behavior and also biphasic regions in PVC rich compositions.

INTRODUCTION

Miscibility can be determined by the calculation of the Flory-Huggins parameter, χ, from the solubility parameter data using a critical parameter χ_{crit} concept (1). Mixtures that have no specific interactions have the parameter $\chi_{crit} \cong 0.002$ (1). PVC/EVA system shows relatively weak interactions registered as infrared shifts smaller than 6 cm^{-1}. Then, for this system a critical value of 0.12 is forecasted. It gives a miscibility window that includes mixtures containing PVAc copolymers with acetate content higher than 45 wt.%. This window is wider than the predicted by the model that considers repulsive interactions where the maximum limit predicted is an acetate content of 85 wt.% (2,3). In this approximation the $\Delta G_H/RT$ term was considered zero and an association model was applied.

The association model, defines the polymer-polymer interaction parameter, χ, as a factor with positive or small negative values. It is unfavorable to mixing and reflects only the non polar intermolecular interaction contributions to total free energy of mixing, ΔG_M, given by the expression

$$\Delta G_M/RT = (\phi_A/X_A)\ln\phi_A + (\phi_B/X_B)\ln\phi_B + \phi_A\phi_B\chi + \Delta G_H/RT \qquad [1]$$

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where ϕ_A and ϕ_B are the volume fractions of the components A and B, X_i is the degree of polymerization of the components A and B, R is the Boltzman constant and T is the temperature.

Favourable contributions to changes in ΔG_M due to specific intermolecular interactions are represented by the $\Delta G_H/RT$ term. It can be equal to zero or assume negative values and there is a balance between the enthalpy ($\Delta G_H/RT$) and the entropy terms ($\phi_A \phi_B \chi$). Equation (1) allows to predict mixing at molecular level. This occurs when χ is very close to zero, and in the absence of specific interaction (the enthalpy term is equal to zero). Then, the $\Delta G_H/RT$ term is given by the expression:

$$\frac{\Delta G_H}{RT} = \phi_B \ln\left(\frac{\phi_{B_1}}{\phi_{B_1}^0}\right) + \phi_1 \ln \phi_{A_1} + \phi_B K_B\left(\phi_{B_1} - \phi_{B_1}^0\right) + \phi_B\left(1 - K_B \phi_{B_1}\right)\left[\frac{\left(K_A \phi_{A_1} / r\right)}{1 + \left(K_A \phi_{A_1} / r\right)}\right] \quad [2]$$

where, K_A and K_B are association constants and r is the molar volume ratio of the components. The index 1 means the component fraction with hydrogen bonding between the two components and the index 2 corresponds to the fraction where self-association occurs.

The free energy of mixing and it second derivatives were related to volume fraction and temperature. The pairs where the second derivative was higher or equal to zero showed the phase diagrams represented by spinodal curves.

EXPERIMENTAL

The poly(vinyl chloride) used in this work was a commercial product of Companhia Petroquímica Camaçari (CPC), with a density of 1.390 gcm^{-3}. Six ethylene-vinyl acetate copolymers were obtained from commercial sources. Pertinent parameters of the polymers studied were described elsewhere (4).

Molecular mechanics, semiempirical calculation and simulated annealing were applied using PC Model and MOPAC (AM1) programs (5,6).

RESULTS AND DISCUSSION

The influence of $\Delta G_H/RT$ was considered in the calculation of ΔG_M. This model it suggests the presence of specific interactions as hydrogen bonding. This kind of interaction was observed using a theoretical molecular modeling calculation made with low molecular weight analogues of the polymers (2,3).

It is necessary to define some parameters to get ΔG_M. ΔH_A is the hydrogen bonding enthalpy, suggested here as the intermolecular bond between the α-hydrogen of PVC and the carbonyl group of EVA (7). The other parameters are the weak self-association enthalpy, ΔH_B, that represents the interaction between the molecules of PVC, the equilibrium constant for association formation, K_A, and the equilibrium constant that corresponds to the self-association of the component, K_B.

These parameters can be obtained from literature (7) or from infrared spectrometric measurements of frequency shifts (8-12). However, the interactions in the PVC/EVA system are weak and no information is available from frequency shifts. These interactions are very small and there are no band splitting that would be useful for quantification of the group fraction that effectively participates. Then, molecular modeling was applied to get these parameters. Molecular mechanics, semi-empirical calculation and simulated annealing were employed.

These calculations gave the heats of formation of ethylene chloride, CE, selected as PVC analogue and ethylene acetate, AE, the EVA analogue. The simulated annealing approach was used to obtain the enthalpy of the CE-CE pair, which indicates the self-association interaction. The interaction between different molecules CE-AE was also determined. These enthalpies were calculated as the difference between the heat of approximation of two molecules and the sum of the heat of formation of pure molecules. Table 1 shows the results.

Table 1
Thermodynamic parameters for analogues of PVC/EVA pair obtained from molecular modeling

Molecule or pair	Heats of formation (ΔH_f) (kcal/mol)	Eq. const. K_A	Eq. const. K_B	Bond enthalpy (kcal/mol)
Ethylene acetate (AE)	-102.21	-	-	-
Ethylene chloride (CE)	-26.16	-	-	-
AE / AE	-206.88	-	-	2.47
CE / CE	-52.84	-	2.41	0.52
AE / CE	-130.28	16.35	-	1.65

The consistency of the values obtained from molecular modeling was verified using another approach. It uses an empirical relation (13) that takes into account the relationship between the enthalpy of formation and the infrared frequency shifts of the proton acceptor group in the presence of another group capable of interaction. The intermolecular enthalpy calculated taking the values of frequency shifts registered for the analogues of PVC/EVA pair reported by Cruz-Ramos and Paul (3) gave a value of 2.1 kcal/mol.

In spite of the empirical relation is not the more appropriate to describe this system the value is near the obtained from modeling calculation. The difference between these two values has no significant interference in the calculations carried out below.

The bonding enthalpies are function of the temperature. However, they were employed as constants because this dependence was not considered significant (14).

The calculation of the equilibrium constants were performed with the Boltzman relation

$$\ln K = - \Delta H/RT + \Delta S/R \qquad [3]$$

The entropy term $\Delta S/R$ was neglected because the calculated values in modeling were negligible as compared with the enthalpy term. Table 1 shows these results.

A computer program was used to calculate ΔG_M, its second derivative and the phase diagrams (10). The effect of self-association was considered only for dimers. In addition, the effect of absence of specific interaction $\Delta G_H/RT = 0$ was considered. The miscibility of the system is described by $\Delta G_M < 0$ and by an additional requirement

$$\partial^2(\Delta G_M / RT) / \partial\phi_A^2 > 0 \qquad [4]$$

When this second derivative is equal to zero a spinodal curve point is reached and it describes in the phase diagram a limit between a monophasic metaestable condition and another completely biphasic. Figure 1 is an example of the behavior of the free energy of mixing and its second derivative as a function of the composition and temperature. The PVC/EVA 50 pair was used with an arbitrary interaction parameter ($\chi = 1.5$).

The assigned temperatures revealed some conditions where $\Delta G < 0$ and its second derivative is higher than zero. It means that the system is thermodynamically miscible. It may occur only at some temperature and composition ranges. The points where the second derivatives are equal to zero correspond to the points in the phase diagram.

The positive values for free energy of mixing and its second derivatives indicate that PVC/EVA 31 and PVC/EVA 41 systems present immiscibility in the whole composition range for all temperatures studied. PVC/EVA 45 and PVC/EVA 45A showed the same behavior shown in Figure 1. It means that molecular weight differences between EVA 45 and EVA 45A are not sufficient to modify the phase behavior. When $\Delta G_H/RT$ is zero, the phase diagram form is strongly dependent of the value arbitrated for χ. The one phase region appears to diminish for higher values of χ.

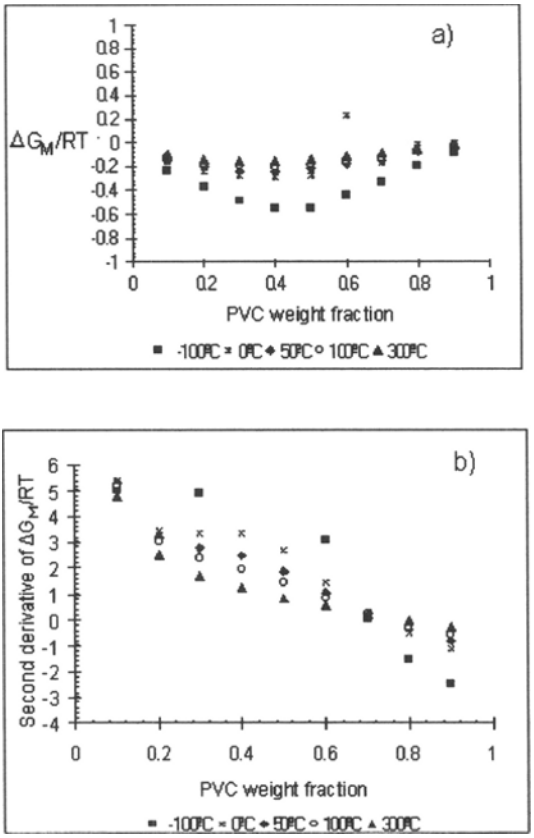

Figure 1. Variation of free energy of mixing, and its second derivative as a function of the PVC composition at different temperatures, for PVC/EVA 50 blends using $\chi = 1.5$. (a) $\Delta G_M/RT$; (b) $\partial^2(\Delta G_M / RT) / \partial\phi_A^2$.

If $\Delta G_H/RT$ is considered zero the system is completely immiscible as depicted in Figure 2 for PVC/EVA 45 blends. The change in the value of bonding enthalpy, H_A, has no significant effect on phase diagram (H_A = 2.1 kcal/mol instead of 1.65 kcal/mol). The phase diagram of PVC/EVA 50 mixtures shows a behavior similar to the PVC/EVA 45 and the χ effect is the same. The interaction parameter has lower value than the estimated for PVC/EVA 45 mixture due to the higher disposability of EVA carbonyl groups to interact with the PVC molecules. Consequently a greater monophasic region appears. The phase diagram shows total miscibility when χ = 0.1 or 0.5.

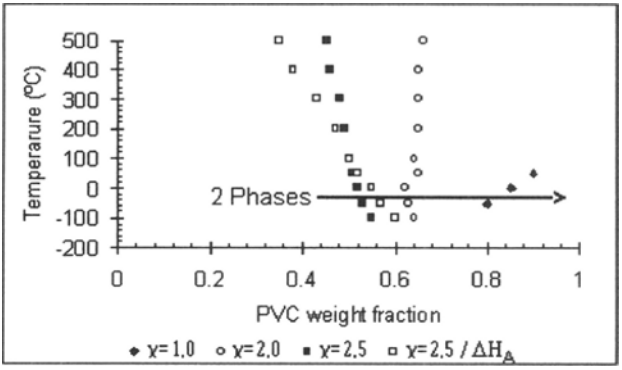

Figure 2. Phase diagrams of PVC/EVA 45 blends using diferent values of χ and $\Delta H_A = 2.1$ kcal/mol.

Figure 3 was obtained using $\Delta G_H/RT = 0$. It demonstrates that the system presents total immiscibility in the absence of specific interaction.

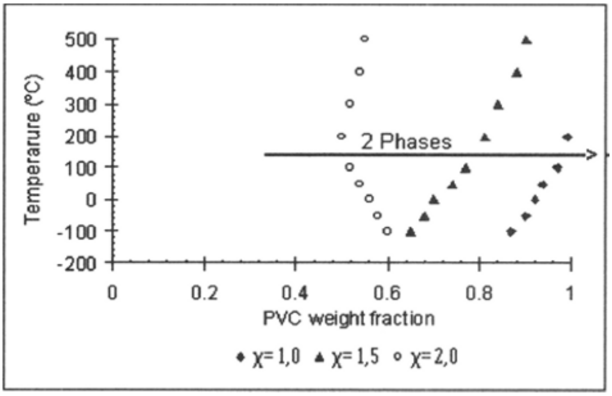

Figure 3. Phase diagrams for PVC/EVA 50 blends using different values of χ.

Figure 4 describes the PVC/EVA 70 pair. The miscibility is almost complete for χ values lower than 0.5. The immiscibility arises when this value is positive and grows with the value of χ. If the $\Delta G_H/RT$ term is negligible the biphasic region is larger and an hourglass shape diagram appears ($\chi = 0.1$).

All pairs investigated have the tendency to show a region with two phases that appears in the PVC rich region. This agrees with the results obtained using differential scanning calorimetry (DSC) (2). The study demonstrated that in blends with copolymers with low vinyl acetate content the miscibility of EVA is small in the PVC rich phase.

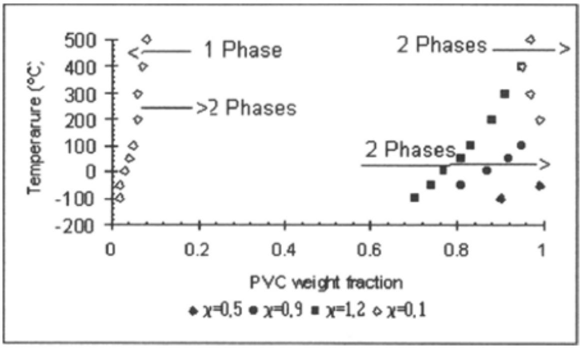

Figure 4. Phase diagrams for PVC/EVA 70 blends using different values of χ.

The applied model works with indirect calculated parameters that may cause significant error. However, the error propagation inserted on the χ parameter, the association constants ($K_{A,}K_B$) and the bonding enthalpy gives no serious changes on the phase diagram behavior(14b-14d).

It was observed that when $\Delta G_H/RT$ is zero the shape of the diagram characterizes the total immiscibility. It means that the enthalpic and entropic terms are in subtle equilibrium. The theoretical phase diagrams of the blends shown a lower critical solution temperature behavior (LCST) that agrees with the shape of the cloud point curve studied before (2). The LCST curve may be shape modified if the free volume contributions are considered in the model (15-16).

CONCLUSIONS

PVC/EVA phase diagrams showed LCST behavior that agrees with previous cloud point investigation (2). Specific interaction magnitude in this system is not in great extension, as indicated by the small frequency shifts obtained (2). The importance of the entropy term in $\Delta G_H/RT$ shows that miscibility is also affected by free volume effects. This was not included in this association model because these contributions were not included in the equation of state. The incorporation of these contributions on the association model for strong interaction systems predicts that the negative contributions to ΔG_M do not give significant changes on phase diagram behavior (12-14).

In spite of these modifications on original model is not the scope of this work it is important to assign that in PVC/EVA system free volume contributions are in any way a determining factor for the phase diagram behavior. A subtle equilibrium occurs between two relatively weak forces; one is associated to volume changes and another is dependent on intermolecular energies as the behavior reported for PS/PVME system (17). The comparison of the modified association model with the original can be useful for the weak interaction pair PVC/EVA. It will be helpful the mismatch with the modified Lattice-Fluid Model (18) that takes into account the effects of specific interactions on some local ordering in the mixture.

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