Group Contribution Method for Predicting Polymer–Polymer Miscibility: Binary Blends of Poly(*p*-vinylphenol) and Ester-Containing Polymers

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ABSTRACT: The ability of the modified Guggenheim quasichemical (MGQ) group contribution method for predicting polymer–polymer miscibility has been tested in blends composed of poly(*p*-vinylphenol) (PVPh) and ester-containing polymers (polyacrylates, polymethacrylates, aliphatic polyesters, and ethylene-*co*-(vinyl acetate) (EVA) copolymers). The model reproduces quite well the experimental miscibility range of these systems and predicts miscibility in the PVPh/poly(dialkyl itaconate) family from poly(dimethyl itaconate) to poly(dioctyl itaconate). Moreover, the MGQ model is able to predict the presence of lower critical solution temperature (LCST) in the PVPh/poly(butyl methacrylate) (PBMA) system, as a consequence of reduced exothermic heats of mixing with increasing temperature. Finally, an attempt was made to relate the nonrandom local fractions in the model to measurable quantities by Fourier transform infrared (FTIR) spectroscopy. Claims about the model limitations are also pointed out.

Introduction

The phase behavior of polymer blends depends primarily on the enthalpic interactions[1,2] between the blend components since the combinatorial entropic contribution to free energy of mixing is usually quite small for mixtures of large molecules, although noncombinatorial entropic terms as well as free volume changes might also have an influence on the free energy of mixing.[3] The enthalpic interactions are mainly determined by the nearest neighbor functional groups. This fact explains why heats of mixing of liquids with an analogous structure to the repeat units of the polymers give useful information about the miscibility of the polymer blend.[4-6] In this way, Lai et al.[7-9] have demonstrated the ability of group contribution methods for predicting polymer–polymer miscibility from heats of mixing of liquids. The interest in using a group contribution method is that it helps to understand the influence of the dissimilar interacting groups on the experimental heat of mixing. Moreover, these methods avoid the need to have close analogues to the polymer repeat units. The results of Lai et al.[7] suggest that the Guggenheim quasichemical model,[10,11] as modified by these authors, seems to be superior to others like UNIQUAC[12] for predicting heats of mixing of polar with nonpolar liquids.

It is known that polymers containing hydroxyl groups are often miscible with ester-containing polymers. It has been found that the MGQ model predicts adequately the miscibility window of the polyhydroxy ether of Bisphenol A with ester-containing polymers.[8,13] Usually, group contribution methods fail to accurately predict heats of mixing in polar and hydrogen bonding systems. The ability of the MGQ model to predict heats of mixing in these systems could be attributed to the quasichemical character of the model, as well as to the formulation of the local nonrandomness of contact sites in the mixture. In this sense, it has been detected by glass transition temperature (T_g) measurements and by Fourier transform infrared spectroscopy that poly(*p*-vinylphenol) forms miscible blends with some acrylic and methacrylic ester polymers.[14-20] The purpose of this paper is to examine the ability of the MGQ group contribution method to predict the miscibility of PVPh with polymethacrylates and polyacrylates. The results will be extended to other ester-containing families.

Summary of the MGQ Model

Group contribution methods that predict heats of mixing of liquids assume that each molecule is a mixture of interacting structural groups. The MGQ model takes into account the formation of i–j contacts from i–i and j–j group pairs through the quasichemical equation

$$(\text{i–i}) + (\text{j–j}) \xrightarrow{2\Delta E_{ij}} 2(\text{i–j})$$

and the chemical equilibrium constant associated with it

$$K_{ij} = A_{ij} \exp(-2\Delta E_{ij}/RT) \tag{1}$$

where ΔE_{ij} is the energy change in the process and A_{ij} is a preexponential factor related to the exchange entropy involved, ΔS_{ij}. The enthalpy of mixing (per unit volume) is given by[7]

$$\Delta H_m/V = H_m - \sum_k \phi_k H_k \tag{2}$$

In this model

$$H_m = \sum_i \sum_{j>i} S\theta_j \Psi_{ij} \Delta E_{ij} \tag{3}$$

$$H_k = \sum_i \sum_{j>i} S^{(k)} \theta_j^{(k)} \Psi_{ij}^{(k)} \Delta E_{ij} \tag{4}$$

where ϕ_k is the volume fraction of pure component k in the solution and S, θ_i, and Ψ_{ij} are the number of contact sites per unit volume, the average area fraction of group i, and the nonrandom local surface fraction of group i in the mixture, respectively. The counter (k) refers the same magnitudes but for pure molecules in the system. The values of S and θ_i can be easily calculated[7] from the densities and the molecular weights of the components and a parameter q_i proportional to the external surface of group i in the mixture.[21] In nonathermal mixtures Ψ_{ij} is related to θ_i through the nonrandom parameter Γ_{ij}:[22]

$$\Psi_{ij} = \Gamma_{ij}\theta_i \tag{5}$$

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also connected with the equilibrium constant by

$$\Gamma_{ij}^2/\Gamma_{ii}\Gamma_{jj} = A_{ij}\exp(-2\Delta E_{ij}/RT) = K_{ij} \quad (6)$$

And since the local surface fractions for each j must be conserved

$$\sum_i \Psi_{ij} = \sum_i \Gamma_{ij}\theta_i = 1 \quad (7)$$

In terms of the model, Ψ_{ij} is the local surface fraction of i available for contact with a central unit j[7] or, equivalently, the fraction of external sites around group j which are occupied by groups i.[12] If the A_{ij} and ΔE_{ij} parameters are known, the above equations allow one to calculate both Γ_{ij} and Ψ_{ij} and then the enthalpy of mixing by means of eqs 2–4. A reverse procedure is employed to obtain the A_{ij} and ΔE_{ij} parameters from fitting the MGQ model to experimental heats of mixing.

Experimental Section

Materials and Procedures. The chemical products were supplied by Aldrich Chemical Co. and were more than 99% pure. They were used without further purification. 4-Ethylphenol (EPH) was selected as a close analogue to poly(*p*-vinylphenol) and ethyl isobutyrate (EIB) was employed as an approximate analogue of poly(ethyl methacrylate). These compounds and two *n*-alkanes (*n*-decane and *n*-dodecane) were chosen because they contain structural groups necessary to the prediction of polymer-polymer miscibility.

A Setaram C.80 D flux-type calorimeter was used for the measurements of heats of mixing at 79 ± 0.1 °C. This temperature is above the melting point of EPH (45 °C) and below the boiling point of EIB (112 °C) and *n*-alkanes employed (>174 °C).

The densities of the chemicals were either obtained from the literature where possible[23] (*n*-decane, *n*-dodecane) or measured with a pycnometer at the selected temperature. Values of 0.965 and 0.801 g/cm^3 were determined for the densities of EPH and EIB, respectively.

The calculational procedure employed to obtain unknown model parameters was developed in the FORTRAN language with two subroutines from the International Mathematical and Statistical Library (IMSL) in a Micro Vax II computer. The first one, called ZXMWD (nonlinear parameter estimation), fits the adjustable parameters A_{ij} and ΔE_{ij} while the second subroutine, called ZSCNT (solve systems of nonlinear equations), is used to determine the values of the nonramdom parameters (eqs 6 and 7).

Results and Discussion

Determination of the Model Parameters. The MGQ model requires the repeat units of the polymers to be divided into structural groups. Previous authors[8,13] recommended employing liquid analogues that closely simulate polymer repeat units (although this model was developed to avoid having close analogues) and dividing the molecules into groups as large as possible with the purpose of alleviating the numerical problems on the procedures of the model. The sorted structural groups are classified in classes and it is assumed that all members (types) in a class interact identically with groups outside the class; however different types in a class differ in surface size which is reflected in the q_i parameter.

For the purpose of predicting the range of miscibility between poly(*p*-vinylphenol) and acrylic ester polymers, these polymers as well as all the analogues used were sorted first into three classes: methylene (CH_2), ester (CH_2COO), and phenol (C_6H_4OH). Consequently, the parameters corresponding to CH_2/CH_2COO, CH_2/C_6H_4OH, and CH_2COO/C_6H_4OH interactions were required according to the model. The values of the parameters for the CH_2/CH_2COO interacting pair were obtained from Lai et al.[7] data,

Table I
Summary of MGQ Parameters

group classes (i/j)	A_{ij}	ΔE_{ij} (cal/mol)	% rms error	data points	sources
CH_2/C_6H_4OH	0.039	290.8	4	17	this work
CH_2/CH_2COO	1.000	137.4	10	123	ref 7
CH_2COO/C_6H_4OH	1.1×10^{-7}	-3560	20	8	this work

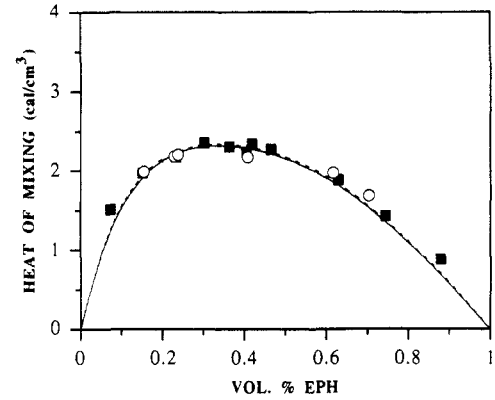


Figure 1. Heats of mixing of EPH with *n*-alkanes at 79 °C: (■, —) EPH with *n*-decane; (○, - - -) EPH with *n*-dodecane. Lines are estimated by MGQ using parameters from Table I.

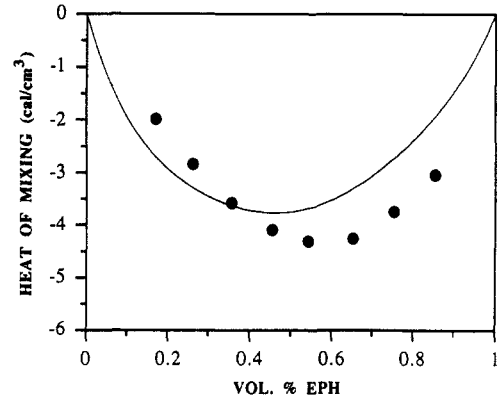


Figure 2. Heats of mixing of EPH with EIB at 79 °C: (●) experimental data; (—) estimate by MGQ using parameters from Table I.

and they are shown in Table I. The values of the parameters for the other interaction pairs were not found in the literature.

Heats of mixing of two alkanes, *n*-decane and *n*-dodecane, with EPH were determined to fit the parameters that characterize the CH_2/C_6H_4OH interaction. Figure 1 shows the comparison between the experimental heat of mixing and the model using the best fit parameter values which are given in Table I.

Then, EPH and EIB were chosen to be mixed because these compounds contain structural groups that allow us to evaluate the third pair of parameters corresponding to the CH_2COO/C_6H_4OH interaction. Attempts to fit the EPH/EIB experimental heats of mixing using the CH_2/CH_2COO and CH_2/C_6H_4OH parameter values previously indicated (Table I) were not very successful, as is shown in Figure 2. The model is not able to reproduce the experimental curve as reflected by the fact that the shapes of the calculated and experimental curves are very different. The calculational procedure attempts to minimize error but the MGQ model cannot skew sufficiently with the composition to fit the experimental curve that leads to a 20% average root-mean-squared error. The failure of the model to describe these heats of mixing could be attributed to an unsuitable assignment of the interacting groups.

Table II
Summary of MGQ Parameters

group classes (i/j)	A_{ij}	ΔE_{ij} (cal/mol)	% rms error	data points	sources
CH_2/CH_2COO	1.000	137.4	10	123	ref 7
$CH_2/PhCOH$	11.95	3745	4	17	this work
$CH_2/PhCH$	0.935	28.8	6	91	ref 7
$CH_2COO/PhCOH$	0.045	260	3	8	this work
$CH_2COO/PhCH$	0.05	−725	3	8	this work
PhCOH/PhCH	9.40	3560	4	17	this work

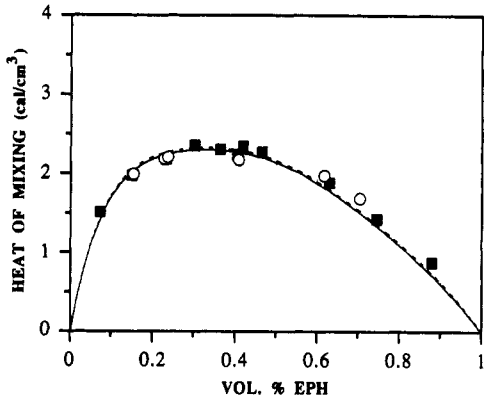


Figure 3. Heats of mixing of EPH with *n*-alkanes at 79 °C: (■, —) EPH with *n*-decane; (○, - - -) EPH with *n*-dodecane. Lines are estimated by MGQ using parameters from Table II.

A more adequate description of the effect of chemical structure on the heat of mixing would be obtained if all the chosen structural groups were sufficiently small to take into account all possible interactions in the mixture. Therefore, the local nonrandomness in the mixture might be better represented with a greater number of structural groups. According to UNIQUAC[12] and UNIFAC[24] setting choices of structural groups, one must sort EIB into methylene (CH_2) and ester (CH_2COO) classes, but now EPH must be divided into methylene, aromatic methine (PhCH), and aromatic hydroxyl (PhCOH) classes. If the above assignment is followed, the number of parameters for all of the unlike binary combination of groups is now greater. However, the setting choice of structural groups should allow us to use the obtained parameters for prediction in other systems. These i–j combinations are contained in Table II, and only the parameters for the $CH_2/PhCH$ and CH_2/CH_2COO interaction pairs are available in the literature.[7] The parameters corresponding to the other interactions can be determined from the previously measured heats of mixing of *n*-alkanes/EPH and EIB/EPH.

The $CH_2/PhCOH$ and PhCOH/PhCH pairs were evaluated simultaneously from the *n*-decane/EPH and *n*-dodecane/EPH experimental heats of mixing. The MGQ model describes these experimental heats of mixing as well as previous ones (see Figures 1 and 3); so it seems that the last group assignment and the procedure employed are adequate. Further results provided us more confidence about their reliability.

Apart from the parameters above mentioned, it is necessary to know the parameters corresponding to PhCH/CH_2COO and PhCOH/CH_2COO interactions which can be obtained from heats of mixing of EIB with EPH. The first of them is given in the literature,[8] but using these values we could not find parameters for PhCOH/CH_2-COO interaction that fit successfully the experimental heats of mixing. The failure might be due to the parameter values obtained from the literature for PhCH/CH_2COO interaction being not appropriate to our case where the aromatic methynes involved in the interaction belong to a phenolic ring. The electron density associated with a hydroxyl aromatic ring is expected to be larger than that associated with an unsubstituted aromatic ring, due to the mesomeric electron-donating effect of the hydroxyl group.[25] Consequently, this fact can affect the parameters for PhCH/CH_2COO interaction. This is why the parameters of both PhCH/CH_2COO and PhCOH/CH_2COO have been evaluated simultaneously. The parameters of Table II lead to an acceptable fit of the data, as can be seen in Figure 4.

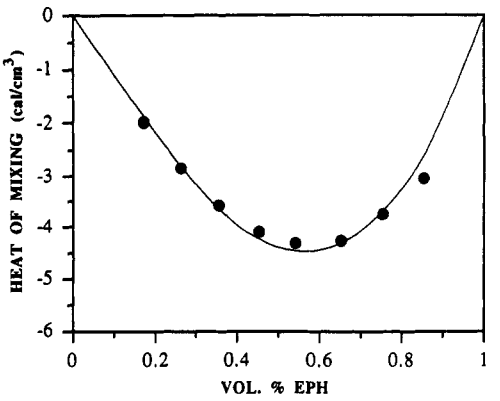


Figure 4. Heats of mixing of EPH with EIB at 79 °C: (●) experimental data; (—) estimate by MGQ using parameters from Table II.

Another way to rationalize the difference between a hydroxyl group attached to an aromatic ring and an hydroxyl attached to an aliphatic hydrocarbon is to compute the heats of mixing of EIB/EPH mixtures using the parameters given in the literature[8] for aliphatic alcohols with esters. Then, using parameters corresponding to CH_2/CH_2OH, CH_2COO/CH_2OH, and CH_2OH/PhCH pairs, we were not able to fit the experimental curve, as was expected for the different reactivity (acidity) between both kinds of alcohols.[26] An endothermic curve was predicted instead of the exothermic one. Therefore, we can conclude that due to the different nature of the mentioned alcohols we must choose adequately the classes of groups to describe EIB/EPH mixtures.

Prediction of Polymer–Polymer Miscibility. From the parameters in Table II one can predict by the MGQ model the miscibility behavior in mixtures of PVPh with different polymers containing ester groups in their repeat units. A knowledge of the repeat unit molecular weights and polymer densities[27] is required for the model calculations. For the prediction, the following criterion is retained in this paper: a polymer–polymer blend is predicted to be miscible if the calculated heat of mixing is exothermic at each composition. Thus, a polymer mixture with positive heats of mixing in a range of composition is considered immiscible even if the calculated heat of mixing at other compositions is negative. We do not have to forget that the simplified nature of a group contribution method and the absence of entropic contributions in this model means that the prediction of miscibility should be taken with reasonable care. Due to the lack of values of thermodynamic magnitudes related to the heat of mixing for PVPh/ester-containing polymer blends we will only predict the miscibility range.

Starting with PVPh/polymethacrylate blends, Serman et al.[15,16] found by Fourier transform infrared spectroscopy and cloud-point measurements that PVPh was miscible with poly(methyl methacrylate) (PMMA), poly(ethyl methacrylate) (PEMA), poly(*n*-propyl methacrylate) (PPMA), and poly(*n*-butyl methacrylate) (PBMA) at room temperature, but the last one showed phase separation at

Table III
Comparison between the Range of Miscibility Predicted by the MGQ Model and That Observed Experimentally[a]

miscibility criterion	polymeth-acrylates	poly-acrylates	aliphatic polyesters	EVA copolymers
DSC	1–3	1–4	2, 3, 4, 5, 7	45–100
FTIR	1–4	1–4		45–100
MGQ model	1–4	1–7	1–12	15–100

[a] For the polymethacrylate, polyacrylate, and polyester families it is expressed in terms of number of methylenes in the polymer repeat unit. For the EVA copolymers the weight percentage of vinyl acetate in the copolymer is used.

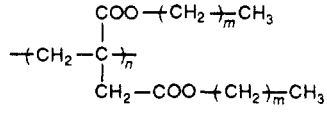
temperatures above 160 °C. However, by T_g measurements only the first three members of the polymethacrylate family were found miscible with PVPh.[14] As we can see in Table III, the range of miscibility predicted by the MGQ model practically agrees with the experimental range.

According to Coleman et al.,[17] PVPh is miscible with polyacrylates from poly(methyl acrylate) (PMA) to poly(*n*-butyl acrylate) (PBA), but poly(*n*-pentyl acrylate) (PPA) is immiscible when the percentage of PVPh is more than 50 wt %. The higher polyacrylates are immiscible with PVPh across the entire composition range. In this case, the range of miscibility predicted by the MGQ model is slightly greater than that obtained experimentally (see Table III).

Regarding linear aliphatic polyesters, only polyesters with CH_2/COO ratios of 2–5 and 7 had been studied by means of T_g measurements, concluding that PVPh is miscible with them.[18,19] In the same work, a melting point depression was detected for these blends, although equilibrium data were not reported. The MGQ model predicts miscibility for the polyesters indicated above, but because we have not found in the literature data for other CH_2/COO ratios, we do not know the model accuracy for predicting the range of miscibility of the PVPh/polyester family. The MGQ model places the miscibility boundary at a CH_2/COO ratio of 12 (Table III). This window seems to be reasonable when compared to that found in other systems as poly(vinyl chloride)/polyester blends, where weaker interactions are present.[28]

Also, PVPh was shown to be miscible with poly(vinyl acetate) (PVAc) and copolymers of ethylene and vinyl acetate (EVA) containing 70% vinyl acetate and to be immiscible with an EVA containing 25% vinyl acetate.[20] In contrast, PVPh appears to form a complicated multiphase system that has a significant degree of mixing with EVA having 45% vinyl acetate.[29] Then, 45% can be considered as the minimal amount of vinyl acetate in the copolymer needed to form a miscible blend with PVPh. Table III shows that the miscibility range calculated by the MGQ model is broader than the range experimentally obtained.

Finally, the model can be used to predict windows of miscibility in systems which have not been tested experimentally yet. In this sense, we will consider the poly(dialkyl itaconate) family (two ester groups per repeat unit):



For PVPh/polyitaconate blends, the MGQ model provides a range of miscibility from poly(dimethyl itaconate) to poly(dioctyl itaconate). Further studies are required to confirm this theoretical prediction.

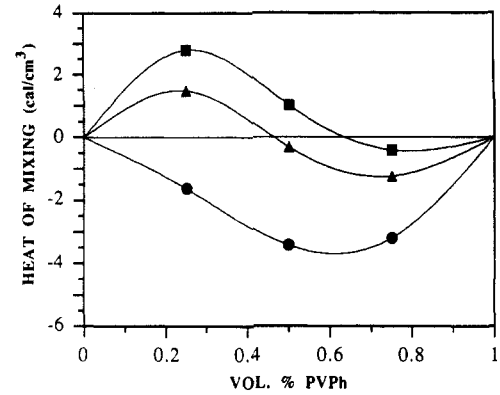


Figure 5. Heats of mixing calculated by the MGQ model as a function of composition at different temperatures: (●) 79 °C; (▲) 165 °C; (■) 200 °C. The parameters employed are shown in Table II.

According to the above exposed experimental data, the range where PVPh is miscible with polymers containing ester groups in their repeat units increase in the order: polymethacrylates < polyacrylates < polyesters. However, the predicted miscibility windows are in all cases broader than experimental results, a fact that points to an overpredicted exothermic heat of mixing by the model. Even with the above limitation, the results in Table III suggest that the MGQ model can be applied to prediction of trends in miscibility for this type of binary polymer blends.

Effect of Temperature on the Heat of Mixing. It is well-known that polymer blends often show phase separation when temperature increases (LCST) and cloud-point measurements are used to obtain information about the temperature where phase instability occurs.[1,30] In this paper, the change of sign of the mixing heat, from exothermic to endothermic, has been taken as the phase instability criterion, neglecting the entropic contributions to the free energy of mixing.[7-9] We can explore the influence of temperature on the predicted heat of mixing by simply changing the temperature in the model equations, in spite of the fact that previous attempts were not successful.[8,13] Implicitly, we are assuming that all A_{ij} and ΔE_{ij} parameters in the model do not change with temperature although we will account for changes in polymer densities.

An increasing temperature causes a reduction in both the magnitude of the heat of mixing and the range of compositions that shows exothermic mixing, as can be seen in Figure 5 for the PVPh/PBMA system. This is a general trend predicted by this model for the polymethacrylate family as well as for the polyacrylate and polyester series. Referring to eqs 2–4, the change of enthalpy upon mixing ($\Delta H_m/V$) is determined by the balance between the enthalpy associated with the mixture of components (H_m) and the enthalpy related to form the pure components as a mixture of interacting structural groups ($\sum_k \phi_k H_k$). In terms of the MGQ model, both H_m and $\sum_k \phi_k H_k$ are positive for the above systems and the miscibility is explained as a consequence of $H_m < \sum_k \phi_k H_k$. In these systems, an increase of temperature leads to a higher H_m value, whereas the $\sum_k \phi_k H_k$ term does not change so much. Consequently, the calculated $\Delta H_m/V$ becomes less exothermic as the temperature is raised.

The temperature variation of the heat of mixing computed by the MGQ model allows one to draw a phase diagram showing the boundary between miscible ($\Delta H_m/V < 0$) and immiscible ($\Delta H_m/V > 0$) regions. Figure 6 shows the predicted $\Delta H_m/V = 0$ boundary for the PVPh/PBMA

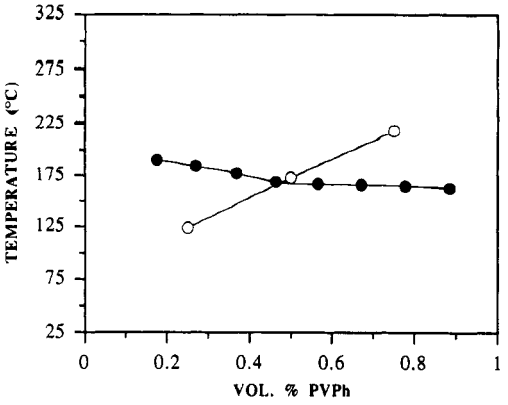


Figure 6. Phase diagram of PVPh/PBMA blends: (●) experimental cloud-point data;[16] (○) miscibility boundary predicted by the MGQ model using the parameters in Table II.

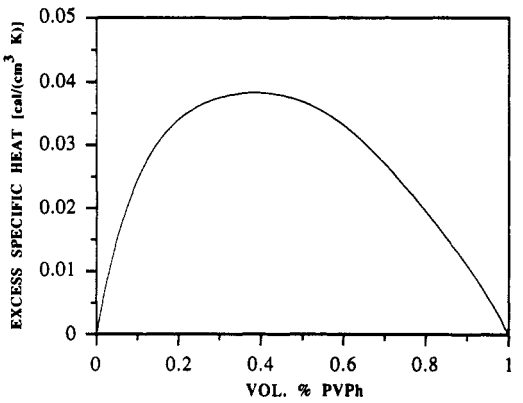


Figure 7. Excess specific heat predicted by the MGQ model as a function of composition in the temperature range between 79 and 200 °C for PVPh/PMMA blends. The parameters employed are shown in Table II.

system and the experimental cloud-point curve.[16] The agreement between experimental and calculated LCSTs is quite poor and is probably due to the simplifications involved in this procedure, so the results must be used with caution. The reasons for this failure can be related to the simplified criterion for phase stability here assumed ($\Delta H_m/V \leq 0$) and probably to the temperature dependence of both A_{ij} and ΔE_{ij} that we have not considered.[13] Recently, a combination of the MGQ model with the lattice-fluid theory has led to accurate LCST predictions for several miscible blends[31] where the heats of mixing computed by the MGQ model do not change significantly with temperature. However, for binary blends of PVPh and ester-containing polymers the MGQ model predicts phase separation in terms of enthalpic considerations only, although the accuracy of the predicted cloud-point curve is poor.

The temperature dependence of the heat of mixing is related to the excess specific heat of the blend (C_p^E) via[32]

$$(\partial(\Delta H_m/V)/\partial T)_p = C_p^E = C_p - (\phi_1 C_{p1} + \phi_2 C_{p2}) \quad (8)$$

Then, reduced exothermic heats of mixing with increasing temperature will lead to positive excess heat capacities, which are shown in Figure 7 as a prediction of the model for the PVPh/PMMA blend. Experimentally, both the heat of mixing and the excess specific heat of several hydrogen-bonded mixtures change strongly with temperature.[33] Note that for the PVPh/PMMA blend no temperature dependence of the excess heat capacity is predicted by the MGQ model and this could be a limitation in applying this model to hydrogen-bonded systems. Similar trends were found for other members in the polymethacrylate family different from PMMA. The MGQ model predicts for the PVPh/polyacrylate and PVPh/polyester series excess heat capacities very similar in magnitude to those calculated for the PVPh/PMMA system. The C_p^E values predicted by this model compare fairly well to those measured in several other miscible blends.[32,34] In this sense, a preliminary study carried out by DSC, has shown a positive C_p^E of the order of 10^{-2} cal/(cm^3 K) for the PVPh/PMMA 50:50 blend.

Nonrandom Local Surface Fractions. The MGQ model tries to account for the microscopic structure of interacting mixtures in terms of the nonrandom local surface fractions, by utilizing the local-composition concept introduced by Wilson.[35] As pointed out before, the nonrandom local surface fraction (Ψ_{ij}) employed in eqs 3–7 is the fraction of external contact sites around a group j which are occupied by groups i. Thus, it is possible to obtain the fraction of external sites around CH_2COO groups occupied by PhCOH groups by means of the corresponding Ψ(PhCOH/CH_2COO). This parameter might be qualitatively related to the fraction of carbonyl groups involved in hydrogen bonding that can be measured by FTIR spectroscopy. When Ψ(PhCOH/CH_2COO) and FTIR results are compared, the trends predicted by the MGQ model as a function of composition and temperature for PVPh/PEMA and PVPh/PPMA blends are correct. However, the absolute values predicted by the MGQ model differ considerably from the experimental ones.[16]

Unfortunately, FTIR data do not permit a measurement of the fraction of hydroxyl groups that are non-hydrogen bonded (free), or alternatively, the fraction of hydrogen-bonded ones.[36] However, some qualitative features have been well established and one can expect an increase of the fraction of free hydroxyl groups both by raising temperature, due to hydrogen bond breaking, or by decreasing the percentage of the ester-containing polymer in the blend, due to the thermodynamic equilibrium between bonded and free species.[36] In this model, the corresponding local area fraction of (free) hydroxyl groups that do not interact with themselves or with carbonyl groups is given by

$$\Psi_{free} = 1 - \Psi(CH_2COO/PhCOH) - \Psi(PhCOH/PhCOH) \quad (9)$$

For PVPh/PEMA and PVPh/PPMA blends the trends predicted by the MGQ model are in agreement with the above considerations.

Finally, it would be interesting to verify if nonrandom local surface fractions can predict more accurately the data for hydrogen-bonded groups in other polymer blend systems.

Summary and Conclusions

The ability of the MGQ group contribution method to predict miscibility of PVPh with ester-containing polymers has been tested. First, analogues similar to the repeat units have been selected to obtain the unknown parameters corresponding to different i–j pairs in the model. If the analogues are sorted into a minimum number of classes of groups, the model is not able to fit EIB/EPH experimental data. The failure could be attributed to an inappropriate structural choice to describe the dissimilar interacting groups in the mixture. A better representation was found when the chosen classes were smaller, as recommended by UNIFAC[24] and UNIQUAC[12] group contribution methods. However, a further modification had to be done for the PhCH/CH_2COO pair parameter, previously reported in the literature,[8] since a PhCH group

in a phenolic ring might interact in a different way that a PhCH group that belongs to an aromatic ring.[25] Moreover, the influence of chemical structure can be shown when the parameters corresponding to aliphatic alcohols[8] are employed. In this case, the experimental and calculated curves for the EIB/EPH mixtures have opposite signs. Apart from the limitation of any group contribution method, it seems that a careful class choice is required to further polymer–polymer miscibility predictions.

In this sense, the parameters obtained in this work allow us to reproduce the miscibility range for PVPh/polyacrylates,[17] PVPh/polymethacrylates,[14-16] and PVPh/EVA[20,29] blends, although the predicted windows seem slightly broader than experimental ones. Also, for all the PVPh/aliphatic polyester blends which experimentally have been found miscible,[18,19] the model predicts exothermic mixing heats but further studies are required to test the predicted miscibility window. Interestingly, in PVPh/polyitaconate blends a window of miscibility is predicted by the MGQ model from poly(dimethyl itaconate) to poly(dioctyl itaconate).

Despite the fact that previous works[7,8,13] suggest that the MGQ model is not able to predict LCST behavior, the results in this work show that at least for PVPh/PBMA blends the model reproduces, poorly, experimental data.[16] Also, relatively high excess specific heats have been predicted by the model, which compare fairly well to those measured in PMMA/poly(styrene-*co*-acrylonitrile)[32] and phenoxy/poly(ethylene oxide) miscible blends.[34]

Finally, we have related the nonrandom local surface fraction of carbonyl groups available for contact with phenolic hydroxyl groups to the fraction of hydrogen-bonded carbonyl groups, which have been determined by FTIR for PVPh/ester-containing polymer blends.[16,36] The model is able to reproduce the general trends with both composition and temperature. However, the difference between the experimental and calculated data suggests that the model does not seem sufficiently adequate to describe the local nonrandom character of the mixture.

In conclusion, despite the fact of the simple nature of a group contribution method and the primitive miscibility criterion ($\Delta H_m/V \leq 0$), the MGQ model appears to reproduce general trends of thermodynamic magnitudes related to mixing heats of polymer blends, but it could be risky to take the calculated data as sufficiently accurate values.

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Registry No. EPH, 97-62-1; EIB, 123-07-9; PBMA, 9003-63-8; PVPh, 24979-70-2; *n*-decane, 124-18-5; *n*-dodecane, 112-40-3.