An Attempt To Predict Phenoxy Resin Miscibility Using a Group Contribution Method

E. Espi* and J. J. Iruin

Departamento de Ciencia y Tecnologia de Polimeros, Facultad de Quimica, Universidad del Pais Vasco, P.O. Box 1072, San Sebastian, Spain

Received March 5, 1991; Revised Manuscript Received July 22, 1991

ABSTRACT: Group contribution methods have been recently proposed as an alternative in the prediction of polymer-polymer miscibility. In this work, some of the possibilities and shortcomings of the so-called modified Guggenheim quasi-chemical method have been analyzed using some previously reported experimental data on phenoxy (a resin from Bisphenol A and epichlorohydrin) blends. More specifically, the experimetal miscibility windows in phenoxy/polyoxide and phenoxy/polyester blends have been used as a test of the validity of the model. A redefinition of the surface parameters and the use of model compounds as similar as possible to the polymers have been employed in order to improve the quantitative predictions of the method. Results have been extended to other ester-containing families, such as poly(vinyl esters), poly(acrylates), and poly(methacrylates).

Introduction

Several attempts have been made in order to have a simple and reliable method of knowing a priori the miscibility or immiscibility of two polymers. Unfortunately, theoretical models used up to this point, e.g. equation of state[1] and lattice fluid model,[2] introduce adjustable, not independently evaluable parameters. One attempt to elude this problem is the evaluation of polymer-polymer interaction parameter using group contribution methods based on segment-segment interaction parameters. This method has proved to be suitable in order to explain the miscibility in copolymer-containing systems.[3] The same method has been applied to some homopolymer-homopolymer blends,[4] but its possibilities are restricted by the limited number of miscible polymer-polymer pairs. Other group contribution methods have used heats of mixing of model compounds to evaluate enthalpy of mixing of a polymer blend. In this last group we can include the modification of the Guggenheim method[5,6] proposed by Lai et al. in a recent paper.[7]

All these methods assume that each molecule can be divided into structural units (CH_2, CH_2O, etc.) so that even a pure component can be defined as a mixture of interacting structural units.

In the above mentioned work,[7] Lai et al. made a comparison of fit between the UNIQUAC[8] method and a modified Guggenheim quasi-chemical model (MGQ)[5,6] and predict heats of mixing of low molecular weight compound mixtures and polymer blends. They proposed two modifications to the Guggenheim method. The first one considers that chemical equilibrium between i-j contacts can be described by a change in the free energy ΔG_{ij}. This implies the introduction of a parameter A_{ij}

$$A_{ij} = \exp(2\Delta S_{ij}/k) \tag{1}$$

in addition to the characteristic energy ΔE_{ij} used in the Guggenheim model

$$\Delta E_{ij} = E_{ij} - (E_{ii} + E_{jj})/2 \tag{2}$$

ΔS_{ij} and ΔE_{ij} are the exchange entropy and energy, respectively, associated with the formation of an i-j contact on mixing i-i and j-j contacts. Thus, in this model, for each class of contacts i-j, two parameters A_{ij} and ΔE_{ij} are needed.

* Author to whom correspondence should be addressed.

The second modification is an attempt to account local nonrandomness in contacts by introducing the nonrandomness factors Γ_{ij} defined by Panayiotou and Vera:[9]

$$\Gamma_{ij} = N_{ij}/\mathcal{N}_{ij} \tag{3}$$

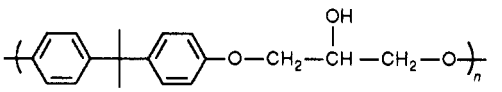
where N_{ij} is the number of i-j pairs in the blend. $\mathcal{N}_{ij}$ has the same meaning, but in a totally random mixture.

This method seems to fit quite well heats of mixing of low molecular weight compounds and it has a better behavior than UNIQUAC for polar mixtures, but it fails in the prediction of the interaction energy density (B) of some polymer blends,[10] assuming that B has only an enthalpic character:

$$\Delta H_m/V = B\Phi_1\Phi_2 \tag{4}$$

where ΔH_m is the enthalpy of mixing and Φ_i the volume fractions of the components. This last assumption rests on the low value of the combinatorial entropy of mixing when the molecular weight of the components is very high.

More specifically, for blends of poly(hydroxy ether) of Bisphenol A (phenoxy) (PH):



and aliphatic polyesters, MGQ predicts a miscibility window for polyesters having a CH_2/COO ratio between 2 and 6. This result agrees aproximately with experimental studies.[11] However, the predicted values of B are less negative than those observed by both melting point depression and solvent probe methods.[12]

Lai et al.[10] attributed this poor agreement to the use of low molecular weight liquids containing structural groups which are not completely equivalent to those of the polymers. MGQ parameters describing interactions between the ether group CH_2O and other groups were calculated using aliphatic ethers, whereas the ether group in the phenoxy resin is contiguous to an aromatic ring. Moreover, Lai et al. assumed that the CHOH group of this polymer could be included in the general class of the CH_2-OH group of the primary alcohols. However, it is reasonable to consider that a secondary hydroxyl group will not have the same ability as a primary one to interact with other groups.

On the other hand, this model does not consider self-association by hydrogen bonding between OH groups in

0024-9297/91/2224-6458$02.50/0

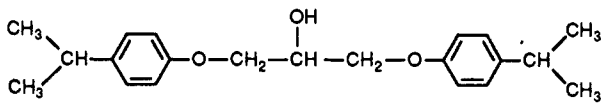
phenoxy. Coleman and Moskala have conclusively demonstrated through Fourier transform infrared spectroscopy (FTIR)[13] that this self-association is nearly complete at room temperature. As we will see later, depending on the alcohols previously selected to evaluate parameters, this effect can have an important influence in the applicability of this model.

In this work, we have examined the feasibility of the MGQ model in predicting miscibility of phenoxy with polyoxides, aliphatic polyesters, polyacrylates and polymethacrylates. Taking into consideration the approximations made in the evaluation of A_{ij} and ΔE_{ij}, previously discussed, we have recalculated them by using model compounds as similar as possible to the structure of the polymers used in the blends.

Experimental Section

Materials and Instrumental Methods. All chemical products used in this work, with the exception of the phenoxy model compound (IPPHP), were supplied by Aldrich Chemical Co. Their purity was at least 98%, and all materials were used without further purification.

The phenoxy model compound, 1,3-bis[4-(2-propyl)phenoxy]-2-propanol (IPPHP) was synthesized in our laboratory from the



reaction between 4-isopropylphenol and epichlorohydrin in a 3:1 ratio and in a basic aqueous solution. The resulting product was recrystallized in a THF/hexane mixture and was characterized by FTIR, ^{1}H NMR, and ^{13}C NMR. Infrared spectra were recorded in a Nicolet 5DXC spectrophotometer. A Varian VXR 300 spectrometer, using deuterated chloroform as solvent, was used for NMR spectra.

Heats of mixing of model compounds were measured at 95 °C in order to obtain parameters in the liquid–liquid state. A Calvet-type calorimeter (Setaram C-80D model) with appropriate mixing cells was used.

All calculations were made with a MicroVax II computer.

Calculation Procedures. In order to estimate A_{ij} and ΔE_{ij} parameters for a pair of groups i and j, heats of mixing of some pairs of liquids containing both classes of groups are required. It is possible to work either with a pair of liquids in several compositions, with several pairs in one composition, or various pairs in several compositions. The final goal is to choose the pair $A_{ij}/\Delta E_{ij}$ in such a way to fit accuratly the experimental results. This choice is made with a FORTRAN International Mathematical and Statistical Library (IMSL) nonlinear parameter estimation subroutine called ZXMWD. The function to minimize is the sum of squared differences between experimental and calculated values of ΔH_m. The enthalpy of mixing per unit volume is calculated according to the equation

$$\Delta H_m/V = \sum_{i}^{}\sum_{j>i}^{} B'_{ij}\theta_i\theta_j - \sum_{k}^{}\sum_{i}^{}\sum_{j>i}^{} \phi_k B'_{ij}{}^{(k)}\theta_i{}^{(k)}\theta_j{}^{(k)} \quad (5)$$

where θ_i and $\theta_i{}^{(k)}$ are the average area fractions of group i in the mixture and in the pure components, respectively, both calculated according to

$$\theta_i = q_i N_i / \sum_{j}^{} q_j N_j \quad (6)$$

where q is a parameter proportional to the group external surface area. It can be calculated according to Abrams and Prausnitz[8] and Bondi.[14] Surface parameters used in this work, with the exceptions pointed out in the text are shown in Table I, ref 10.

B'_{ij} and $B'_{ij}{}^{(k)}$ are the group interaction densities in the mixture and in the k component, respectively, calculated as

$$B'_{ij} = S\Gamma_{ij}\Delta E_{ij} \quad (7)$$

where S is the number of contact sites per unit volume

$$S = (\sum_{m}^{} z q_m N_m)/V \quad (8)$$

and Γ_{ij} and ΔE_{ij} have been already introduced.

Previously, for each composition, nonrandom parameters Γ_{ij} had to be evaluated. This estimation was made by the simultaneous resolution of the following equation set for every i–j pair in the mixture:

$$\Gamma_{ij}{}^2\theta_i\theta_j/(1 - \sum_{j\neq i}^{}\theta_j\Gamma_{ij})(1 - \sum_{i\neq j}^{}\theta_i\Gamma_{ij}) = A_{ij}\exp(-2\Delta E_{ij}/kT) \quad (9)$$

A FORTRAN IMSL ZSCNT subroutine was used for this purpose.

Equations 5–9 can be used in the inverse sense. From tabulated values of A_{ij} and ΔE_{ij} for each pair of groups interacting in the mixture it is possible to calculate ΔH_m of the mixture.

Results and Discussion

Polymer–Polymer Miscibility Predictions from Heats of Mixing of Simple Liquids. Miscibility of phenoxy blends with polyoxides[15] and polyesters[11] can be attributed to the ability of the phenoxy hydroxyl group to form hydrogen bond interactions. Taking into account some of the approximations made by Lai et al.,[7,10] we have decided to recalculate the parameters of those interactions in which the groups of the PH molecule are involved. For this purpose we have used liquids containing similar groups to those of phenoxy, polyoxides, and aliphatic polyesters, particularly the secondary alcohol and the aliphatic–aromatic ether in PH. Our first step was to use one pair of simple liquids in several compositions. We mixed a secondary alcohol (cyclohexanol) with an alkane (decane), an aromatic hydrocarbon (ethylbenzene), an aliphatic–aromatic ether (methyl phenyl ether), an aliphatic ether (diethylene glycol diethyl ether, DEGDEE), and an aliphatic ester (diethylene succinate). In our procedure, only one pair of parameters A_{ij} and ΔE_{ij} was estimated per system studied. Every pair of compounds were mixed in seven different compositions 20/80, 30/70, 40/60, 50/50, 60/40, 70/30, and 80/20 in weight. Extreme compositions were obviated in order to minimize the error.

Table I shows the heats of mixing of each pair of mixed liquids at all compositions. As usual, all systems showed a maximum for intermediate compositions. Heats of mixing evaluated from parameters obtained with primary alcohols (Table II, ref 7, and Table II, ref 10) differ between 5 and 40% from experimental results. By fitting the model to the data sets obtained from these mixtures we have estimated other values of these parameters which predict experimental results with a deviation between 1.4 and 2.7%. As is shown in Figures 1 and 2, by changing these parameters it is possible to improve the agreement between calculated and experimental results, but not radically. A comparison of MGQ parameters calculated by Lai et al.[7,10] and those calculated in this work is shown in Table II.

In the following paragraphs we will discuss the observed changes in the predictions of phenoxy/polyoxides and phenoxy/aliphatic polyesters miscibility when we use our parameters instead of those of Lai et al.

Phenoxy/Polyoxides. Phenoxy was reported[15,16] to be miscible with poly(ethylene oxide) (PEO) and immiscible with poly(propylene oxide) (PPO).[15] In a recent work of our group, we have found evidences of immiscibility with poly(methylene oxide) (PMO).[17] Thus, the experimental miscibility window is placed around CH_2/–O– ratios of 2. Misleadingly, at 60 °C MGQ predicts positive enthalpies of mixing for blends of phenoxy with all the studied polyoxides (PMO, PEO, PPO, and poly(butylene

Table I
Measured Heats of Mixing Using Cyclohexanol (A)

vol % B	$\Delta H_m/V$, cal/mL
A + Decane (B)	
7.07	1.96
14.07	2.90
21.95	3.28
35.72	3.65
47.86	3.36
62.48	2.87
75.73	2.12
A + Ethylbenzene (B)	
24.67	2.39
31.03	2.87
42.04	3.65
51.47	4.02
63.75	4.07
71.04	3.96
80.33	3.42
A + DEGDEE (B)	
20.94	1.25
31.40	1.61
40.68	1.95
50.72	2.11
61.34	2.08
70.68	2.00
81.12	1.48
A + Methyl Phenyl Ether (B)	
19.09	2.842
30.47	3.967
39.28	4.296
50.08	4.761
58.79	4.892
69.60	4.331
79.09	3.580
A + Diethyl Succinate (B)	
18.99	2.607
28.60	3.420
38.93	3.986
48.23	4.193
57.34	4.190
68.68	3.821
79.15	2.856

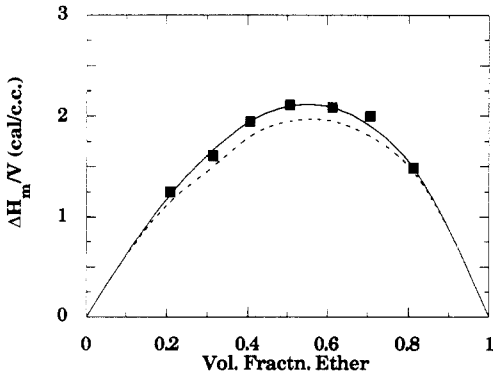


Figure 1. Heats of mixing of cyclohexanol with DEGDEE at 95 °C: ■, data from Table I; —, estimated by MGQ using parameters from this work (Table II); - - -, estimated by MGQ using parameters from refs 7 and 10.

oxide) (PBO)) when both our parameter set and that of Lai et al.[7,10] was used. Nevertheless, some differences between both sets must be pointed out. Practically similar values of B are predicted for blends of PH with PPO and PBO: 2.5 and 4.0 cal/mL, respectively. With PEO and PMO a shift toward less positive values is observed. For PEO, B shifts from 1.8 to 0.4 and for PMO, from 4.0 to 0.7 cal/mL. Values predicted for PMO must not be taken into account since the PMO melting point is near 180 °C.[18] Thus, in order to make predictions about this system

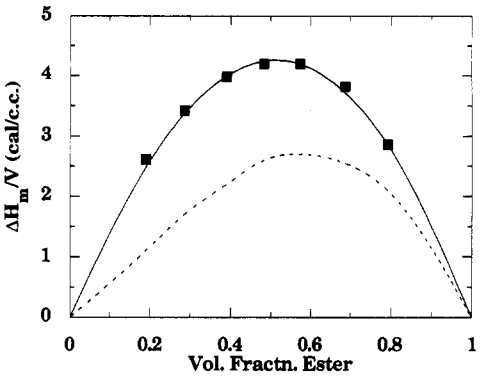


Figure 2. Heats of mixing of cyclohexanol with diethylene succinate at 95 °C: ■, data from Table I; —, estimated by MGQ using parameters from this work (Table II); - - -, estimated by MGQ using parameters from refs 7 and 10.

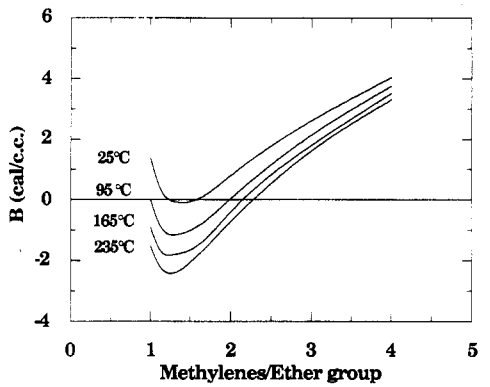


Figure 3. Effect of temperature on predicted binary interaction densities for phenoxy blends with polyoxides having various CH_2/–O– ratios in their repeating units, using parameters from this work (Table II).

Table II
Summary of MGC Parameters

	Lai et al.		this work	
groups	A_{ij}	ΔE_{ij}, cal/mol	A_{ij}	ΔE_{ij}, cal/mol
CHOH/CH_2	14.17	3837	0.413	818
CHOH/PhCH	9.643	3550	0.481	648
CHOH/CH_2O	0.583	143.9	0.980	217.2
CHOH/CH_2O[a]			0.719	268.9
CHOH/CH_2COO	0.546	163.4	2.040	326.4

[a] Aliphatic/aromatic ether.

in the true liquid–liquid state, parameters should be calculated above this temperature. The only member of the family miscible with phenoxy (PEO) coincides with the predicted B minimum value. In the case of our set this value is near zero. This indicates, at least, a qualitative predictive character of the model.

An attempt to obtain negative values for PH/PEO blends by changing the temperature was made. Figure 3 shows the behavior of PH/polyoxide blends at several temperatures, as a function of the CH_2/–O– ratio in the polyoxide. At 95 °C (temperature at which heats of mixing were measured) the model forecasts a miscibility window for CH_2/–O– ratios between 1 and 2, corresponding to poly(methylene oxide) (PMO) and poly(ethylene oxide) (PEO), respectively. Then, the most favorable enthalpy for miscibility corresponds to copolymers of methylene oxide and ethylene oxide. Until now, mixtures of phenoxy and these copolymers have not been reported.

In order to check the evolution of this window with the temperature, we have calculated heats of mixing for the same polymers at 25, 165, and 235 °C. As is shown in

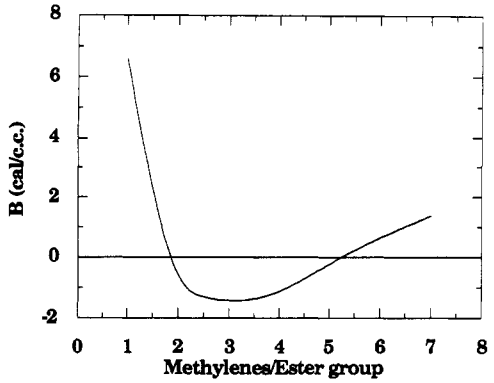


Figure 4. Predicted binary interaction densities at 95 °C for phenoxy blends with aliphatic polyesters having various CH_2/COO ratios in their repeating units, using parameters from this work (Table II).

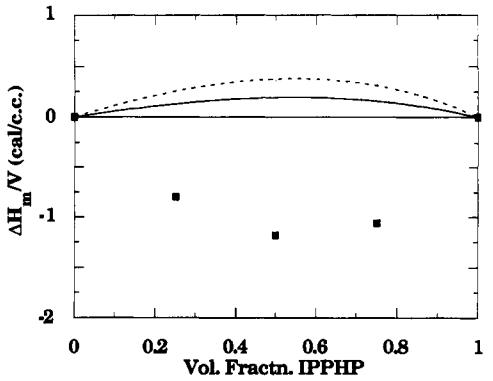


Figure 5. Heats of mixing of IPPHP with DEGDEE at 95 °C: ■, data from Table III; —, estimated by MGQ using parameters from this work (Table II); - - -, estimated from MGQ using parameters from refs 7 and 10.

Figure 3, the curve tends to more negative values with increasing temperature, the minimum shifting slightly toward PMO. This tendency predicts a more miscible system at higher temperatures contrary to the general behavior observed in high molecular weight polymers, that is, the existence of a lower critical solution temperature (LCST). This failure is general for every polymer family studied: polyoxides, aliphatic polyesters, polyacrylates, and polymethacrylates. It can be attributed to the independence of A_{ij} and ΔE_{ij} parameters on temperature, assumed by Lai et al.[7,10] In our opinion, a variation of A_{ij} and ΔE_{ij} with temperature cannot be neglected.

Phenoxy/Aliphatic Polyesters. The curve calculated for this family of blends using our parameters does not differ widely from that evaluated by Lai et al. (see Figure 4) previously mentioned. The miscibility window is predicted for CH_2/COO ratios between 2 and 5 at 95 °C. Miscibility has been experimentally demonstrated with poly(ethylene adipate) (PEA), poly(polybutylene adipate) (PBA), and poly(ϵ-caprolactone) (PCL) with CH_2/COO ratios of 3, 4, and 5, respectively, whereas immiscibility is the rule in the case of poly(ethylene succinate) (PES) and poly(hexamethylene sebacate) (PHS) with CH_2/COO ratios of 2 and 6. A less favorable enthalpy of mixing is predicted for phenoxy/PCL blends than for phenoxy/PES. Therefore in this case the predictive character of the model is only approximate, even qualitatively.

Polymer–Polymer Miscibility Predictions from Heats of Mixing of Model Compounds. Experimental Heats of Mixing of Model Compounds. In order to test the predictions of the model working with our parameter set previously calculated, we have mixed two model compounds containing all the groups present in the mixture of phenoxy and polyoxides. We have chosen a commercialy available product, diethylene glycol diethyl ether (DEGDEE) as a model compound of polyoxides. The model compound of phenoxy: 1,3-bis[4-(-2-propyl)-phenoxy]-2-propanol (IPPHP) was synthesized in our laboratory (see details in the Experimental Section). As is shown in Figure 5, using our parameters, the model predicts an endothermic mixing, but lower than that calculated by using Lai's parameters. These results contrast with the exothermic mixing measured for three compositions (25/75, 50/50, and 75/25 in weight) (see Table III). It seems that this fact cannot be attributed to the parameters used, but to the model. Variations in the surface parameter for the hydroxyl group, due to hydrogen bonding, were explored. A q_m reduction from 0.812 to 0.400 gave heats of mixing near zero, but it was impossible to fit the experimental results changing this parameter value.

Table III
Measured Heats of Mixing Using IPPHP

vol % B	$\Delta H_m/V$, cal/mL
IPPHP + DEGDEE (B)	
28.92	−1.06
54.97	−1.18
78.55	−0.80
IPPHP + Dimethyl Succinate (B)	
49.92	0.486
IPPHP + Diethyl Succinate (B)	
52.97	−0.176
IPPHP + Dimethyl Adipate (B)	
51.15	−0.122
IPPHP + Diethyl Adipate (B)	
51.16	−0.715
IPPHP + Dibutyl Adipate (B)	
49.59	−0.681

In our opinion this disappointing result can be explained by the self-association effect. All parameters affecting the hydroxyl group were calculated using low molecular weight and no sterically hindered alcohols. Both phenoxy and IPPHP have high molecular weight and bulky groups around the hydroxyl group (aromatic rings, isopropyl groups, etc.) which would hinder self-association. Therefore, the energy neccesary to destroy the association should be smaller in this case. This explains why mixtures of cyclohexanol/DEGDEE are endothermic, whereas IPPHP/DEGDEE are exothermic. In order to elude this problem the ability of each molecule to form self-association should be considered. This implies that it is not correct to place all types of alcohols in the same class, due to their different capability to form hydrogen bonds. This also emphasizes the importance of choosing model liquids as similar as possible to the polymers studied.

Attempts to find another parameter set for the CHOH/CH_2O interaction able to fit heats of mixing of IPPHP/DEGDEE were made, but many pairs $A_{ij}/\Delta E_{ij}$ produced in practice the same heat of mixing versus composition curve. An alternative way was to fit experimental enthalpies from mixtures of IPPHP with a series of ethers, rather than only one. Unfortunately, ethers having boiling temperatures above 110 °C and adequate CH_2/–O– ratios were not available. Conversely, this is possible in the case of aliphatic esters.

Therefore, the next step in our work was to mix, in a 50/50 composition, the model compound of phenoxy (IPPHP) with a series of esters having CH_2/COO ratios between 2 and 6. This series of mixtures were endother-

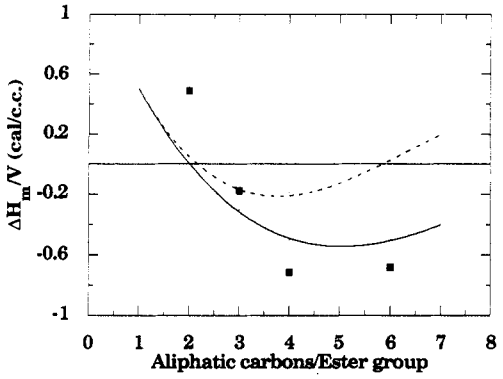


Figure 6. Heats of mixing at 95 °C of IPPHP with esters having various CH_2/COO ratios: ■, data from Table III; —, using parameters from this work (Table II), but A_{ij} = 1000, ΔE_{ij} = 380 cal/mol for the hydroxyl/ester interaction; - - -, using A_{ij} = 2.04, ΔE_{ij} = 326.4 cal/mol (this work as well).

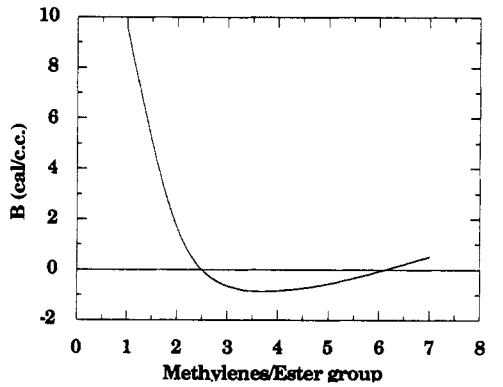


Figure 7. Predicted binary interaction densities at 95 °C for phenoxy blends with aliphatic polyesters having various CH_2/COO ratios in their repeating units, using parameters from this work (Table II), but A_{ij} = 1000, ΔE_{ij} = 380 cal/mol for the hydroxyl/ester interaction.

mic or exothermic depending on the number of aliphatic carbons in the ester (see Table III). The curve predicted by the model using our parameters (basically the same as that of Lai et al.) did not fit experimental results, especially in the cases of diethylene adipate and dibutylene adipate (see Figure 6). Changes were made in the value of parameters A_{ij} and ΔE_{ij} corresponding to the interaction between hydroxyl and ester groups, the others being fixed. It was observed that ΔE_{ij} affects the values of heats of mixing but not significantly the position of the minimum. This position and the shape of the curve were determined by A_{ij}. Values of A_{ij} near 1000 are necessary to fit experimental results. The best parameters found were A_{ij} = 1000 and ΔE_{ij} = 380 cal/mol. It is important to point out that, in this case, no other pairs of parameters could give the same curve.

These A_{ij} values contrast with those calculated by Lai et al.[7,10] and by us with simple liquids. The extreme values of A_{ij} previously used are 0.129 and 14.17. It is necessary to consider that because A_{ij} has an exponential dependence with ΔS_{ij}, the variation in the exchange entropy is much less than the drastic change in A_{ij}. Nevertheless we have not tried to give a physical interpretation of these parameters.

Phenoxy/Linear Aliphatic Polyesters. Surprisingly, the new large parameter values, given above, predict negative enthalpies of mixing for phenoxy with PEA, PBA, and PCL and positive ones with PES and PHS (see Figure 7). These predictions agree perfectly with the experimental miscibility window. This positive result raises our confidence in the predictive character of the model and confirms the validity of our new parameter set.

Table IV
Surface Parameters for Ester Class

type	q_m Lai et al.	q_m this work
C-COO-CH_2	0.880	1.150
C-COO-CH_3	0.880	1.304
CH-COO-CH_2	1.108	1.264
CH-COO-CH_3	1.108	1.418
CH_2-COO-CH_2	1.420	1.420
CH_3-COO-CH	1.728	1.418

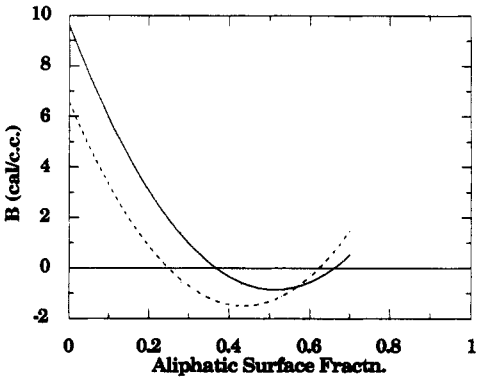


Figure 8. Binary interaction densities for phenoxy blends with polyesters, polyacrylates, and polymethacrylates at 95 °C: —, using parameters from this work (Table II), but A_{ij} = 1000, ΔE_{ij} = 380 cal/mol for the hydroxyl/ester interaction; and - - -, using A_{ij} = 2.04, ΔE_{ij} = 326.4 cal/mol.

Phenoxy/Polyacrylates and Polymethacrylates. The choice of interacting groups made by Lai et al. follows the rules of the UNIQUAC[8] and UNIFAC[19] methods. This allows the placement of the ester group of an aliphatic polyester and that of polyacrylate, polymethacrylate, or poly(vinyl acetate) in the same general class. This simple approximation does not consider the location of the group either in the main chain or in a lateral branch. Accordingly, it is correct to group all these polymers in a "super-family" formed by aliphatic carbons (CH_2) and ester groups (CH_2-COO). However, a comparison based on the number of methylenes per ester group is impossible since there are primary, tertiary, and quaternary carbons next to the ester group in these polymers. In order to compare all of them, we have chosen the fraction area of aliphatic carbons (θ_1) in the polyester as the reference variable. Lai et al.[7,10] have calculated the surface parameter (q_m) of the ester group as formed by the ester itself and the aliphatic carbon next to the carbonyl group. This choice is absolutely arbitrary, and it creates drastic differences between the surface parameters of an ester group next to a quaternary carbon (0.880) and next to a methyl group (1.728) (see Table IV). Transferring this inconsistency to the calculation procedure in the case of polymers we can see that θ_1 values corresponding to two polymers having the same groups in their repeat unit, such as poly(vinyl acetate) (PVAc) and poly(methyl acrylate) (PMA), are 0.308 and 0.556, respectively. Thus, we decided to evaluate q_m of the ester group considering an average of the aliphatic carbons next to the carbonyl and to the oxygen of the ester. Values of q_m calculated using this procedure are shown in Table IV. By using this new criterion, q_m of an ester group placed in an acrylic or methacrylic polymer, has more well-balanced values and both PVAc and PMA have an aliphatic fraction of 0.432.

Figure 8 displays the interaction density coefficient B predicted for this broad family versus the aliphatic surface fraction in the polyester. As is shown, a single curve fits all results for each parameters set. This allows the

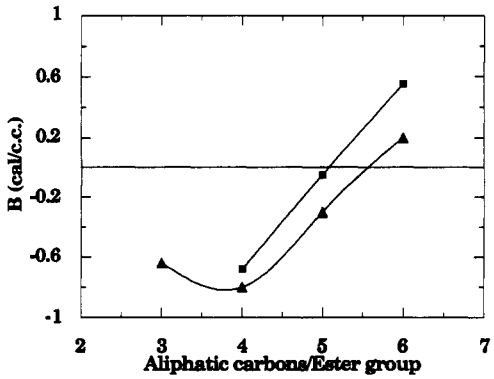


Figure 9. Predicted binary interaction densities at 95 °C for phenoxy blends with polyacrylates (▲) and polymethacrylates (■) having various aliphatic carbons/ester group ratios in their repeating units, using parameters from this work (Table II), but $A_{ij} = 1000$, $\Delta E_{ij} = 380$ cal/mol for the hydroxyl/ester interaction.

comparison of curves calculated using parameters from cyclohexanol and from IPPHP. At first glance, no drastic changes are observed, but it is important to point out the shift in the minimum of q_1 from 0.43 to 0.51. In addition to a superior agreement in the miscibility window of blends with linear aliphatic polyesters, as mentioned above, this shift produces an improvement in the predictive character of the model. The first parameter set locates the more negative values of B in the aliphatic surface fraction corresponding to PVAc or PMA (see Figure 9). With the second set, the minimum coincides with poly(methyl methacrylate) (PMMA) and poly(ethyl acrylate) (PEA). Evidence of miscibility in phenoxy/PMMA blends has been detected in recent tests made in our department by using calorimetry (DSC) and spectroscopy (FTIR and ^{13}C CP-MAS and ^{1}H NMR)[20] and studying mechanical properties.[21] Other authors have reported phase diagrams for this mixture.[22] Up to now no other PH miscible blends have been reported with polyacrylates, polymethacrylates, or PVAc, although difficulties in finding an adequate solvent for phenoxy/PMMA blends allow us to suspect that other miscible pairs are possible.

Conclusions

In this work, four limitations of the MGQ model have been considered. In the first place, parameters which fit heats of mixing of model compounds are not able to reproduce experimental values of B for polymer blends. In our opinion, this is only a consequence of considering B with an exclusively enthalpic character, especially in blends involving strong directional interactions, e.g. hydrogen bonding. Secondly, MGQ does not reflect properly the temperature dependence. In the future, variations of A_{ij} and ΔE_{ij} with temperature or a combination of aspects of MGQ with "equation of state" theories could be attempted in order to predict LCST. Until then, the model should be applied only at the temperature at which parameters have been calculated. Moreover, interacting groups, as well as their surface parameters must be carefully chosen, if a comparison between polymers containing similar but not identical groups is to be made. Lastly, liquids chosen to evaluate parameters have also a large importance. These must be as similar as possible to the polymers studied given that the nature of the contiguous groups, and of the whole molecule, on the parameters assigned to an interacting group impair the predictive character of this model. It is also more convenient to use different pairs of models than to use a single one at different compositions.

However, not all the conclusions are negative. More favorable enthalpies of mixing predicted in a polymer family can be taken as indicative of miscibility. The excellent results in the prediction of PH/PMMA miscibility[22] encourage us to carry out similar studies with other model compound series of polymer families.

Acknowledgment. The authors thank the University of the Basque Country (Project number 203.215-51/88) for the initial financial support of this work, as well as the funds to adquire the flow calorimeter. Further support of the CICYT (Project number MAT89-0187) is also acknowledged. E.E. thanks a Ph.D. grant of the Basque Goverment.

References and Notes

(1) McMaster, L. P. *Macromolecules* **1973**, *6*, 670.

(2) Sanchez, I. C. *Encyclopedia of Physical Science and Technology*; Academic Press: New York, 1987; Vol XI, p 1.

(3) Paul, D. R.; Barlow, J. W. *Polymer* **1984**, *25*, 487.

(4) Ellis, T. S. *Macromolecules* **1989**, *22*, 742.

(5) Guggenheim, E. A. *Proc. R. Soc. London: A* **1944**, *183*, 213.

(6) Guggenheim, E. A. *Mixtures*; Clarendon: Oxford, 1952.

(7) Lai, C. H.; Paul, D. R.; Barlow, J. W. *Macromolecules* **1988**, *21*, 2492.

(8) Abrams, D. S.; Prausnitz, J. M. *AIChE J.* **1975**, *21*, 116.

(9) Panayiotu, C.; Vera, J. H. *Fluid Phase Equilib.* **1980**, *5*, 55.

(10) Lai, C. H.; Paul, D. R.; Barlow, J. W. *Macromolecules* **1989**, *22*, 374.

(11) Harris, J. E.; Goh, S. H.; Paul, D. R.; Barlow, J. W. *J. Appl. Polym. Sci.* **1982**, *27*, 839.

(12) Harris, J. E.; Paul, D. R.; Barlow, J. W. *Polym. Eng. Sci.* **1983**, *23*, 676.

(13) Coleman, M. M.; Moskala, E. J. *Polymer* **1983**, *24*, 251.

(14) Bondi, A. *Physical Properties of molecular crystals, liquids and gases*; Wiley: New York, 1968.

(15) Robeson, L. M.; Hale, W. F.; Merriam, C. N. *Macromolecules* **1981**, *14*, 1644.

(16) Iriarte, M.; Iribarren, J. I.; Etxeberria, A.; Iruin, J. J. *Polymer* **1989**, *30*, 1160.

(17) Fernandez-Berridi, M. J.; Martinez de Ilarduya, A.; Valero, M.; Espi, E.; Iruin, J. J. *Polymer*, to be published.

(18) Suzuki, H.; Grebowitz, J.; Wunderlich, B. *Makromol. Chem.* **1985**, *186*, 1109.

(19) Fredenslund, A.; Rasmussen, P. *Fluid Phase Equilib.* **1985**, *24*, 115.

(20) Iruin, J. J.; Espi, E.; Fernandez-Berridi, M. J.; Valero, M. Reunion Nacional de Materiales Polimericos; Valencia, Spain; Junio 1989.

(21) Erro, R.; Gaztelumendi, M.; Nazabal, J. *New Polym. Mater.*, to be published.

(22) Chiou, J. S.; Paul, D. R. *J. Appl. Polym. Sci.* **1991**, *42*, 279.

Registry No. PH (copolymer), 25068-38-6; IPPHP, 136795-25-0; DEGDEE, 112-36-7; PEO, 25322-68-3; PPO, 25322-69-4; PMO, 9002-81-7; PBO, 25190-06-1; PEA (SRU), 24937-05-1; PEA (copolymer), 24938-37-2; PBA (SRU), 24936-97-8; PBA (copolymer), 25103-87-1; PCL (SRU), 25248-42-4; PCL (homopolymer), 24980-41-4; PES (SRU), 25667-11-2; PES (copolymer), 25569-53-3; PHS (SRU), 26762-10-7; PVAc, 9003-20-7; PHS (copolymer), 26745-88-0; PMA, 9003-21-8; PMMA, 9011-14-7; PEA, 9003-32-1; cyclohexanol, 108-93-0; decane, 124-18-5; ethylbenzene, 100-41-4; methyl phenyl ether, 100-66-3; dimethyl succinate, 106-65-0; diethyl succinate, 123-25-1; dimethyl adipate, 627-93-0; diethyl adipate, 141-28-6; dibutyl adipate, 105-99-7.