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Enthalpies of Mixing in Polymer Blends of Chlorinated Polymers: Application of a Group Contribution Method

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ABSTRACT: A modified Guggenheim quasichemical method (MGQ) has been applied to calculate enthalpies of mixing in mixtures based on chlorinated polymers such as poly(epichlorohydrin) (PECH) or poly(vinyl chloride) (PVC). The required parameters have been determined from experimental heats of mixing in mixtures of model compounds. Using the MGQ method, enthalpies of mixing of PECH/ester containing polymer mixtures and PVC/polyoxide blends have been simulated. In PECH/ester containing polymer blends, the MGQ method gives an adequate picture of the evolution of the miscibility with the polyester CH_2/CH_2COO ratio. Similarly, in PVC/polyoxide blends, the variation of the heat of mixing along the polyoxide family seems to agree with the miscibility window of these blends. However, in PVC/poly(ethylene oxide) blends, the MGQ method was not able to predict accurately the experimentally observed dependence of the miscibility on the composition.

Introduction

Different factors should be taken into account in considering the miscibility of polymer blends. The presence of specific interactions is particularly relevant due to the small contribution of the combinatorial entropy.[1,2] However, other terms such as the noncombinatorial entropy or the free-volume effects can play an important role in the free energy of mixing.[3] In this sense, a magnitude such as the enthalpy of mixing allows us to know more about the nature of the interactions and their role in the miscibility of these systems. Unfortunately, it is not possible to measure accurately enthalpies of mixing in polymer blends.[4] Some alternative ways have been proposed to solve this problem. The use of the Hess cycle[5,6] and the use of mixtures of analogue compounds[7−9] can provide an acceptable approach to the heat of mixing and to the polymer−polymer miscibility.

In this framework, Lai et al.[10] have compared the possibilities of some group contribution methods to quantify thermodynamic magnitudes in mixtures with specific interactions. They have demonstrated the major ability of a modified Guggenheim quasichemical method (MGQ)[11,12] to reproduce the enthalpy of mixing of polar mixtures. Like in any other group contribution method, each molecule has to be divided into some structural groups, and the formation of a contact (i−j) between two different groups (i−i and j−j) is defined through the quasichemical reaction

$$\frac{1}{2}\,\mathrm{i{-}i} + \frac{1}{2}\,\mathrm{j{-}j} \xrightarrow{A_{ij},\ \Delta E_{ij}} \mathrm{i{-}j}$$

where A_{ij} and ΔE_{ij} are the exchange entropy and energy, respectively. In order to generalize the model, it is necessary to define an additional parameter, Γ_{ij}, which takes into account the nonrandomness of the mixture. Γ_{ij} is defined by Panayiotou and Vera[13] as

$$\Gamma_{ij} = \mathrm{N}_{ij}/N_{ij} \qquad (1)$$

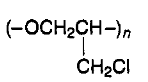
where N_{ij} is the number of i−j contacts in the mixture and N_{ij} has the same meaning but in a totally random mixture.

In a simplified picture of the thermodynamic factors involved in polymer−polymer miscibility, Lai et al.[10] identified the enthalpy of mixing, calculated by this method, with the so-called interaction energy density (B) of the polymer blend,

$$\Delta H_m/V = B\phi_A\phi_B \qquad (2)$$

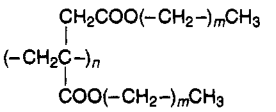
In eq 2 V is the total volume of the mixture and ϕ_i the volume fraction of component i. B is a magnitude directly related to the excess free energy of mixing. In writing eq 2 the combinatorial entropy is neglected as well as other contributions to the free energy of mixing such as free volume or noncombinatorial entropic terms. In spite of some successful results,[10,14,15] this last assumption would probably fail in systems where these other contributions play an important role.[16] A later combination of the MGQ method and the lattice fluid theory had tried to improve the possibilities of the method in predicting phase diagrams.[17] In this work we will restrict the use of the MGQ method to calculations of the enthalpy of mixing.

Along this work, we will study systems containing a chlorinated component as the first component. More specifically, we will consider poly(vinyl chloride) (PVC)/polyoxide blends and poly(epichlorohydrin) (PECH) mixtures in which the second component is an ester-containing polymer such as acrylates, methacrylates, aliphatic esters, and dialkyl itaconates (the repeating units of PECH and itaconates are presented below).



$(-OCH_2CH(CH_2Cl)-)_n$

PECH



$(-CH_2C(CH_2COO(-CH_2-)_mCH_3)(COO(-CH_2-)_mCH_3)-)_n$

poly(itaconates); when $m = 0$; PDMI; $m = 1$; PDEI, ...

We are interested in these systems for several reasons. The polymer−polymer mixture composed of PECH and poly(methyl acrylate) (PMA) is a qualified member of the blend family involving PECH and polyesters, which has been extensively studied by Fernandes et al.[18−20] As far as the PECH/PMA blend is concerned, it has been studied in the literature[18,21,22] and in our laboratory[23] in a wide range of temperatures and compositions. There is an open discussion in the literature about the nature of the interactions relating

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to the α-hydrogen of an alkyl chloride and ester groups.[24-26] This interaction, probably responsible for the stability of these mixtures, seems to be in the border between dipole–dipole and hydrogen bond type interactions.[27]

In PVC/polyoxide blends and, more specifically, in the PVC/PEO blend, a strong dependence of the miscibility on the blend composition has been found.[28-32] Thus, melting point depression (MPD),[28,29,31] CP-MAS RMN,[31] and inverse gas chromatography (IGC)[32] seem to indicate that blends with PEO concentrations higher than 70% (in weight fraction) are immiscible, becoming miscible in the rest of the compositions. Measurements of enthalpies of mixing can help us to understand why these blends show such a strong composition dependence.

Experimental Section

Materials. All the chemical products were supplied by Aldrich and used without further purification. Heats of mixing at 79 ± 0.1 °C were measured in a Setaram C-80D flux type calorimeter with appropriate mixing cells. The experimental temperature was selected to ensure that all the model compounds were in the liquid state and to avoid high vapor pressures in some liquids. Moreover, at that temperature most of the polymer blends discussed in the text would be in the liquid state. Densities, except that of diethylene glycol diethyl ether (DEGDEE),[33] were determined with a pycnometer at the temperature at which heats of mixing were measured.

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

$$\Delta H_m/V = \sum_{i}\sum_{j>i} B_{ij}\theta_i\theta_j - \sum_{k}\sum_{i}\sum_{j>i}\phi^{(k)}B_{ij}{}^{(k)}\theta_i{}^{(k)}\theta_j{}^{(k)} \qquad (3)$$

where $\phi^{(k)}$ is the volume fraction of component k in the mixture and 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

$$\theta_i = q_iN_i/\sum^{j} q_jN_i \qquad (4)$$

where q is a parameter proportional to the group external surface area. It can be calculated according to Abrams and Prausnitz[34] and Bondi.[35] B parameters are defined as

$$B_{ij} = s\Gamma_{ij}\Delta E_{ij}$$

$$B_{ij}{}^{(k)} = s^{(k)}\Gamma_{ij}{}^{(k)}\Delta E_{ij} \qquad (5)$$

where z is the coordination number and s is the number of contact sites per unit volume

$$s = [\sum^{m} zq_mN_m]/V \qquad (6)$$

Previously, for each composition, the nonrandomness parameters, Γ_{ij}, have to be calculated. This estimation was made by the simultaneous resolution of the following equation set

$$\frac{\Gamma_{ij}{}^2\theta_i\theta_j}{(1 - \sum_{j\neq i}\theta_i\Gamma_{ij})(1 - \sum_{i\neq j}\theta_i\Gamma_{ij})} = A_{ij}\exp\{-2\Delta E_{ij}/kT\} \qquad (7)$$

written for every i–j pair in the mixture. The number of contact sites for each component must be conserved

$$\sum_{j}\theta_i\Gamma_{ji} = 1 \qquad (8)$$

The FORTRAN IMSL ZSCNT subroutine was used for this purpose. This set of equations 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 the enthalpy associated to blend formation.

Table 1. Values of Parameters A_{ij} and ΔE_{ij} Taken from the Literature[10,14]

groups i/j	A_{ij}	ΔE_{ij} (cal/mol)
CH_2/CH_2COO	1.000	137.4
CH_2/CH_2O	0.612	70.3
CH_2/CH_2Cl	0.501	88.3
$CH_2/CHCl$	0.752	148.8
CH_2O/CH_2COO	0.700	−46.5
CH_2Cl/CH_2COO	2.110	6.55

All the calculations were made in a MicroVax II computer.

Results and Discussion

Determination of the MGQ Parameters. Before any calculation, the use of the MGQ method requires one to define the structural groups (classes in the author's[10] terminology), in which polymer repeat units are divided. Classes are divided into types (for instance, CH_2Cl and $CHCl$ are two types of the same class). It is assumed that all the members of a class have the same interaction with other groups, sharing the values of the pair A_{ij} and ΔE_{ij}. Different types of a given class differ in the surface offered to the interactions, which is taken into account in the q parameter. In order to calculate enthalpies of mixing, A_{ij} and ΔE_{ij} parameters corresponding to all the possible different pairs involved in a given mixture should be known. Some of these parameters have been previously reported.[10,14] However, in our blends, the values of A_{ij} and ΔE_{ij} corresponding to the CH_2O/CH_2Cl interaction have still not been calculated. Other required parameters are shown in Table 1.

As previously mentioned, the MGQ method permits one to calculate these parameters by the inverse procedure: eq 3 allows us to select the A_{ij} and ΔE_{ij} pair which best fits the experimental heats of mixing of low molecular weight liquids containing the functional groups involved in the unknown interaction. Some authors[16,36] have recommended the use of liquids with chemical structures as close as possible to the corresponding polymer repeat units although this is not a prerequisite in the MGQ formulation. In our mixtures, the CH_2O/CH_2Cl interaction is present in different ways. In PVC/polyoxide blends this interaction has an intermolecular character, while in PECH/polyester blends it is an intramolecular interaction. It seems reasonable to think that the interactions in these systems have to be different, but MGQ does not distinguish them.

Our study started by choosing an ether (DEGDEE) and a chlorinated compound (1,4-dichlorobutane, DClB) and measuring their heats of mixing at several compositions (Table 2) as the best way to determine the required parameters in the MGQ analysis. Initially, a homemade software, which simultaneously used both ZXMWD and ZSCNT subroutines, was employed. Although the program was able to find a pair of $A_{ij}/\Delta E_{ij}$ parameters that accurately fits the experimental data, these values depended slightly on the initial conditions given to the computer. This fact seems to reflect that many $A_{ij}/\Delta E_{ij}$ pairs fit experimental data with similar error. Figure

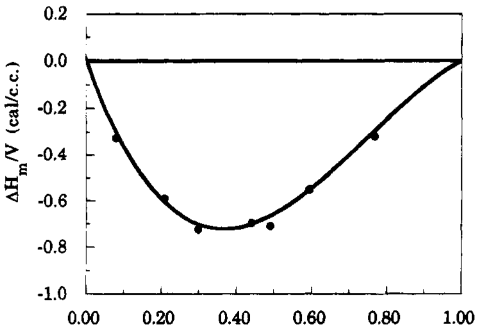

Figure 1. Heats of mixing DClB/DEGDEE blends at 79 °C: (●) experimental data. The line is estimated using the $A_{ij}/\Delta E_{ij}$ pair $A_{ij} = 2.575$ and $\Delta E_{ij} = -23.3$ cal/mol.

Table 2. Experimental Heats of Mixing of 1,4-Dichlorobutane with Ethers (B)

% volume of B	ether	$\Delta H_m/V$ (cal/cm^3)	CH_2/O ratio in B
	DEGDBE		4
0.54*		−0.38	
0.59		−0.41	
0.66		−0.42	
	EGDEE		3
0.44		−0.61	
0.58*		−0.75	
0.74		−0.66	
	DEGDEE		2.67
0.23		−0.32	
0.41		−0.55	
0.51		−0.71	
0.56*		−0.70	
0.70		−0.73	
0.79		−0.59	
0.92		−0.33	
	MEE		2
0.44		−1.20	
0.53*		−1.31	
0.55		−1.28	
0.64		−1.26	
0.74		−1.09	
	DX		2
0.53*		−0.39	
	TX		1
0.50*		1.29	
0.57		1.27	

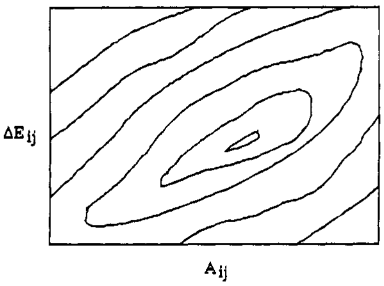

Figure 2. Map method of estimation of the MGQ parameters. Contours of level join pairs of $A_{ij}/\Delta E_{ij}$ parameters with the same value of rms error.

Table 3. Values of A_{ij} and ΔE_{ij} Obtained for the Interaction CH_2O/CH_2Cl from the Different Tested Methods

	A_{ij}	ΔE_{ij}	rms error[c]
DClB/DEGDEE[a]	2.575	−23.3	52
DClB/DEGDEE[b]	3.026	−21.1	49
DClB/Ethers[b]	182	12.6	29
$\Delta H_m/V$ vs CH_2/O ratio	400	19.6	31

[a] Fitted by using the ZXMWD subroutine. [b] Fitted by a map as Figure 2. [c] Error calculated with all the experimental heats of mixing.

1 shows one of these fits with $A_{ij} = 2.57$ and $\Delta E_{ij} = -23.3$ cal/mol.

A better alternative, similar to that used by Lai et al.[10,14] is to use different pairs of analogue compounds with different compositions. For this purpose we measured heats of mixing of DClB with several aliphatic and cyclic ethers such as diethylene glycol dibutyl ether (DEGDBE), ethylene glycol diethyl ether (EGDEE), 2-methoxyethyl ether (MEE), dioxane (DX), and 1,3,5-trioxane (TX). Results are presented in Table 2. Most of the experiments have been done at concentrations near 50/50 in volume, the region where higher thermal effects are expected. The previously cited data of the mixture DClB/DEGDEE have been included in this calculation.

In this case, the computer was not able to find a unique $A_{ij}/\Delta E_{ij}$ pair fitting all the experimental data, even though the interval where it had to look for the pair was changed and narrowed. In some cases, the system was solved but one or more Γ parameters had negative values, with no physical meaning. As a possible alternative, we changed the ZSCNT subroutine by another one based on the classical Newton–Raphson method,[37] but results were similar. We have speculated that, because of the rough changes introduced by the ZXMWD subroutine in the values of A_{ij} and ΔE_{ij}, the ZSCNT subroutine was unable to solve the system of equations giving the nonrandomness parameters. In fact, both ZXMWD and ZSCNT subroutines worked well when they were used independently. For instance, when any values of A_{ij} and ΔE_{ij} were fixed, the solutions of ZSCNT and Newton–Raphson subroutines were always satisfactory.

Another alternative was used to fit experimental data. Given that the ZSCNT subroutine was able to find real values for the Γ parameters when A_{ij} and ΔE_{ij} were fixed, we decided to draw maps where the countour lines join pairs that have the same error of the function to minimize (root mean square (rms) error). This can be seen in Figure 2, where the minimum of rms error is located in the depression of the map and corresponds to the $A_{ij}/\Delta E_{ij}$ pair which best fits experimental data. The method was tested with the data of the DClB/DEGDEE mixture, the values being similar to those previously found using only the ZXMWD subroutine (see Table 3). Using all the heats of mixing summarized in Table 2, the best values obtained with the aid of the above-described procedure were $A_{ij} = 182$ and $\Delta E_{ij} = 12.6$ cal/mol.

Finally, Espi and Iruin,[16] in a paper studying Phenoxy blends, have proposed another alternative way. Using experimental enthalpies of several esters with an analogue compound of the poly(hydroxyether of Bisphenol A, Phenoxy), the authors calculated MGQ parameters by fitting experimental heats of mixing at approximately the same composition in a plot against the CH_2/CH_2COO ratio in the ester compound.

We have enough experimental data to try a similar fitting. For this purpose we have selected heats of mixing measured close to a 0.55 volume fraction in the ether compound (they are marked with an asterisk in Table 2). The results of this attempt are shown in Figure 3. In this figure it can be observed that many different pairs of $A_{ij}/\Delta E_{ij}$ (especially different in the value of the A_{ij} parameter) can reproduce, with similar accuracy, the experimental data, although the $A_{ij}/\Delta E_{ij}$ pair calculated by the map method is within the same

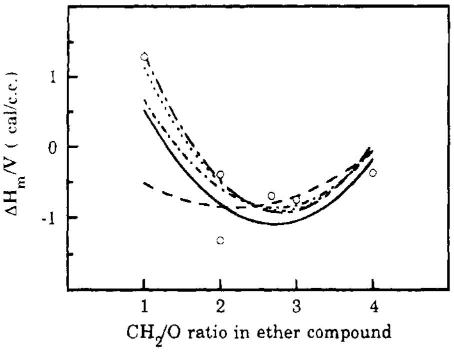

Figure 3. Different $A_{ij}/\Delta E_{ij}$ pairs obtained by the fitting method proposed by Espi and Iruin.[16] The fitted pair obtained with all the experimental (map) data is also given: (O) experimental. (—) A_{ij} = 182, ΔE_{ij} = 12.6 (map); (– –) A_{ij} = 10, ΔE_{ij} = 4.93; (– • –) A_{ij} = 100, ΔE_{ij} = 13.3; (• • •) A_{ij} = 400, ΔE_{ij} = 19.6; (- — -) A_{ij} = 1000, ΔE_{ij} = 22.49.

range of values. Moreover, when the rms error is calculated with all the experimental data, none of the $A_{ij}/\Delta E_{ij}$ pairs obtained by the last fitting method improve the rms error calculated with the pair A_{ij} = 182 and ΔE_{ij} = 12.6 cal/mol.

In conclusion, this pair has been fitted using the largest number of heats of mixing and it has the lowest rms error (see Table 3). Consequently, we will use it in our simulations of the polymer–polymer heat of mixing.

Polymer–Polymer Enthalpies. Now we have all the parameters required to predict enthalpies of mixing of polymer blends by the MGQ method. Additionally, we need polymer repeat unit molecular weights and polymer densities which have been measured in our laboratory[23] or taken from the literature.[38–40] However, before any prediction, a point must be clarified. As it has been previously mentioned, different types of a class group share, in principle, an $A_{ij}/\Delta E_{ij}$ pair, with differences arising from the different surfaces offered to the contact. However, Lai et al.[10] have determined two different pairs to characterize alkyl/alkyl chloride interaction depending on the nature of the second component, i.e., CHCl or CH_2Cl. In Table 1 both parameter pairs are presented and both will be employed in our work: the pair CH_2/CHCl will be used in blends of PVC, whereas the pair CH_2/CH_2Cl will be employed in PECH blends. In a similar way, it would be reasonable to calculate the $A_{ij}/\Delta E_{ij}$ pair both for the CH_2O/CHCl and CH_2O/CH_2Cl pairs, but technical problems in using the required analogue compounds have restricted our analysis to the CH_2O/CH_2Cl pair. In this sense, results concerning PVC blends are more questionable.

Starting with the PECH mixtures, we will predict enthalpies of mixing of PECH with polymers containing an ester group in their repeat unit, as is the case of acrylates, methacrylates, aliphatic esters, and itaconates. Excepting itaconates, the other families of mixtures have been studied by Fernandes et al.[18–20] using glass transition temperatures, phase diagrams, excess volume, and melting point depression measurements in crystalline/amorphous mixtures. The authors found that PECH was miscible with linear polyacrylates until poly(butyl acrylate) which showed a single glass transition temperature only at low PECH compositions.[18] In the case of polymethacrylates, PECH was found to be miscible with methyl, ethyl, propyl, butyl, and cyclohexyl polymethacrylates and partially miscible with poly(isopropyl methacrylate).[19] Finally, aliphatic polyesters with a CH_2/CH_2COO ratio between 3 and 9, both included, were miscible with PECH, the maximum level of the interactions corresponding to PECH/poly(butylene sebacate), with a CH_2/CH_2COO ratio of 6.[20]

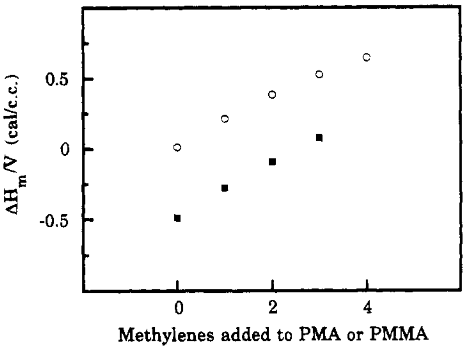

Figure 4. Influence of the CH_2/CH_2COO ratio in the predicted heats of mixing for PECH/polyacrylate (■) and PECH/polymethacrylate (O) mixtures at 50:50 volume fraction and 79 °C.

Table 4. Comparison between the Experimental Miscibility Windows of PECH/Ester-Containing Polymer (exptl) and Blends of These Series for Which the MGQ Method Predicts a Negative Enthalpy of Mixing (MGQ)

	poly-acrylates[a]	poly-methacrylates[a,b]	aliphatic polyesters[c]	poly-itaconates[a]
exptl	1–3	1–4, 6[a]	3–9	not tested
MGQ	1–3	none	1–6	1–4

[a] 1 corresponds to PMA, PMMA, and PDMI, respectively.[18] [b] 6 corresponds to poly(cyclohexyl methacrylate).[19] [c] CH_2/CH_2COO ratio: 1 corresponds to poly(ethylene succinate).[20]

In Figure 4 the enthalpies of mixing of PECH with polyacrylates and polymethacrylates are given against the polyester CH_2/CH_2COO ratio. From this figure, the interactions decrease when the lateral alkyl group is larger, possibly because there are less favorable interactions in the same volume of mixing, as could be expected. Enthalpies of mixing for the polyacrylates are more negative than those for the polymethacrylates although the miscibility window of the last family is larger.[18] This behavior could be related to the donor effect of the methyl group in the α-carbon which increases the carbonyl proton-acceptor nature. This result would reflect the inability of the MGQ method for predicting accurately enthalpies of mixing with the same set of parameters when the present interactions have the same nature but different strength. Therefore, a new $A_{ij}/\Delta E_{ij}$ parameter set would be necessary for the PECH/polymethyacrylates. This conclusion is in agreement with the recommendation cited in the literature,[16,36] according to which it would be better to determine those parameters from experimental data of analogue compounds of the polymer repeat units, although this requirement restricts the original possibilities of the MGQ method.

In Table 4 we have summarized the blends of PECH and ester-containing polymers for which the MGQ method predicts negative enthalpies of mixing at a 50:50 volume fraction composition. Experimental miscibility windows are also summarized. Although both magnitudes are not directly comparable, the MGQ method reproduces adequately the tendency of the interactions in such mixtures, showing that they play an important role in the phase behavior.

Two more comments are needed: First, in the case of aliphatic polyesters the minimum of the enthalpy is slightly shifted to a minor value of the CH_2/CH_2COO ratio.[20] This can be a consequence of either the used

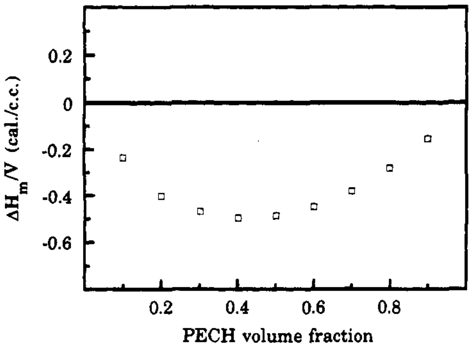

Figure 5. MGQ calculated heats of mixing for PECH/PMA blends at 79 °C.

set of parameters not being sufficiently accurate or the fact that there are a significant weight of other contributions in the free energy of mixing. Second, an interesting result was obtained with the polyitaconates, where the first four members of the family would have negative heats of mixing. If the predictions of the MGQ method are correct, it would be indicative of new miscible polymer blends in this series, although previous experimental attempts with the first two members of the family have not been successful.[41]

Regarding to the PECH/poly(methyl acrylate) (PMA) blend, Figure 5 shows the dependence of the enthalpy of mixing on the composition. The tendency is usually exhibited by the excess magnitudes.

Interaction energy densities (B) of this mixture at two temperatures (76 and 125 °C) have been determined by Al-Saigh and Munk[21] using inverse gas chromatography (IGC). Although the values are subject to large errors, B does not vary appreciably in the considered temperature range, giving an enthalpy of mixing close to zero. Such a difference with the calculated values would imply that other contributions, such as the free volume, can have an important role in the thermodynamic magnitudes of this mixture.[42]

Changing to the PVC/polyoxide mixtures, it is known that the ether group has been classified as a proton-acceptor, while PVC has a proton-donor nature. Moreover, PVC is one of the most common components in polymer blends due to its miscibility with other polymer families. However, PVC/polyoxide blends have not been widely studied in the literature and there are reasonable doubts about the localization of the miscibility window of these pairs. In this sense, data of Margaritis and Kalfoglou using DMA, DSC, and TOA seem to indicate that these blends are very sensitive to the composition, poly(tetramethylene oxide) (PTMO) being the most qualified member to form a miscible blend.[29,30] However, this experimental conclusion must be taken with caution. Recent association models have divided the contributions to miscibility into two terms: the unfavorable one comes from the differences in solubility parameters, whereas the favorable one arises from specific interactions.[27] In this family, the minimum value of the solubility parameter difference corresponds to a CH_2/O polyoxide ratio around 2–3, that is, between PEO and poly(trimethylene oxide) (PTrO).[32] On the other hand, recent results of this laboratory on PVC/PEO blends have shown that the miscibility of this pair has a strong composition dependence, as mentioned above.[31,32]

Values of the heats of mixing of PVC/polyoxide blends are presented in Figure 6. As it can be observed, the MGQ method also predicts the major level of interactions close to the PVC/PEO blend. In this figure we have included not only linear polyoxides but also those with lateral groups such as poly(propylene oxide) (PPO) and poly(butylene oxide) (PBO). Furthermore, the variation of the enthalpies of mixing with the CH_2/O ratio is in agreement with the miscibility window reported before.[32]

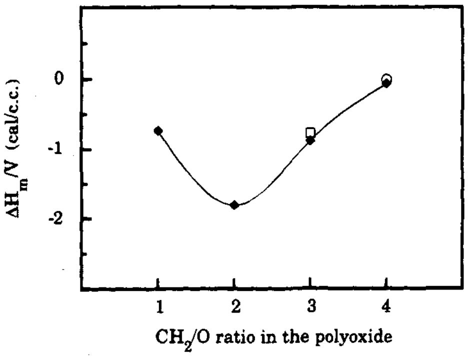

Figure 6. Variation of the heats of mixing for mixtures of PVC and linear polyoxides (◆), PPO (□), and PBO (○) at 50:50 volume fraction and 79 °C.

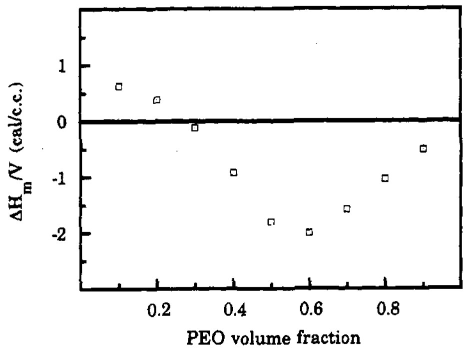

Figure 7. Dependence of the heat of mixing on the composition predicted by the MGQ method for a PVC/PEO blend at 79 °C.

The composition dependence of the enthalpy of mixing of the PVC/PEO blend is shown in Figure 7. In previous papers[28,29,31,32] it has been reported that this blend is only miscible at high PVC compositions, in opposition to the the enthalpy behavior predicted by the MGQ method.

These S-shaped heat of mixing diagrams are rare. They are possible in two cases: First, in mixtures where one or both components are near the critical point[43] and, second, in mixtures where a component self-associates and the other does not but can form specific interactions with the first component.[44–46] In these last systems there are three contributions to the heat of mixing: (1) dispersive forces, (2) the loss of self-association through dilution, and (3) specific interactions between both components. The two first contributions are endothermic, whereas the third one is favorable to exothermic heats of mixing. The S-shaped diagrams are possible, assuming that only the dispersive forces have a parabolic dependence on the composition. Then, at self-associated component high compositions, heats of mixing are exothermic because of the formed favorable interactions between both components of the mixture, while at low concentrations the disrupted self-associated interactions become greater driving to endothermic heat of mixing values. This behavior reflects that these systems are near their phase separation temperature.

Mixtures of ketones with chlorinated compounds have S-shaped heat of mixing diagrams. It is supposed that ketone molecules form strong dipole–dipole interactions with the other component.[44] In chlorinated compound/ether mixtures a similar behavior should be expected. If this assumption is true, in ether-poor concentration mixtures the dipole–dipole disrupt contribution would be more important and endothermic heats of mixing should be expected. However, when the ether compound fraction in the mixture is increased, the new favorable interactions overcome that contribution. Predictions of the MGQ method, shown in Figure 7, are in good agreement with the above comments.

If we restrict our comparison to the 50:50 composition (the more relevant composition), its enthalpy of mixing (-1.81 cal/cm^3) is in reasonable agreement with the change of the interaction energy density (B) with temperature, experimentally determined. When this B parameter is determined by melting point depression[31] and inverse gas chromatography[32] at 66.1 and 100 °C, respectively, its values were -1.27 and -0.115 cal/cm^3. If we suppose that the change is only due to the dependence of the interactions on the temperature, and disregarding the combinatorial entropic term, it would imply an enthalpy of mixing of -3.1 cal/cm^3. Both values are similar considering the assumptions made in both methods. At this point, however, it is necessary to point out again that predictions for this blend can be taken with caution, given the model compounds used to calculate the model parameters.

Summary and Conclusions

Using several ethers and a chlorinated compound, the A_{ij} and ΔE_{ij} parameters required to apply the MGQ method[10,14] have been calculated. They have been used to simulate polymer–polymer enthalpies of mixing in systems where the interaction ether–α-hydrogen of an alkyl chloride is present. Alternative ways to determine those parameters have been tested, the best fitting of experimental heats of mixing being obtained by working with a major number of different experimental data of different model compounds at different compositions.

Enthalpies of mixing for PECH/ester-containing polymer mixtures and PVC/polyoxides have been predicted. First, heats of mixing of PECH with ester-containing polymers reflect adequately the tendency of the interactions along each ester family. The generally small values of the heats of mixing are also a sign of favorable but not very strong interactions.

On the other hand, the calculated enthalpies of mixing for PVC/PEO blends do not reflect accurately the strong dependence of the miscibility on the composition. Considering only the values of the enthalpies at 50:50 composition, the MGQ method reproduces reasonably well the variation of the miscibility along the polyoxide family as well as the variation of the interaction energy density with temperature for the PVC/PEO blend.

Although the method MGQ was conceived to use the same set of parameters for polymer blends containing the same groups, the predictions can be improved by fitting the $A_{ij}/\Delta E_{ij}$ parameters with low molecular weight compounds, reproducing, as close as possible, the chemical structure of the polymer repeating unit. However, this implies the loss of the best advantage of the MGQ method.

Finally, it has been recently shown[47] that the number of specific interactions in high molecular weight polymer mixtures are different from those occurring in mixtures of their low molecule weight analogues. So, in applying the MGQ method to polymer blends with specific interactions, like PVC and polyoxides, this factor has to be considered and some kind of refinement should be introduced.

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