

## COMPATIBILITY RANGE IN POLYMER MIXTURES An approach using analogue calorimetry and group contribution procedures

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### Abstract

The mixing enthalpies of blends of polymethylmethacrylate (PMMA) with poly(styrene-co-acrylonitrile) (SAN) were investigated by analogue calorimetry through the determination of the excess enthalpies of pseudobinary model mixtures corresponding to the addition of methyl-*i*-butyrate to a binary mixture of acetonitrile or propionitrile plus toluene or ethylbenzene.

A group contribution procedure, based on UNIQUAC equation, was also devised and the polymeric mixing enthalpies were calculated from properly defined group contributions. Enthalpies for polymeric interactions were introduced into the Flory–Huggins equation and the miscibility window of PMMA-SAN mixtures was calculated.

The results show a qualitative agreement with the experimental miscibility data and indicate that both the analogue calorimetry and the group contribution procedures yield correct results when acetonitrile, and not propionitrile, is chosen as the model for the polyacrylonitrile repeat unit of the copolymer.

**Keywords:** analogue calorimetry, binary and ternary mixtures, excess enthalpies, group contributions, model compounds, polymer blends

### Introduction

It has been found [1–3] that polymethylmethacrylate (PMMA) is miscible with random poly(styrene-co-acrylonitrile) (SAN), while no miscibility is observed between any pair of the three homopolymers PMMA, polyacrylonitrile (PAN) and polystyrene (PS). Others [4] measured a value of negative mixing enthalpy between PMMA and SAN copolymer with a specific composition. In order to evidence the PMMA-SAN enthalpic behaviour over the whole composition range, in a previous paper [5] we determined the excess enthalpies of two ternary systems made up with small molecules able to mimic these polymeric mixtures. Methyl-*i*-butyrate (MIB) was chosen to simulate the repeat unit of PMMA, while toluene (Tol) and acetonitrile (AN) or, alternatively, ethylbenzene (EB) and propionitrile (PN) were chosen as representative of the styrene and nitrile repeat units, respectively. Accurate measurements of the heats of

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mixing over the whole composition of the ternary mixtures evidenced an interesting phenomenology. In the case of mixtures {methyl-*i*-butyrate(1)+toluene(2)+acetonitrile(3)} negative mixing enthalpies could be obtained when adding MIB to {toluene+acetonitrile} mixtures, over a large range of compositions of the latter binary, although all of the relevant binaries exhibited repulsive interactions, e.g. positive excess enthalpies. The same feature could not be observed in the other ternary system {methyl-*i*-butyrate(1)+ethylbenzene(2)+propionitrile(3)} which in all cases exhibited positive pseudobinary mixing heats even if the molecular structure of EB and PN seems to better mimic the repeat units of the macromolecular chain. Application of some common predictive rules of empirical nature [6] showed that the enthalpy properties of the ternary mixtures could be calculated, in nice agreement with experimental values, using enthalpy data relative to six binary systems involving the model compounds above considered [5].

In order to provide a rationale to this phenomenology, in this work we measured the heats of mixing of the two binary mixtures (ethylbenzene+acetonitrile) and (toluene+propionitrile), necessary to calculate the enthalpy behavior of the two further ternary mixtures {methyl-*i*-butyrate(1)+toluene(2)+propionitrile(3)} and {methyl-*i*-butyrate(1)+ethylbenzene(2)+acetonitrile(3)}, able to simulate the PMMA-SAN polymeric blends. A general criterion is proposed to establish which conditions are to be met in order to observe pseudobinary negative excess enthalpies starting from binaries characterized by positive mixing heats. This corresponds to the existence of concavities of the excess enthalpy in the ternary composition space. A group contribution procedure based on the UNIQUAC equation [7] is also here proposed. A provisional list of group contributions is presented, whose values were calculated from heats of mixing data of numerous binary mixtures taken from the literature or experimentally determined in this work. Use of these contributions permits an easy and fast calculation of the enthalpy of mixing of macromolecular species.

Finally, the Gibbs energies of mixing per unitary volume of PMMA-SAN blends were calculated through the Flory–Huggins equation [8] using interaction enthalpies obtained both from model compounds and group contributions. The corresponding miscibility windows, calculated as a function of the SAN acrylonitrile content, were compared with those experimentally observed by various authors.

## Experimental

### *Calorimetric measurements*

The heats of mixing of the binary systems were measured by means of a Calvet type differential calorimeter Mod. BT-200 from SETARAM (France). This old model has been updated and its performance improved by connecting the output of the thermocouples to a home built high stability DC amplifier with variable gain (50–5000) and interfacing it to a PC using a 16 bit resolution ADAM-4012 analog-to-digital converter. Mixing of the liquids was performed using the flow technique by means of two syringe pumps COLE-PARMER Mod. 74900. The mixing cell, designed and constructed in our labora-

tory, is schematically represented in Fig. 1. Liquids coming from the pumps through the stainless steel capillary tubes, pass first through a heat exchanger (not represented in the figure) in order to attain the same temperature, then they are mixed at the entry of the cell and are forced to flow through a narrow and winding flat groove across a number of gold plated copper plates (Fig. 1, on the right). The volume of the cell is less than 1 cm<sup>3</sup>. The various compositions of the mixtures are obtained by changing the flow ratio of the two pumps while maintaining the total flow almost constant (0.05–0.12 cm<sup>3</sup> min<sup>-1</sup>). The low overall liquid flow, permitted by the high sensitivity of the Calvet apparatus, allowed to use much lower quantities of the reagents as compared with the previously used [1] flow calorimeter. Excess enthalpies  $H^E$  were calculated through the following equation:

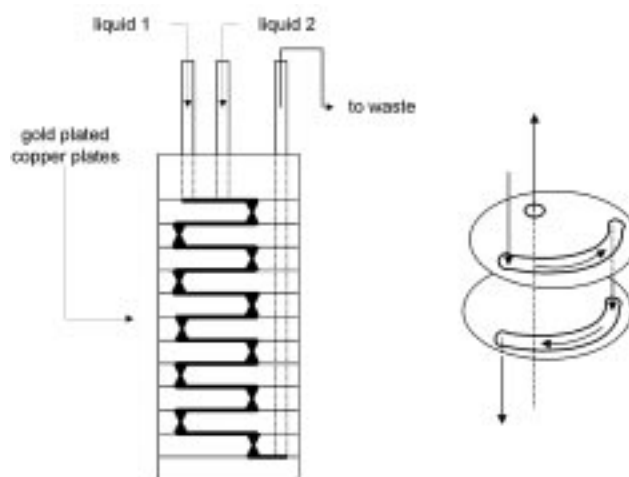
$$H^E = \frac{K_{\text{cal}} S}{\left( \frac{\phi_1 \rho_1}{MW_1} + \frac{\phi_2 \rho_2}{MW_2} \right)} \quad (1)$$

where  $\phi_i$ ,  $\rho_i$  and  $MW_i$  ( $i=1, 2$ ) are the flow rate (cm<sup>3</sup> s<sup>-1</sup>), the density (g cm<sup>-3</sup>) and molecular mass of the liquid  $i$  respectively.  $K_{\text{cal}}$  and  $S$  are, respectively, the calorimeter constant ( $K_{\text{cal}}=3.61 \cdot 10^{-3}$  WV<sup>-1</sup> determined by electrical calibrations at the maximum gain value,  $G=5000$ ) and the stationary signal (V) registered during the mixing run.

Densities  $\rho$  of all examined compounds were measured with an Anton–Paar vibration densimeter Mod. DMA-60 equipped with a cell Mod. DMA-602.

The observed power threshold of the apparatus is about 20  $\mu$ W. The overall precision, given as percent error on mixing heat,  $\Delta Q_{\text{mix}}/Q_{\text{mix}}\%$ , can be calculated with the following relationship:

$$\frac{\Delta Q_{\text{mix}}}{Q_{\text{mix}}}\% = 10(H^E \phi_1)^{-1} + 0.3 \quad (2)$$



**Fig. 1** Home built mixing cell employed for measurements of excess enthalpies with Calvet calorimeter

being  $H^E$  ( $\text{J mol}^{-1}$ ) the value of the excess enthalpy at the examined composition of the mixture and  $\varphi_t$  ( $\text{cm}^3 \text{min}^{-1}$ ) the total flow.

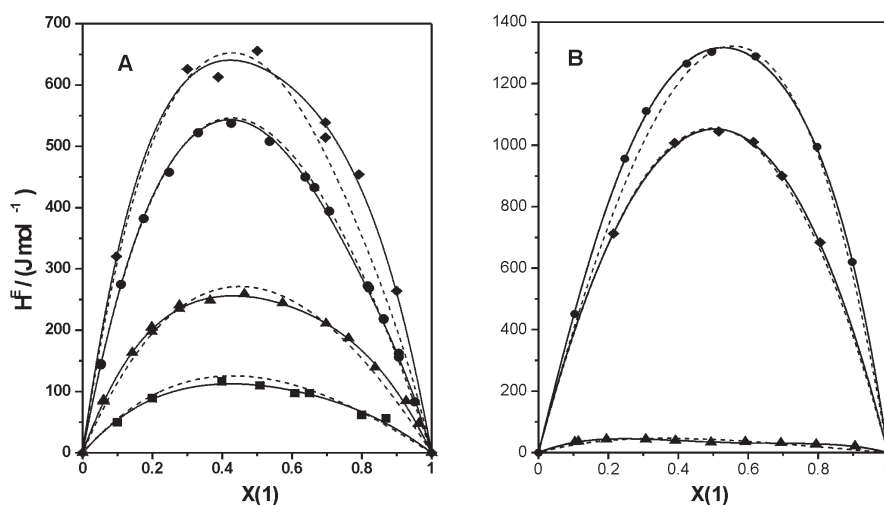
### Materials

The purity and origin of the products was as follows: ethylbenzene (EB) and propionitrile (PN) 99% Aldrich reagents; methyl isobutyrate (MIB) and *n*-dodecane (Dod) 99% Fluka; acetonitrile (AN) 99.8% and *n*-heptane (Hep) 99.5% Carlo Erba; benzene (B) 99.8% and toluene (Tol) 99.9% Baker. All reagents were used without further purification. Their purity was checked by gas-chromatography. The water mass fraction content (Karl–Fischer) was always less than 0.1%. The densities ( $\text{g cm}^{-3}$ ) of the pure compounds at  $T=298.15$  K were: 0.88462 (MIB), 0.77677 (AN), 0.77674 (PN), 0.8737 (B), 0.86223 (Tol), 0.86249 (EB), 0.6840 (Hep), 0.7490 (Dod).

### Results

Experimental values of the excess molar enthalpies,  $H_{ij}^E$ , for binary mixtures considered in this work are reported in Table 1. They were represented by a Redlich–Kister type equation:

$$H_{ij}^E = x_i x_j \sum_{k=1}^K a_k (x_i - x_j)^{k-1} \quad (3)$$



**Fig. 2** Experimental values (points), fitted to Eq. (3) (full lines), and predicted by group contribution method (dashed lines) of the enthalpies of mixing,  $H_{ij}^E$ , for binary mixtures

- A. {Tol(1)+AN(2)} (●), {Tol(1)+PN(2)} (■), {EB(1)+AN(2)} (◆)  
and {EB(1)+PN(2)} (▲)  
B. {MIB(1)+Dod(2)} (●), {MIB(1)+Hep(2)} (◆) and {MIB(1)+B(2)} (▲)

**Table 1** Excess molar enthalpies,  $H_{ij}^E$  (J mol<sup>-1</sup>), of binary mixtures at 298.15 K<sup>a</sup>

$x_1$	$H^E$	$x_1$	$H^E$	$x_1$	$H^E$
MIB(1)+Hep(2)		MIB(1)+Dod(2)		MIB(1)+B(2)	
0.2149	712.1	0.1036	450.8	0.1040	35.5
0.3897	1007.0	0.2468	955.9	0.1143	36.8
0.5156	1044.4	0.3082	1110.8	0.1948	44.2
0.6149	1010.2	0.4243	1265.3	0.3067	42.5
0.6969	900.0	0.4957	1303.2	0.3067	44.0
0.8059	683.3	0.6209	1288.4	0.3922	39.7
		0.7972	994.6	0.4936	34.0
		0.8978	620.1	0.5921	35.8
				0.6937	31.7
				0.7947	26.4
				0.7947	27.5
				0.9063	21.6
				0.9063	20.7
EB(1)+AN(2)		Tol(1)+PN(2)			
0.0969	320.3	0.0996	50.0		
0.3003	625.8	0.1993	89.3		
0.3889	612.9	0.3989	116.6		
0.5004	655.8	0.5079	110.0		
0.6960	514.5	0.6076	97.4		
0.6960	538.9	0.6501	97.2		
0.7914	454.0	0.7993	62.2		
0.8998	263.9	0.8690	56.2		

<sup>a</sup>Mole fractions were calculated from known volumetric flows and the experimental densities

**Table 2** Coefficients  $a_k$  (J mol<sup>-1</sup>) of Eq.(3) and standard deviation of the fit,  $\sigma$  (J mol<sup>-1</sup>)

Binary mixture	$a_1$	$a_2$	$a_3$	$a_4$	$\sigma$
Methyl <i>i</i> -butyrate(1) + <i>n</i> -heptane(2)	4211.00	87.04	233.84	–	6.0
Methyl <i>i</i> -butyrate(1) + <i>n</i> -dodecane(2)	5257.00	458.70	984.66	1167.1	8.6
Methyl <i>i</i> -butyrate(1) + benzene(2)	138.88	–82.67	252.33	–	1.7
Ethylbenzene(1) + acetonitrile(2)	2530.10	–464.50	1218.9	–	17.5
Toluene(1) + propionitrile(2)	443.12	–108.20	119.11	–	4.4

Table 2 reports values of the parameters  $a_k$  and the standard deviation  $\sigma$  of the fit, obtained by solving Eq. (3) through a non-linear least-squares treatment. Fitting functions and experimental data are reported in Fig. 2, together with other data for

relevant binary systems already studied by us [5]. To our knowledge, no data are reported in the literature for the mixtures here considered.

Figure 2 shows that all binaries here examined display positive excess enthalpies. Particularly large  $H^E$  values are observed for mixtures of MIB with aliphatic hydrocarbons, with larger effects associated to longer hydrocarbon chains, while very low values with benzene (Fig. 2A). In the mixtures of nitriles with aromatic hydrocarbons (Fig. 2B) the larger positive enthalpies are exhibited by mixtures containing the smaller nitrile, again with larger effects associated to the larger hydrocarbon. These positive effects are probably to be attributed to the breaking of polar interactions in the neat nitriles.

Excess molar enthalpies,  $H_{123}^E$ , of the ternary mixtures of our interest can be calculated through proper combinations of triplets of binary data (i.e. Redlich–Kister–Muggianu procedure [9]) through the equation:

$$H_{123}^E = \sum_{i=1}^2 \sum_{j=i+1}^3 H_{ij}^E \quad (4)$$

where  $H_{ij}^E$  are the excess properties of the relevant binaries, obtained through Eq. (3) using mole fractions of the ternary mixture. Manipulation of ternary excess data given by Eq. (4) allows then to calculate mixing enthalpies of proper pseudobinary mixtures chosen such as to mimic polymeric blends of our interest (see next section).

### Miscibility of polymeric blends

It is well known that the formation of a homogeneous mixture between two polymers is determined by the trend of the Gibbs mixing energy,  $\Delta G_{\text{mix}}$ , as a function of composition. Particularly, the following conditions need to be met:

$$\Delta G_{\text{mix}} < 0 \quad \text{and} \quad \left( \frac{\partial^2 \Delta G_{\text{mix}}}{\partial x^2} \right)_{T,P} > 0 \quad (5)$$

Following the Flory–Huggins theory [8], the quantity  $\Delta G_{\text{mix}}$  of a binary polymeric mixture can be calculated as:

$$\frac{\Delta G_{\text{mix}}}{RTV_{\text{mix}}} = \frac{\Delta H_{\text{mix}}}{RTV_{\text{mix}}} + \left[ \frac{\phi_1 \ln \phi_1}{V_1 N_1} + \frac{\phi_2 \ln \phi_2}{V_2 N_2} \right] \quad (6)$$

where  $V_i$ ,  $\phi_i$  and  $N_i$  are the molar volume, volume fraction and polymerization degree of component  $i$ , respectively.  $V_{\text{mix}}$  is the molar volume of the mixture and  $\Delta H_{\text{mix}}$  its mixing enthalpy. The two terms of the right hand side of Eq. (6) are the enthalpic and the entropic (combinatorial) contributions to the Gibbs energy of mixing per unit volume, respectively. Estimates of the enthalpy term can be realized according to the following procedures.

*Analogue calorimetry*

The enthalpy term of Eq. (6),  $\Delta H_{\text{mix}}$ , can be estimated from the excess enthalpies of model molecules of the repeat units of the polymers, following the procedure of analogue calorimetry [10].

The mixing enthalpy of the system here investigated, polymethylmethacrylate plus poly(styrene-co-acrylonitrile) (PMMA-SAN), can be estimated from the mixing enthalpies of ternary mixtures obtained by adding methyl-*i*-butyrate (MIB) used as a model for PMMA, to binary mixtures of an aromatic hydrocarbon and a nitrile. Using toluene (Tol) or ethylbenzene (EB) as model compounds for the styrenic units of SAN, while acetonitrile (AN) or propionitrile (PN) for the nitrilic units, the PMMA-SAN blends can be simulated by the following four ternary mixtures: MIB(1)+Tol(2)+AN(3) (I), MIB(1)+EB(2)+PN(3) (II), MIB(1)+Tol(2)+PN(3) (III) and MIB(1)+EB(2)+AN(3) (IV). Excess enthalpies of ternaries I and IV have been experimentally measured [5]. Those of ternaries II and III can be estimated through empirical or semiempirical procedures which make use of the mixing enthalpies of the relevant binaries. It was in fact demonstrated that enthalpy data thus calculated for ternary mixtures made up with these compounds are in good agreement with experimental data [5]. Excess enthalpies  $H_{\text{ps}}^{\text{E}}$  of pseudobinary mixtures obtained by adding MIB to binary mixtures of an aromatic hydrocarbon plus a nitrile, calculated from the excess enthalpies of the above four ternary systems, can therefore be considered a reasonable estimate for the enthalpy of mixing of PMMA with SAN. Negative values of  $H_{\text{ps}}^{\text{E}}$  are thus indicative of favorable conditions for the formation of a blend between these polymers.

A general rule for blend miscibility can be formulated as follows.

If one applies the Redlich–Kister–Muggianu [9] symmetrical rule (Eq. (4)), the excess enthalpies of a ternary system,  $H_{123}^{\text{E}}$ , can be expressed as a function of the molar fraction of component 1 (MIB in the present case) and of the ratio  $R=x_3/x_2$  of the molar fractions of the other components, through the following relationship:

$$H_{123}^{\text{E}} = \frac{x_1(1-x_1)}{R+1}(A_{12}+RA_{13}) + \frac{(1-x_1)^2 RA_{23}}{(R+1)^2} \quad (7)$$

where the quantities  $A_{ij}$  ( $i, j=1, 2, 3$  with  $j>i$ ) are the polynomials of the Redlich–Kister equation (Eq. (3)), i.e.

$$A_{ij} = \sum_{k=1}^4 a_k (x_i - x_j)^{k-1} \quad (8)$$

The excess enthalpies,  $H_{\text{ps}}^{\text{E}}$ , of the various pseudobinary mixtures  $\{x_1(1)+(1-x_1)[x_2(2)+x_3(3)]\}$  can then be obtained through

$$H_{\text{ps}}^{\text{E}} = H_{123}^{\text{E}} - \frac{(1-x_1)RA_{23}}{(R+1)^2} \quad (9)$$

By introducing expression (7) into Eq. (9) one obtains

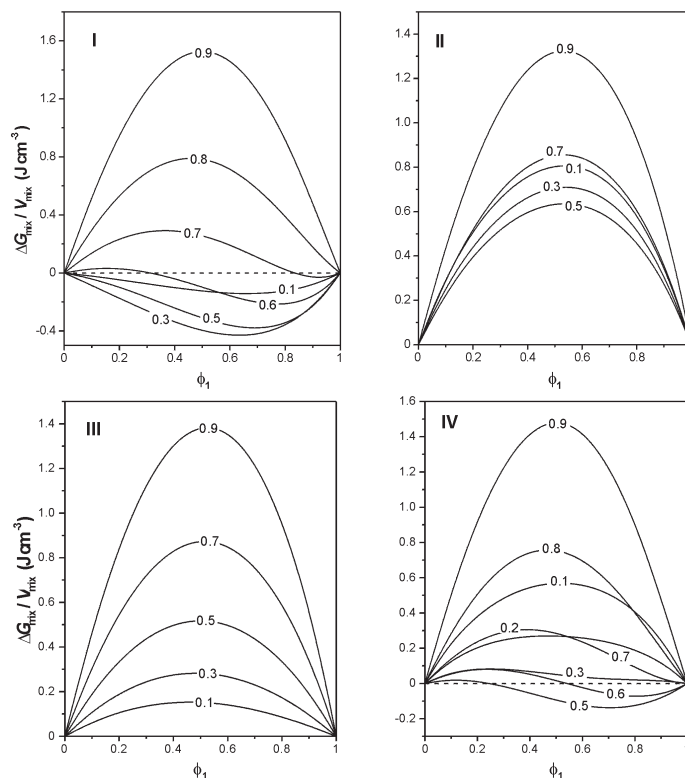
$$H_{ps}^E = \frac{x_1(1-x_1)}{(R+1)}Z \quad (10)$$

where the factor  $Z$  has the form

$$Z = \left[ (A_{12} + RA_{13}) - \frac{R}{R+1}A_{23} \right] \quad (11)$$

It is thus obvious from Eq. (10) that exothermic values of  $H_{ps}^E$  can only be obtained when  $Z$  values, calculated from Eq. (11), result negative. A practical criterion to search for the presence of negative  $H_{ps}^E$  values, valid only for nearly symmetric binary mixtures, is expressed by the condition

$$Z^* = \left( H_{12}^{E*} + \frac{x_3}{1-x_3} H_{13}^{E*} \right) - x_3 H_{23}^{E*} < 0 \quad (12)$$



**Fig. 3** Mixing Gibbs energies per unit volume ( $\Delta G_{\text{mix}}/V_{\text{mix}}$ ) obtained using pseudo-binary excess enthalpies  $H_{ps}^E$  calculated by Eq. (6) for the addition of MIB(1) to binary mixtures ( $x_2+x_3=1$ ) of {Tol(2)+AN(3)} (I), {EB(2)+PN(3)} (II), {Tol(2)+PN(3)} (III), and {EB(2)+AN(3)} (IV) with different binary compositions. Numbers quoted inside the figures represent  $x_3$



where  $H_{ij}^{E*}$  are the values of the excess enthalpies of binaries  $i-j$  at  $x_i=0.5$  and  $x_3$  is the molar fraction of component 3 in the ((2)+(3)) binary.

Finally, if  $H_{ps}^E$  values calculated through Eq. (10) are substituted for  $\Delta H_{\text{mix}}$  of Eq. (6), the latter equation allows to calculate the Gibbs energy  $\Delta G_{\text{mix}}$  of any polymeric mixture using a proper model system. In the calculation of the combinatorial term an average polymerisation degree  $N_i=500$  was used.

Figure 3 shows the trend of the property  $\Delta G_{\text{mix}}/V_{\text{mix}}$  as a function of the molar fraction of component 1 (MIB) for different compositions of the binary ((2)+(3)) as it is reproduced from the four model systems here adopted. Table 3 reports values of  $Z$  and  $Z^*$  as a function of the composition of the ((2)+(3)) binary mixtures. Negative values of  $Z^*$ , related to the miscibility window, clearly parallel corresponding negative values of  $Z$ , thus indicating the reliability of the approximate criterion above proposed (Eq. (12)). This is very useful since, in principle, it requires the knowledge of only one experimental value of the mixing enthalpy (at  $x_i=x_j$ ) for each of the relevant  $i-j$  binary mixtures.

**Table 3** Values of  $Z$ , Eq. (11), and  $Z^*$ , Eq. (12), calculated at  $x_i=0.5$ , for ternary mixtures I {MIB(1)+Tol(2)+AN(3)} and IV {MIB(1)+EB(2)+AN(3)}<sup>a</sup>

$x_3$	Ternary system			
	I		IV	
	$Z$	$Z^*$	$Z$	$Z^*$
0.1	-63	-17	293	70
0.2	-166	-42	151	34
0.3	-248	-60	29	5
0.4	-294	-66	-62	-13
0.5	-280	-53	-95	-11
0.6	-152	-8	-17	22
0.7	219	103	298	121
0.8	1221	375	383	1239
0.9	1333	4807	1324	4758

<sup>a</sup>In the case of ternaries II and III (see text) values of  $Z^*$  and  $Z$  are always positive

#### Group contribution method (modified UNIQUAC)

Enthalpy properties of real macromolecules and their mixtures can be estimated following a general group contribution procedure which allows to construct a large number of polymeric species through a limited number of molecular segments (groups). This procedure should take advantage from the fact it eliminates the possibly critical choice of the model compounds and permits to construct the real structure of the repeat unit of the polymers.

The UNIQUAC equation for excess energy  $U^E$  of molecular systems [7] can be easily transformed into an analogous expression for the calculation of the enthalpy of

a mixture of molecular segments (conventional groups), following the same criterion used for deriving the UNIFAC model for Gibbs energy [11].

For present procedure we made use of the following form of the UNIQUAC equation for a mixture containing  $c$  compounds and  $n$  groups:

$$\frac{\Delta H_{\text{mix}}}{R} = \sum_{j=1}^n Q_j x_j \left[ \frac{\sum_{i=1}^m Q_i x_i \delta_{ij} \exp\left(\frac{-\alpha_{ij} \delta_{ij}}{T}\right)}{\sum_{i=1}^m Q_i x_i \exp\left(\frac{-\alpha_{ij} \delta_{ij}}{T}\right)} \right] - \sum_{k=1}^c x_k \sum_{j=1}^n Q_j x_j^{(k)} \left[ \frac{\sum_{i=1}^m Q_i x_j^{(k)} \delta_{ij} \exp\left(\frac{-\alpha_{ij} \delta_{ij}}{T}\right)}{\sum_{i=1}^m Q_i x_j^{(k)} \exp\left(\frac{-\alpha_{ij} \delta_{ij}}{T}\right)} \right] \quad (13)$$

where  $Q_i$  and  $x_i$  are the conventional surface area and molar fractions of the  $i$  group in the mixture, and  $x_i^{(k)}$  and  $x_k$  are the molar fractions of the  $i$  group in the pure compound  $k$  and of compound  $k$  in the mixture, respectively. Parameters  $\delta_{ij}$  (expressed in Kelvin) represent the group contributions, and are a measure of the interactions between the various groups present in the system under study. The coefficients  $\alpha_{ij}$  ( $\alpha_{ij} = \alpha_{ji} = \alpha$ ) have been introduced to make a few interactions more specific through modification of the exponential term which determines the local composition.

Molar fractions  $x_i$  and  $x_i^{(k)}$  can be calculated through the following relationships:

$$x_i = \frac{\sum_k x_k v_{i,k}}{\sum_k x_k \sum_m v_{m,k}} \quad x_i^{(k)} = \frac{v_{k,i}}{\sum_i v_{k,i}} \quad (14)$$

where  $v_{ik}$  is the number of  $i$  groups in the compound  $k$ . The second term on the right hand side of Eq. (13) is necessary to fulfill the condition of a null  $\Delta H_{\text{mix}}$  value for all pure compounds.

Use of Eq. (13) requires to determine the values of  $\delta_{ij}$  and  $\alpha_{ij}$  parameters for the interactions of a series of groups necessary to build up the most important macromolecular chains. Unfortunately, it is not possible to use the known UNIFAC values [12] since the latter are valid for Gibbs energy. A few attempts to calculate enthalpy contributions through the Gibbs–Helmholtz equation

$$\left[ \frac{\partial(G^E/T)}{\partial(1/T)} \right]_{P,x} = H^E \quad (15)$$

applied to a recent UNIFAC data base [13] able to describe the Gibbs energy as a function of temperature, were unsuccessful. Unsatisfactory results were also obtained when using UNIFAC contributions for enthalpy given by Dang and Tassios [14]. The use of

**Table 4** Values of group contributions,  $\delta_{ij}$ , for use in Eq. (3)

Groups	$Q_i$	$CH_x$	COO	ACH	AC(CH <sub>3</sub> )	AC(CH <sub>2</sub> )	CN(CH <sub>3</sub> )	CN(CH <sub>2</sub> )
CH <sub>3</sub>	0.848							
CH <sub>2</sub>	0.540	0	500	110	110	110	410	420
CH	0.228							
$\alpha^a$			-0.5				0.5	0.5
COO	2.10	180	0	-46.5	15.3	330	27.5	29.5
ACH	0.40	53	71.5	0	0	0	65	120
$\alpha$							1.35 <sup>b</sup>	
AC(CH <sub>3</sub> )	0.12	50	220	0	0	0	50	-390
AC(CH <sub>2</sub> )	0.40	50	95	0	0	0	220	-120
CN(CH <sub>3</sub> )	1.5 <sup>c</sup>	220	8.5	250	50	150	0	0
$\alpha$				1.35 <sup>b</sup>				
CN(CH <sub>2</sub> )	1.6 <sup>c</sup>	250	8.5	120	-35	-45	0	0

<sup>a</sup> $\alpha = \alpha_{ij} = \alpha_{ji}$  Eq. (13). Quoted  $\alpha$  values are to be used only when the  $CH_x$  group belongs to a paraffin. In all other cases  $\alpha = 1$

<sup>b</sup>The value of  $\alpha_{ij} = 1.35$  has to be used only for mixtures of acetonitrile with benzene. In all other cases  $\alpha = 1$

<sup>c</sup> $Q_i = 2$  when  $CN(CH_x)$  interacts with paraffins

UNIQUAC equation for identifying group contributions appropriate for macromolecules was already faced a few years ago by Lai *et al.* [15]. However, the results were not considered satisfactory by the authors themselves. Addition of the  $\alpha_{ij}$  parameter into Eq. (13) aims to obtaining better results.

**Table 5** Binary mixtures employed for calculation of group contributions to excess enthalpies (see Table 4)

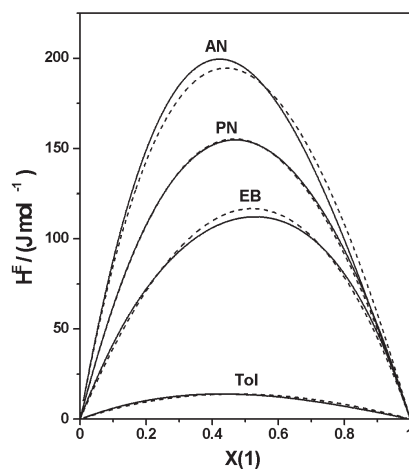
Binary mixture	$\sigma$ (J mol <sup>-1</sup> ) <sup>a</sup>	Ref.
Methyl isobutyrate + <i>n</i> -heptane	6.0	b
Methyl isobutyrate + <i>n</i> -dodecane	8.6	b
Methyl isobutyrate + benzene	1.7	b
Acetonitrile + ethylbenzene	17.5	b
Propionitrile + toluene	4.4	b
Acetonitrile + methyl isobutyrate	1.5	[5]
Acetonitrile + toluene	3.2	[5]
Methyl isobutyrate + toluene	2.1	[5]
Propionitrile + methyl isobutyrate	3.4	[5]
Propionitrile + ethylbenzene	3.8	[5]
Methyl isobutyrate + ethylbenzene	2.2	[5]
Ethyl isobutyrate + methyl isobutyrate	0.8	[15]
<i>n</i> -hexane + propionitrile	6.9	[16]
<i>n</i> -butyronitrile + <i>n</i> -dodecane	9.3	[16]
Propionitrile + <i>n</i> -heptane	6.2	[16]
Propionitrile + <i>n</i> -butyronitrile	1.7	[17]
Benzene + cyclohexane	1.3	[18]
Benzene + acetonitrile	2.5	[19]
Acetonitrile + 1,4-dimethylbenzene	2.1	[19]

<sup>a</sup>Standard deviation; <sup>b</sup>This work

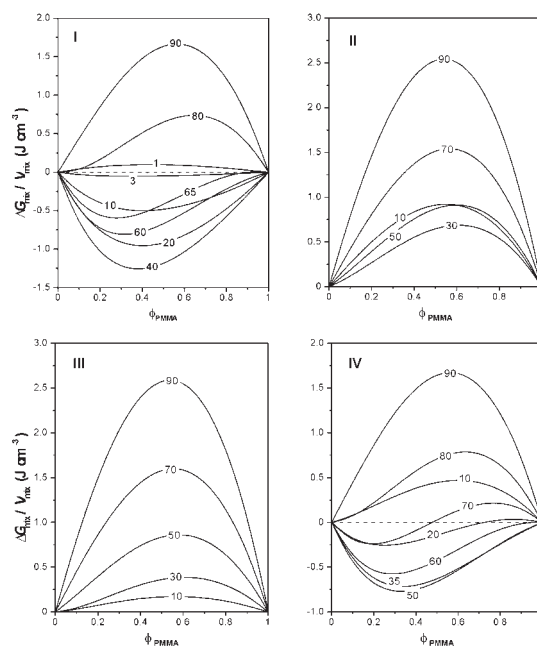
A series of group contributions  $\delta_{ij}$  and coefficients  $\alpha_{ij}$  have been determined by fitting Eq. (13) to experimental excess enthalpies of a series of binary mixtures. Values of these contributions are reported in Table 4, while Table 5 lists all the mixtures from which they were derived.

As a further modification to the original procedure the CN group has been defined as a separate group, with its contribution value depending on the nature of the adjacent hydrocarbon group. Furthermore, this group was assigned a slightly different  $Q_1$  value which better fits mixing enthalpies of the relevant mixtures of Table 5.  $Q_1$  values of all other groups are those reported in the UNIFAC tables [12].

Values of parameters reported in Table 4 are obviously to be considered as provisional. Refinement of these values, using a more extended data base supported by calorimetric measurements on further binary systems, is in progress.



**Fig. 4** Excess enthalpies,  $H_{ij}^E$ , fitted to Eq. (3) (full lines) and predicted by group contribution method (dashed lines) for binary mixtures of MIB(1) with Tol, EB, AN and PN. Experimental data from [5]



**Fig. 5** Mixing Gibbs energies per unit volume ( $\Delta G_{\text{mix}}/V_{\text{mix}}$ ) obtained using  $\Delta H_{\text{mix}}$  values calculated with group contribution method (Eq. (13)) for different PMMA-SAN blends, as a function of PMMA volume fraction ( $\phi$ ). Numbers in the figures represent acrylonitrile content (mass%) in the copolymer. Cases (I)–(IV) refer to the use of different contributions for AC (aromatic carbon), and CN (nitrile) groups: AC(CH<sub>3</sub>) and CN(CH<sub>3</sub>) (I); AC(CH<sub>2</sub>) and CN(CH<sub>2</sub>) (II); AC(CH<sub>3</sub>) and CN(CH<sub>2</sub>) (III); AC(CH<sub>2</sub>) and CN(CH<sub>3</sub>) (IV)

The excess enthalpies of binary mixtures measured in this work are compared with the corresponding values calculated with present group contribution procedure in Fig. 2. The analogous comparison for pertinent binary mixtures studied in our previous work [5] is presented in Fig. 4. The nice agreement with experimental data found for binary mixtures containing hydrocarbons (Fig. 2), when compared with the lack of agreement found for analogous systems by others [15] clearly indicates the improvements obtained by introducing the modifications of present procedure. Figure 5 finally compares the trend of the function  $\Delta G_{\text{mix}}/V_{\text{mix}}$  obtained via Eq. (6) using for  $\Delta H_{\text{mix}}$  the  $H_{\text{ps}}^{\text{E}}$  values of the pseudobinary mixtures calculated from group contributions.

## Discussion

The trend of the function  $\Delta G_{\text{mix}}/V_{\text{mix}}$  calculated using values of pseudobinary enthalpy,  $H_{\text{ps}}^{\text{E}}$ , according to different model systems is represented in Fig. 3 for different compositions of the binary ((2)+(3)). The plots indicate that only ternary systems containing acetonitrile display regions of composition characterized by negative values of Gibbs energy. The analogous data obtained through group contributions (Fig. 5) show a similar trend, again displaying a miscibility window only when  $\text{CN}(\text{CH}_3)$  is used as the nitrile group contribution.

If we compare the results obtained through the predictive calculation with experimental data, we can make the following considerations:

1. The miscibility of homopolymers with copolymers, as already observed by others [20], is greatly conditioned by the different extent of repulsive energies between pairs of repeat units as compared when they are separate groups inside different model compounds. Attenuation of the repulsion between components 2 and 3, following addition of component 1, takes place when the binary interaction energies, represented by terms  $A_{ij}$ , fulfill the following condition:  $A_{23} > A_{12}/x_3 + A_{13}/(1-x_3)$ . The composition range where attenuation takes place will be wider the larger is the above inequality.

2. Model molecules more appropriate to simulate the real behaviour of a blend should preferentially be the simplest ones which contain the relevant pendant group of the polymer. This can be understood in view of the fact that the hydrocarbon residues which are part of the macromolecular chain lose most of their degrees of freedom and thus give a much lower contribution to the overall interactions. Others [21] suggested that the proper model compound should have a solubility parameter  $\delta$  the most similar to that of the corresponding polymeric system. Our choice of model compounds for the poly(styrene-co-acrylonitrile), acetonitrile or propionitrile to mimic the polyacrylonitrile repeat unit and toluene or ethylbenzene to mimic the polystyrene unit, indicates that acetonitrile should be preferred over propionitrile while toluene and ethylbenzene work equally well:  $\delta=24.1 \text{ (MPa)}^{1/2}$  for AN and  $22.1 \text{ (MPa)}^{1/2}$  for PN against  $25.6 \text{ (MPa)}^{1/2}$  of PAN;  $18.2 \text{ (MPa)}^{1/2}$  for Tol and  $18.0 \text{ (MPa)}^{1/2}$  for EB against  $18.4 \text{ (MPa)}^{1/2}$  of PS [22]. Therefore, in the case of blends here considered, both criteria suggest acetonitrile as a better choice compared with propionitrile.

**Table 6** Miscibility window for the polymeric system PMMA/SAN at 298.15 K

	System	Miscibility window (acrylonitrile mass% in SAN)		Method	Ref.
		Lower limit	Upper limit		
Experimental	PMMA–SAN	8.9–9.4	34.4–36.9	Light scattering blends cast from CHCl <sub>3</sub>	[1]
	PMMA–SAN	8–12.9	37.0–39.3	Refractive index blends cast from MEK	[2]
	PMMA–SAN	6.3–9.5	28	Refractive index blends cast from THF	[3]
Calculated from model compounds <sup>a</sup>	{MIB+Tol+AN }	2	49	$H^E$ data of ternary system	[5]
	{MIB +EB+AN}	21	44	Combination of binary $H^E$ data	c
Calculated from group contributions <sup>b</sup>	PMMA–SAN	3	70	Using AC(CH <sub>3</sub> ) and CN(CH <sub>3</sub> )	c
	PMMA–SAN	17	68	Using AC(CH <sub>2</sub> ) and CN(CH <sub>3</sub> )	c

<sup>a</sup>No miscibility window was found when PN was used as a model compound<sup>b</sup>No miscibility window was found when CN(CH<sub>2</sub>) value was used as parameter for the CN group<sup>c</sup>This work

3. Results obtained with model molecules and group contributions based on UNIQUAC procedure are only qualitative. The miscibility window calculated for different acetonitrile contents in the copolymer results rather larger than observed experimentally (Table 6).

Finally, we tested the capability of our group contribution method to account for the specific behaviour of the macromolecule structure. Taking as the reference the miscibility window (3% to 70%) calculated using the AC(CH<sub>3</sub>) contribution value (Table 6), we checked the response of the mixing free energy to the following modifications:

a) Decrease of the number of interactions between the pendant groups and the main chain of the macromolecule. This was accomplished through the decrease of the surface area  $Q_i$  of CH and CH<sub>2</sub> groups which determines, coupled with the coordination number  $z$ , the number of the nearest neighbours to the main chain .

b) Change of the temperature value and consequent change of the coordination number, according to the equation proposed by Dang and Tassios [14]. This change ( $z=7$  at 373 K;  $z=14$  at 220 K) causes a modest change on local composition, while a marked change of the number of nearest neighbours and thus of the number of interactions between polymeric species.

The modification of point 'a' was suggested from the fact that the repeat units are bound to each other in the real polymer, and thus not free to move independently as the model molecules. A 50% decrease of the surface area shifts the upper miscibility limit from 70 to 65% of acrylonitrile content. A zero surface area shifts this limit to 53%. No appreciable change is observed in the 3% lower limit.

The modification of point 'b' should instead take care of the different physical state of the real system, amorphous solid, as compared to the liquid model. A temperature change from 298 to 220 K (a temperature value at which the liquid may turn to amorphous solid) causes an increase of the lower limit from 3 to 14%, and a decrease of the upper limit to 66%. A contrary effect is obviously observed for increasing temperature.

It is our hope that this phenomenon can be observed in other polymeric blends, so as to suggest possible correction factors which enable the group contributions, calculated from small molecules, to be more correctly applied to real mixtures of macromolecules.

\* \* \*

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