

## **EXCESS MOLAR ENTHALPIES OF THE TERNARY SYSTEMS (ACETONITRILE+METHYL ISOBUTYRATE+TOLUENE) AND (PROPIONITRILE+METHYL ISOBUTYRATE+ETHYLBENZENE) AT 298.15 K**

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### **Abstract**

Excess molar enthalpies were measured at 298.15 K with a flow calorimeter built in our laboratory for the two ternary systems (acetonitrile+methyl isobutyrate+toluene) and (propionitrile+methyl isobutyrate+ethylbenzene). Experimental data were nicely predicted by some empirical and semi-empirical procedures, exception made for UNIFAC group contribution method. The latter equation proved unsatisfactory for all mixtures containing methyl isobutyrate. The first ternary set proved a good model system to simulate mixing enthalpies reported in the literature for mixtures of poly(styrene-co-acrylonitrile) with polymethylmethacrylate.

**Keywords:** analogue calorimetry, excess enthalpies, mixtures, model compounds, polymer blends

### **Introduction**

In previous papers [1–3] we have determined the excess thermodynamic properties ( $G^E$ ,  $H^E$ ,  $V^E$ ,  $C_p^E$ ) of a number of multicomponent mixtures made up with compounds of different polarity and proticity. Aim of the research was to investigate the possibility of predicting these properties through application of empirical and semiempirical procedures which make use only of experimental data relative to the pertinent binary mixtures.

Application of the upper strategy to mixtures of compounds which can mimic the interactions between polymeric molecules might be useful to make predictions about the thermodynamic properties of polymeric blends, which certainly deserve a large interest in modern technology. Examples exist in the literature of such an approach [4–9], but generally authors do not examine the behavior of the mixtures involved over the whole composition range. For instance, Pfennig *et al.* [9] found that the addition of methyl isobutyrate to proper binary mixtures of (acetonitrile+toluene) is accompanied by an exothermic effect which parallels the negative enthalpy of mixing of polymethylmethacrylate (PMMA) with a poly(styrene-co-acrylonitrile) [10], while polyacrylonitrile and

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polystyrene homopolymers are completely immiscible with PMMA. The possibility of predicting mixing enthalpies of polymers might be particularly useful in view of the dominant contribution of this property to the Gibbs energy of polymer mixing [11] and thus of the possible prediction of their mutual solubility.

In the present work we determined the excess molar enthalpies,  $H^E$ , of mixtures of small molecules which might be of interest for the above polymers: acetonitrile (ACN), propionitrile (PrCN), toluene (Tol), ethylbenzene (EtBz) and methyl isobutyrate (MiB). We choose to examine the ternary systems (ACN+MiB+Tol) (set A) and (PrCN+MiB+EtBz) (set B) and measured their  $H^E$  values over the whole concentration space, including the relevant binary mixtures. The main aim of the work was to examine the possibility of predicting the enthalpic behavior of the ternary mixtures from the corresponding data of the simpler binary mixtures. Secondly, we wanted to check whether the experimental observation made by Pfennig *et al.* [9] at a single specific composition is consistent with the behavior over the whole composition range.

Experimental data of the ternary mixtures were generally nicely reproduced by binary data using both empirical and semiempirical methods. As the empirical procedures of mixing binary data we adopted those summarized by Pando *et al.* [12] and Lopez *et al.* [13]. As the semiempirical procedures we adopted Wang [14] and UNIQUAC [15] equations. We also used the UNIFAC group contribution method [16], which proved unable to reproduce acceptably the  $H^E$  data of all binary mixtures involving methyl isobutyrate.

## Experimental

Excess enthalpies were measured by means of a flow calorimeter and an experimental procedure already described [17, 18]. Experimental uncertainty was estimated as  $\pm(0.2+0.005H^E)$  J mol<sup>-1</sup>.

The distribution of the measured experimental data over the ternary composition space is shown in Fig. 1. Almost all of the measurements have been realized by adding methyl isobutyrate to preformed mixtures of the other two components. The densities of the latter mixtures and those of the pure components at  $T=298.15$  K were measured with an Anton–Paar vibrating-tube densimeter DMA-60 equipped with a cell DMA602.

The purity and origin of the products was as follows: MiB, EtBz and PrCN 99% Aldrich reagents; ACN 99.8% Carlo Erba; 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%.

## Results

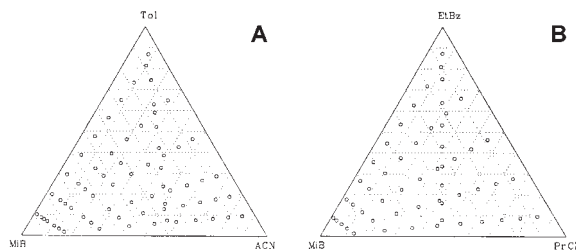
Experimental values of the excess molar enthalpies,  $H^E$ , for binary mixtures considered in this work are reported in Table 1. They were represented by a Redlich–Kister type equation:

$$H_{ij}^E = x_i x_j \sum_{k=1}^{k=5} A_k (x_i - x_j)^{k-1} \quad (1)$$

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

$x_1$	$H^E$	$x_1$	$H^E$	$x_2$	$H^E$
ACN(1)-MiB(2)		ACN(1)-Tol(3)		MiB(2)-Tol(3)	
0.1953	98.4	0.0482	83.2	0.0933	10.0
0.3532	159.5	0.0940	162.3	0.1879	11.7
0.4835	192.1	0.0940	156.2	0.2840	12.3
0.5929	201.7	0.1377	217.9	0.3816	10.7
0.6860	189.1	0.1377	218.7	0.3816	11.2
0.7662	165.7	0.1794	268.7	0.3816	14.8
0.8360	131.4	0.1835	272.3	0.4807	14.9
0.8973	89.8	0.2937	394.1	0.4807	14.1
0.9516	44.1	0.3358	432.6	0.5813	13.0
		0.3621	449.9	0.6835	11.1
		0.4643	508.1	0.6835	8.8
		0.5742	537.6	0.7874	7.6
		0.6691	522.3	0.7874	10.4
		0.7521	457.7	0.8928	3.6
		0.8251	382.0		
		0.8900	274.8		
		0.9479	145.6		
		0.9479	143.5		
PrCN(1)-MiB(2)		PrCN(1)-EtBz(3)		MiB(2)-EtBz(3)	
0.0366	13.8	0.0373	47.2	0.1059	41.7
0.0721	36.8	0.0735	84.7	0.2105	78.4
0.1532	75.3	0.1617	139.4	0.3136	94.3
0.1532	79.0	0.2382	187.0	0.4155	106.5
0.2359	110.9	0.3025	211.0	0.5160	113.6
0.2359	110.6	0.4266	244.4	0.6153	108.8
0.2893	121.4	0.5364	259.0	0.7133	100.6
0.2893	119.3	0.6345	248.6	0.8101	76.5
0.4110	143.0	0.7225	240.8	0.9056	47.3
0.5205	154.3	0.7225	234.6		
0.6195	152.1	0.8020	205.5		
0.6195	151.3	0.8020	204.3		
0.7095	135.3	0.8020	197.7		
0.7916	113.3	0.8576	163.5		
0.8669	79.8	0.9398	84.3		
0.9361	38.1	0.9398	86.6		
		0.9398	83.7		

<sup>a</sup>Molar fractions were calculated from known volumetric flows and the experimental densities (g cm<sup>-3</sup>): ACN (0.77677), MiB (0.88462), Tol (0.86223), PrCN (0.77674), EtBz (0.86249)



**Fig. 1** Distribution of experimental  $H^E$  data over the composition space of ternary systems A (acetonitrile+methyl isobutyrate+toluene) and B (propionitrile+methyl isobutyrate+ethylbenzene)

Table 2 reports values of the parameters  $A_k$  and the standard deviation  $\sigma$  of the fit, obtained by solving Eq. (1) through a non-linear least-squares treatment. Fitting functions and experimental data are reported in Fig. 2. To our knowledge, the only complete binary data reported in the literature are those on the mixtures acetonitrile-toluene [19, 20] and methyl isobutyrate-ethylbenzene [21]. Concerning the first system, the data by Di Cave *et al.* [19] are in very good agreement with ours, while those by Li *et al.* [20] are about 8% larger (Fig. 2). A slightly worse agreement is observed for the second system, since the data by Greenhill *et al.* result about 20% smaller than ours.

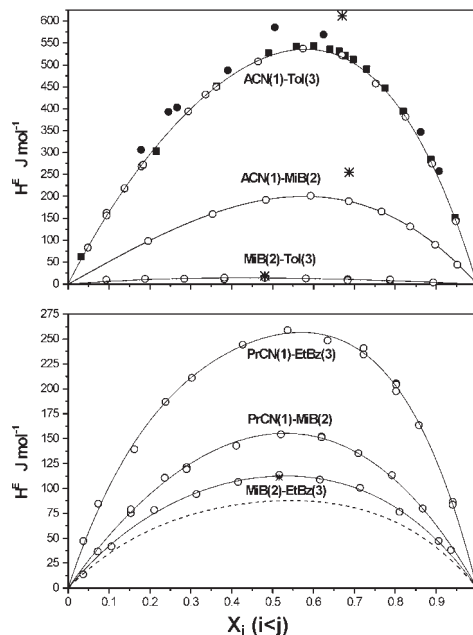
**Table 2** Coefficients  $A_k$  ( $\text{J mol}^{-1}$ ) of Eq. (1) and standard deviation of the fit,  $\sigma$  ( $\text{J mol}^{-1}$ )

Binary mixture	$A_1$	$A_2$	$A_3$	$\sigma$
Acetonitrile(1)+methyl isobutyrate(2)	780.59	261.41	–	1.5
Acetonitrile(1)+toluene(3)	2092.1	613.30	355.66	3.2
Methyl isobutyrate(2)+toluene(3)	54.809	–16.714	–	2.1
Propionitrile(1)+methyl isobutyrate(2)	619.03	72.375	37.399	3.4
Propionitrile(1)+ethylbenzene(3)	1013.1	185.70	411.22	3.8
Methylisobutyrate(2)+ethylbenzene(3)	448.67	45.105	85.447	2.2

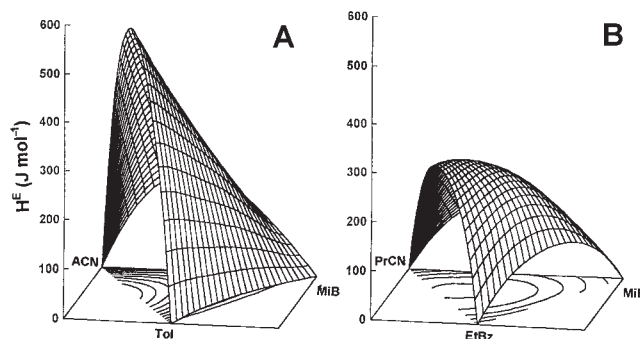
Excess molar enthalpies,  $H^E$ , of the ternary mixtures  $\{\text{ACN}(1)+\text{MiB}(2)+\text{Tol}(3)\}$  (set A) and  $\{\text{PrCN}(1)+\text{MiB}(2)+\text{EtBz}(3)\}$  (set B) are reported in Tables 3 and 4, respectively. Values of the observed pseudobinary excess enthalpies,  $H_{\text{obs}}^E$ , are also given for convenience.  $H^E$  values were fitted to the polynomial equation:

$$H_{123}^E = x_1 x_2 x_3 \sum_{m=0}^3 \sum_{n=0}^m B_{mn} x_1^{m-n} x_2^n + \sum_{i=1}^2 \sum_{j=i+1}^3 H_{ij}^E \quad (2)$$

where  $H_{ij}^E$  are the corresponding binary excess properties obtained through Eq. (1) using mole fractions of the ternary mixture. The optimal values of the parameters  $B_{mn}$  and standard deviations  $\sigma$  of the fit are reported in Table 5.



**Fig. 2** Molar excess enthalpies of the binary mixtures : (—) calculated from Eq. (1) using  $A_k$  coefficients of Table 2; (---) [21]; (o) exptl. data from this work; (\*) [6]; full symbols:  $H^E$  data for binary ACN(1)-Tol(3), (■) [19] and (●) [20]



**Fig. 3** Molar excess enthalpies for the ternary systems A and B.  $H^E$  surfaces were calculated through Eq. (2) using parameters of Tables 2 and 5

A graphical representation of the calculated excess quantities over the whole composition domain is given in Fig. 3. The curves on the triangle base represent contour lines at constant values of  $H^E$ .

**Table 3** Experimental pseudobinary molar enthalpies,  $H_{\text{obs}}^{\text{E}}$  ( $\text{J mol}^{-1}$ ), and excess molar enthalpies,  $H^{\text{E}}$  ( $\text{J mol}^{-1}$ ), of the ternary system ACN(1)-MiB(2)-Tol(3) at 298.15 K<sup>a</sup>

$x_1$	$x_2$	$H_{\text{obs}}^{\text{E b}}$	$H^{\text{E}}$	$x_1$	$x_2$	$H_{\text{obs}}^{\text{E b}}$	$H^{\text{E}}$
$x_1=0.2953$ $d=0.8497$ $H_{13}^{\text{E}}=395.5$				$x_1=0.8984$ $d=0.7929$ $H_{13}^{\text{E}}=253.2$			
0.2716	0.0803	-6.9	356.8	0.8507	0.0531	25.6	268.2
0.2716	0.0803	-10.8	352.9	0.7977	0.1121	45.7	273.2
0.2468	0.1642	-17.6	313.0	0.7385	0.1780	67.3	277.9
0.2209	0.2519	-28.2	267.7	0.6721	0.2519	81.4	273.1
0.1938	0.3437	-35.3	224.3	0.5969	0.3356	92.8	263.0
0.1938	0.3437	-37.3	222.3	0.5111	0.4311	91.9	237.7
0.1654	0.4399	-40.0	181.5	0.5111	0.4311	90.8	236.6
0.1356	0.5409	-41.5	140.1	0.4124	0.5410	86.4	204.0
0.1356	0.5409	-43.6	138.0	0.4124	0.5410	83.7	201.3
0.1042	0.6470	-45.5	94.1	0.2974	0.6689	68.5	153.3
0.0713	0.7586	-41.9	53.6	0.2974	0.6689	69.3	154.1
0.0366	0.8761	-25.0	24.0	0.1620	0.8197	39.7	85.9
0.0366	0.8761	-26.5	22.5				
$x_1=0.1075$ $d=0.8586$ $H_{13}^{\text{E}}=175.6$				$x_1=0.8000$ $d=0.8062$ $H_{13}^{\text{E}}=414.1$			
0.0980	0.0885	-1.4	158.7	0.7539	0.0577	10.3	400.5
0.0882	0.1794	-1.1	143.0	0.7032	0.1210	17.6	381.6
0.0782	0.2726	-9.9	117.8	0.6472	0.1910	23.8	358.8
0.0679	0.3682	-14.5	96.4	0.5851	0.2686	28.5	331.4
0.0574	0.4665	-18.0	75.7	0.5158	0.3552	27.1	294.1
0.0465	0.5674	-18.6	57.4	0.4381	0.4524	27.9	254.7
0.0354	0.6710	-17.9	39.9	0.3501	0.5624	20.5	201.7
0.0239	0.7776	-18.0	21.1	0.2497	0.6878	13.7	143.0
0.0121	0.8872	-12.5	7.3	0.1343	0.8322	4.4	73.9
$x_1=0.5006$ $d=0.8360$ $H_{13}^{\text{E}}=523.2$				$x_1=0.3942$ $d=0.8437$ $H_{13}^{\text{E}}=472.4$			
0.4650	0.0712	-8.3	477.6	0.2267	0.4250	-42.6	229.0
0.4270	0.1471	-18.6	427.6	0.1869	0.5258	-49.4	174.6
0.3864	0.2282	-23.7	380.1	0.1447	0.6330	-50.2	123.2
0.3429	0.3150	-35.7	322.7	0.0996	0.7473	-43.9	75.5
0.2963	0.4082	-41.1	268.5	0.0515	0.8693	-29.5	32.2
0.2460	0.5085	-44.5	212.7				
0.1918	0.6168	-43.9	156.6				
0.1332	0.7340	-41.2	98.0				
0.0695	0.8613	-31.5	41.1				

**Table 3** Continued

$x_1$	$x_2$	$H_{\text{obs}}^{\text{E b}}$	$H^{\text{E}}$	$x_1$	$x_2$	$H_{\text{obs}}^{\text{E b}}$	$H^{\text{E}}$
$x_1=0.6943 \quad d=0.8183 \quad H_{13}^{\text{E}}=506.0$				$x_1=0.6002 \quad d=0.8429 \quad H_{12}^{\text{E}}=199.9$			
0.6509	0.0625	-2.3	472.1	0.5555	0.3698	79.8	264.8
0.6038	0.1304	-11.4	428.6	0.5080	0.3383	144.9	314.1
0.5523	0.2045	-10.6	391.9	0.4577	0.3048	192.4	344.8
0.5523	0.2045	-16.2	386.3	0.4044	0.2693	227.3	362.0
0.4960	0.2857	-17.1	344.3	0.3477	0.2315	244.9	360.7
0.4960	0.2857	-11.3	350.1	0.2872	0.1913	242.1	337.8
0.4340	0.3750	-14.1	302.2	0.2227	0.1483	219.7	293.9
0.4340	0.3750	-19.7	296.6	0.1537	0.1023	177.4	228.6
0.3655	0.4736	-18.7	247.7	0.0796	0.0530	108.7	135.2
0.2893	0.5833	-21.9	189.0				
0.2042	0.7058	-26.0	122.9				
0.1085	0.8437	-23.9	55.2				

<sup>a</sup>Measurements performed by successive additions of pure MiB to a binary ACN-Tol, except for the last set of data where Tol was added to an ACN-MiB mixture. For each set of data the composition, density ( $\text{g cm}^{-3}$ ) and excess molar enthalpy ( $\text{J mol}^{-1}$ ) of the starting binary is given

<sup>b</sup>Experimentally observed molar enthalpy ( $H_{ij}^{\text{E}}=0$  for the starting binary)

**Table 4** Experimental pseudobinary molar enthalpies,  $H_{\text{obs}}^{\text{E}}$  ( $\text{J mol}^{-1}$ ), and excess molar enthalpies,  $H^{\text{E}}$  ( $\text{J mol}^{-1}$ ), of the ternary system PrCN(1)-MiB(2)-EtBz(3) at 298.15 K<sup>a</sup>

$x_1$	$x_2$	$H_{\text{obs}}^{\text{E b}}$	$H^{\text{E}}$	$x_1$	$x_2$	$H_{\text{obs}}^{\text{E b}}$	$H^{\text{E}}$
$x_1=0.2720 \quad d=0.8495 \quad H_{13}^{\text{E}}=200.8$				$x_1=0.7007 \quad d=0.8151 \quad H_{13}^{\text{E}}=242.0$			
0.2463	0.0947	34.4	216.2	0.6469	0.0768	27.1	250.5
0.2202	0.1904	59.3	221.9	0.5903	0.1575	48.1	252.0
0.1938	0.2874	77.3	220.4	0.5307	0.2427	63.0	246.3
0.1938	0.2874	79.6	222.7	0.4676	0.3327	73.3	234.8
0.1672	0.3855	84.5	207.9	0.4009	0.4278	78.2	216.7
0.1401	0.4848	86.8	190.3	0.3303	0.5287	75.4	189.5
0.1128	0.5853	81.3	164.6	0.2553	0.6357	69.7	157.9
0.0851	0.6871	69.6	132.4	0.1756	0.7494	57.4	118.0
0.0571	0.7901	49.1	91.2	0.0906	0.8707	35.0	66.3
0.0287	0.8944	26.8	48.0				

**Table 4** Continued

$x_1$	$x_2$	$H_{\text{obs}}^{\text{E b}}$	$H^{\text{E}}$	$x_1$	$x_2$	$H_{\text{obs}}^{\text{E b}}$	$H^{\text{E}}$
$x_1=0.4941 \quad d=0.8340 \quad H_{13}^{\text{E}}=252.7$				$x_1=0.8983 \quad d=0.7916 \quad H_{13}^{\text{E}}=129.9$			
0.4519	0.0854	25.1	256.2	0.8369	0.0683	30.8	151.8
0.4083	0.1736	53.4	262.2	0.7711	0.1416	59.1	170.6
0.3633	0.2648	70.2	256.0	0.7003	0.2204	80.2	181.5
0.3167	0.3591	86.1	248.1	0.6239	0.3054	97.0	187.2
0.3167	0.3591	85.9	247.9	0.5413	0.3974	106.0	184.3
0.2685	0.4567	82.2	219.5	0.4515	0.4973	105.9	171.2
0.2186	0.5577	77.3	189.1	0.3538	0.6061	100.0	151.2
0.1669	0.6623	71.2	156.5	0.2469	0.7251	84.9	120.6
0.1133	0.7707	46.6	104.5	0.1295	0.8558	61.1	79.8
0.0577	0.8832	28.6	58.1	0.1295	0.8558	53.8	72.5
$x_1=0.0989 \quad d=0.8584 \quad H_{13}^{\text{E}}=100.6$				$x_1=0.4962 \quad d=0.8448 \quad H_{12}^{\text{E}}=154.6$			
0.0889	0.1018	45.4	135.8	0.4577	0.4647	40.4	183.0
0.0788	0.2032	75.1	155.3	0.4172	0.4236	87.5	217.5
0.0689	0.3042	92.3	162.3	0.3746	0.3803	118.7	235.4
0.0589	0.4048	102.2	162.1	0.3297	0.3348	137.4	240.1
0.0490	0.5050	99.1	148.9	0.2823	0.2866	153.0	241.0
0.0391	0.6048	95.1	134.9	0.2323	0.2358	154.6	227.0
0.0293	0.7042	78.7	108.5	0.1793	0.1820	142.5	198.4
0.0195	0.8032	60.2	80.0	0.1231	0.1250	118.9	157.3
0.0097	0.9018	31.7	41.6	0.0635	0.0644	78.3	98.1

<sup>a</sup>Measurements performed by successive additions of pure MiB to a binary PrCN-EtBz, except for the last set of data where EtBz was added to a PrCN-MiB mixture. For each set of data the composition, density ( $\text{g cm}^{-3}$ ) and excess molar enthalpy ( $\text{J mol}^{-1}$ ) of the starting binary is given

<sup>b</sup>Experimentally observed excess molar enthalpy ( $H_{ij}^{\text{E}}=0$  for the starting binary)

**Table 5** Ternary coefficients  $B_{mn} \cdot 10^{-3}$  ( $\text{J mol}^{-1}$ ) of Eq. (2)

	ACN(1)+MiB(2)+Tol(3)	PrCN(1)+MiB(2)+EtBz(3)
$B_{00}$	0.6930	2.3623
$B_{10}$	–	–16.806
$B_{11}$	–9.0232	–
$B_{20}$	–9.0350	34.272
$B_{21}$	20.069	24.997
$B_{22}$	19.592	–4.3024
$B_{30}$	8.7454	–19.757
$B_{31}$	–11.173	–38.405
$B_{32}$	–23.243	–8.1318
$B_{33}$	–13.606	–
$\sigma$ ( $\text{J mol}^{-1}$ )	2.7	3.4



## Discussion

All mixtures examined here display positive values of excess enthalpies (Fig. 3). These mixtures appear therefore always destabilized, from an enthalpic point of view, with respect to the pure compounds. The less stabilized mixtures are those involving interactions between the nitriles and the aromatic hydrocarbons, probably owing to the destruction of the favourable self-interactions of the nitriles (dipolar) and the aromatic ring (stacking). Practically ideal behavior is instead exhibited by mixtures of methyl isobutyrate with toluene.

The excess enthalpy data of the ternary mixtures were nicely predicted by empirical rules which properly combine the  $H^E$  data of corresponding binary systems. We adopted methods by Redlich–Kister–Muggianu, Kohler, Lakhanpal, Colinet, Mathieson–Thynne, Toop, Tsao–Smith, Hillert, Scatchard and Knobloch–Schwartz. The relative equations can be found in [12] and [13]. The chosen procedures, except for Knobloch–Schwartz, are able to reproduce the experimental data with a root mean square deviation, *rmsd*, of about  $10 \text{ J mol}^{-1}$ . No significant *rmsd* difference was displayed by unsymmetrical procedures when changing the numbering of the components.

We also applied semiempirical equations such as Wang [14] and UNIQUAC [15], as well as the Modified UNIFAC group contribution method [16]. The last procedure gave satisfactory results only for binary mixtures acetonitrile+toluene and propionitrile+ethylbenzene. Predicted  $H^E$  values of mixtures of the nitriles with methyl isobutyrate were four times larger in the case of acetonitrile and about half for propionitrile. Mixtures of methyl isobutyrate with the benzene derivatives were predicted as exothermic. The interaction parameters of the UNIFAC Data Bank [16] involving the ester group are probably altered by steric or/and inductive effects in the case of methyl isobutyrate.

Table 6 reports molecular parameters of UNIQUAC and Wang procedures as well as the parameters obtained by fitting to these models the experimental data of the binary mixtures. These equations are able to reproduce experimental  $H^E$  data of the mixtures of both ternary sets within acceptable error limits. The *rmsd* value calculated for the ternary ACN-MiB-Tol was  $19 \text{ J mol}^{-1}$  for UNIQUAC and  $20 \text{ J mol}^{-1}$  for Wang equations, while the analogous values in the case of mixtures PrCN-MiB-EtBz were  $16 \text{ J mol}^{-1}$  and  $6 \text{ J mol}^{-1}$ , respectively.

The fact that several predictive procedures based on binary data, independently of their empirical or semiempirical nature, all predict within acceptable accuracy (less than 5% of the maximum value observed) the data of the different ternary mixtures here examined, indicates that probably the enthalpic behavior of mixtures made up with these or analogous compounds (same functional groups) is mainly governed by a statistical distribution of binary interactions. The enthalpy data of analogous complex mixtures might thus be confidently predicted with no needs of collecting laborious experimental data over the whole composition range.

The  $H^E$  data of present ternary systems could also be used to predict enthalpies of mixing of polymeric molecules containing analogous chemical structures. It has been found that poly(styrene-co-acrylonitrile) (SAN), containing 38.3% moles of

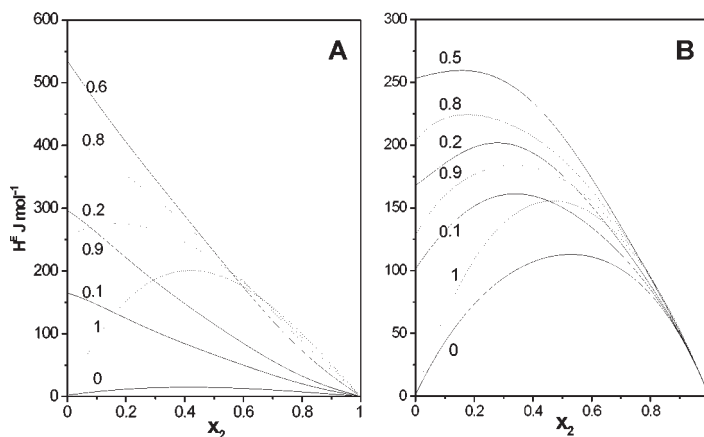
**Table 6** Parameters used in the UNIQUAC and Wang models for  $H^E$ 

Mixture	$i, j$	UNIQUAC <sup>a</sup>		Wang <sup>b</sup>		
		$\delta_{ij}$	$\sigma^c$	$\alpha$	$\Delta\epsilon_{ij}$	$\sigma^c$
Acetonitrile(1) + methyl isobutyrate(2)	1,2	0.002449	3.1	0.360825	-240.990	2.9
	2,1	0.136729			297.847	
Acetonitrile(1) + toluene(3)	1,3	0.243821	6.2	-8.08450	144.987	4.2
	3,1	0.200371			178.468	
Methyl isobutyrate(2) + toluene(3)	2,3	-0.109227	1.9	152.026	75.2305	1.7
	3,2	0.130547			25.4118	
Acetonitrile(1) + methyl isobutyrate(2) + toluene(3)			19.2			20.4
Propionitrile(1) + methyl isobutyrate(2)	1,2	-0.066518	3.2	13.6262	82.3476	3.2
	2,1	0.170744			72.7643	
Propionitrile(1) + ethylbenzene(3)	1,3	0.090461	11.0	-41.5399	68.1027	4.7
	3,1	0.074575			67.1914	
Methyl isobutyrate(2) + ethylbenzene(3)	2,3	0.144904	3.2	27.7613	87.7952	2.0
	3,2	-0.079497			64.7833	
Propionitrile(1) + methyl isobutyrate(2) + ethylbenzene(3)			16.0			6.1

<sup>a</sup>Molecular parameters  $q_i$  were 1.724 (ACN), 2.264 (PrCN), 3.652 (MiB), 2.968 (Tol) and 3.508 (EtBz);  $\delta_{ij}$  interaction parameters (adimensional values) refer to the UNIQUAC expression given in [17] with  $\delta_{ij}^* \equiv \delta_{ij}$ , which is equivalent to differentiate with respect to the temperature the original equation for  $G^E$  [15] in the hypothesis that  $\Delta\epsilon_{ij}$  are temperature independent

<sup>b</sup>Molecular collision diameters  $\sigma_{ij}$  of Wang equation were taken as being proportional to the cubic root of the volume UNIQUAC parameters  $r_i$ , taking  $r_i$  as 1.8701 (ACN), 2.5445 (PrCN), 4.1522 (MiB), 3.9228 (Tol), 4.5972 (EtBz);  $\Delta\epsilon_{ij}$  are interaction parameters ( $\text{J mol}^{-1}$ )

<sup>c</sup>Standard deviation of the fit ( $\text{J mol}^{-1}$ ) for binary mixtures or root mean square deviation ( $\text{J mol}^{-1}$ ) for ternary mixtures

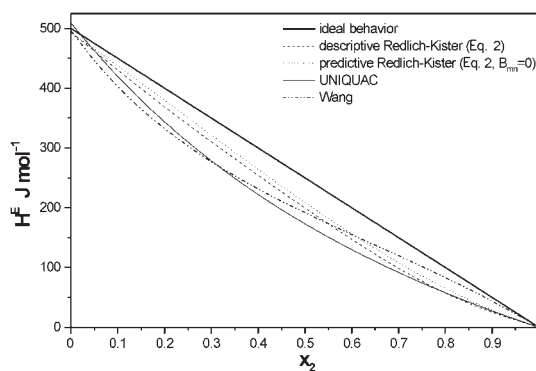


**Fig. 4**  $H^E$  pseudobinary curves for the addition of MiB(2) to ACN(1)-Tol(3) (A) and to PrCN(1)-EtBz(3) (B) mixtures at different binary compositions. Single curves are characterized by  $x_1$  of the starting binary

acrylonitrile, can be mixed 50:50 by mass with polymethylmethacrylate producing an exothermic heat effect [10]. Under the hypothesis that energetic interactions in the above polymeric mixture can be simulated by addition of methyl isobutyrate to a defined binary mixture of a chosen nitrile with a proper aromatic molecule, we calculated the above mixing heat by proper analysis of  $H^E$  data of ternary sets A and B of present work. In Fig. 4 are plotted pseudobinary curves obtained by intersecting the  $H^E$  surfaces of Fig. 3 with proper vertical planes passing through pure MiB and defined compositions of the opposite binary. These sections display a clear concavity upwards in case of the ternary ACN-MiB-Tol, while always convex curves for the ternary PrCN-MiB-EtBz. The concavity of the curves of set A is exhibited over a large range of compositions,  $0.05 < x_1 < 0.70$ , of the binary ACN(1)-Tol(3). In view of the fact that ideal behavior ( $\Delta H_{\text{mix}} = 0$ ) of these pseudobinary mixtures is represented by straight lines connecting  $H^E$  values of the binary to the conventional zero value of pure MiB, it can be easily deduced that mixing pure MiB with ACN-Tol mixtures characterized by the above composition range would always yield an exothermic effect.

Thus model system A would predict a favorable enthalpic contribution to the stability of mixtures of PMMA with SAN copolymer, over a large composition range of the latter. The same indication cannot be obtained from the enthalpic behavior of set B, which would always predict positive mixing heats. But this appears reasonable, if one assumes that the interactions between the pendant groups of the macromolecules are better simulated by model compounds characterized by a skeleton equal to that of the macromolecules pendant chains, with exclusion of the carbon atoms immobilized on the polymer backbone.

The analysis of the pseudobinary curves of Fig. 4 A allows to calculate a value  $\Delta H_{\text{mix}} = -44 \text{ J mol}^{-1}$  as the value for the mixing of MiB(2) and ACN(1)-Tol(3) binary, with  $x_1 = 0.383$ , to form a final mixture with  $x_2 = 0.458$ . This value is consistent with the slightly negative mixing enthalpy experimentally measured by Frezzotti and Ravanetti at 302.6 K [10].



**Fig. 5** Pseudobinary curves for the addition of MiB(2) to a binary ACN(1)-Tol(3) with  $x_1 = 0.43$ , as calculated by different procedures

As a consequence of the general agreement between experimental ternary  $H^E$  data and those calculated through binary data alone, negative heats of mixing would have been also predicted by all of the methods mentioned above, as shown by Fig. 5 for the pseudobinary curve at  $x_1=0.43$  which displays the maximum exothermic effect. In particular heats of mixing ranging from  $-40$  to  $-60$  J mol $^{-1}$  can be computed by Wang, UNIQUAC and Redlich–Kister–Muggianu [22] equations, the latter equation chosen as representative of the empirical procedures.

It should be interesting to check whether consistent conclusions might be drawn by examining other possible model compounds.

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