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ANALOG CALORIMETRY AND UNIQUAC GROUP CONTRIBUTIONS APPROACHES TO THE MISCIBILITY OF PVC WITH EVA COPOLYMERS

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Abstract

The miscibility of blends of poly(vinyl-chloride) (PVC) with poly(ethylene-*co*-vinyl acetate) (EVA) was investigated through analog calorimetry and a group contribution procedure based on the UNIQUAC model. The group contribution parameters quantifying the pair interactions between the structural features of the above polymers were calculated from experimental excess enthalpies of a series of binary mixtures of chlorocompounds, esters and hydrocarbons. Enthalpy data were also collected for the ternary mixtures (2-chloropropane+ethyl acetate+*n*-heptane) and (2-chlorobutane + methyl acetate+*n*-heptane), chosen as possible models for the studied macromolecular mixtures. The miscibility window of the PVC-EVA blends is fairly predicted by the group contribution method. It is also acceptably predicted by the enthalpic behaviour of the first ternary set, but only when the latter is calculated with binary data. A slightly narrower miscibility range is predicted by the binary interaction model. The results of these procedures are compared and the higher reliability of the group contribution procedure is emphasized in terms of its capability to reproduce the exact structure of the macromolecules and the non-univocal choice of the model molecules involved in the analog calorimetry approach.

Keywords: analog calorimetry, excess enthalpies, group contributions, mixtures, model compounds, polymer blends

Introduction

Polymeric blends are very important from a practical point of view and different approaches have been tried to predict their miscibility. Owing to the small entropic contribution to the mixing Gibbs energy of macromolecular species it is common to assume that miscibility is conditioned by a negative mixing enthalpy. The direct experimental determination of the heat associated to the formation of the blends is unfortunately unfeasible. Thus many authors have tried to simulate the heat of mixing

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of polymers through the mixing enthalpies of proper model compounds. This approach, known as *analog calorimetry*, did produce some promising results [1–6] though showing the possible critical choice of the proper model molecules [7, 8]. It was already applied with fair results to the formation of blends between the polymers here investigated, i.e. poly(vinyl-chloride) (PVC) with poly(ethylene-*co*-vinyl acetate) (EVA) [9], whose miscibility window has been previously reported [10].

Heats of polymer blend formation can also be determined indirectly through a thermodynamic cycle which involves the measurements of the solution heats in the same solvent of the separate polymers and their blends [11–13]. This approach, since requiring the preparation of the blends, does not solve the problem of predictability but is very useful to check the quality of the above predictions. It requires, however, a high precision of the calorimetric measurements.

When one is interested in the blend formation between a homopolymer and a random copolymer, as for the present case of PVC with EVA, another useful approach is the binary interaction model [14]. This approach, which is an extension of the original Flory–Huggins treatment of polymeric mixtures [15], is able to interpret the partial miscibility of the above two polymers, apparently impossible in view of the complete immiscibility of all the corresponding pairs of homopolymers, in terms of the repulsive energy between the repeat units of the copolymer. Such an approach has been already applied to PVC–EVA mixtures by Cruz-Ramos and Paul [9], who were able to give a qualitative explanation of the experimental miscibility window of this system [10].

A further possible approach is a group contribution procedure based on the UNIQUAC model [16], originally devised by Lai *et al.* [17] and recently applied to study the formation of poly(methylmethacrylate)–poly(styrene-*co*-acrylonitrile) blends (PMMA–SAN) [13, 18].

In the present work we applied this group contribution procedure, in a form based on a modified UNIQUAC equation [18], to the PVC–EVA blends. To this purpose we needed to extend the data base necessary for the calculation of group contributions and thus we measured the excess enthalpies at 298.15 K of a number of binary mixtures of compounds (chloroalkanes, esters, alkanes) containing groups which simulate the repeat units of the above polymers.

We also applied to the above blends the same procedure already applied to PMMA–SAN blends [7, 18], which consists in simulating the heats of mixing of PVC with EVA through the study of the enthalpic behaviour of ternary mixtures of model compounds. We measured experimentally the excess enthalpies at 298.15 K of the following ternary systems, over the whole composition range: (2-chloropropane+ethyl acetate+*n*-heptane) (set A) and (2-chlorobutane+methyl acetate+*n*-heptane) (set B). In the above mixtures 2-chloropropane (ClPr) and 2-chlorobutane (ClBu) may be considered model compounds of the PVC repeat unit, while methyl acetate (AcOMe) and ethyl acetate (AcOEt) should mimic the ester unit, and *n*-heptane (Hep) the ethylene unit, of the EVA copolymer. A more sophisticated choice of the model compounds, which never reproduces the exact structure of the polymeric repeat units, was already shown to yield practically the same results as with simple molecules [9].

The results are discussed in terms of the capability of the adopted models to predict the known PVC–EVA miscibility window [10].

Experimental

Excess enthalpies were measured by means of a flow calorimeter and an experimental procedure already described [18]. Experimental uncertainty, given as percent of the measured heat, was estimated as $\pm(0.3+100/H^{E})\%$, when working with an average volumetric flow of 0.1 cm^3 min^{-1}.

The distribution of the measured experimental data over the composition space for the ternary mixtures is shown in Fig. 1. The measurements have been realized by adding the chlorocompound to pre-formed mixtures of the other two components. The densities of the pure compounds at 298.15 K were measured with an Anton-Paar vibrating-tube densimeter DMA-60 equipped with a cell DMA602. The densities of the binary mixtures (ester+heptane) were calculated from excess volumes reported by Vidal *et al*. [19] for ethyl acetate and by Dusart *et al.* [20] for methyl acetate.

The origin and purity of the products was as follows. Within parentheses is reported the experimental density (g cm^{-3}): 2-chloropropane Fluka ≥99.5% (0.85533); 2-chlorobutane Aldrich ≥99% (0.86724); *n*-hexane Carlo Erba >99% (0.65479); *n*-heptane Carlo Erba 99.7% (0.67943); ethyl acetate Carlo Erba 99.8% (0.89431); methyl acetate Aldrich 99.5% (0.92695); all other esters were Aldrich reagents with purity ≥99%: ethyl propanoate (0.88416), methyl butanoate (0.89238), ethyl butanoate (0.87344), methyl hexanoate (0.87956), ethyl hexanoate (0.86608). 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%.

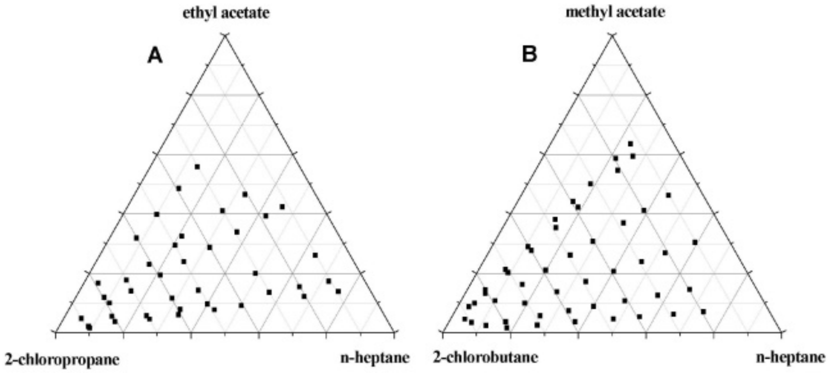

Fig. 1 Distribution of experimental H^{E} data over the composition space of ternary mixtures A (chloropropane+ethyl acetate+*n*-heptane) and B (chlorobutane+methyl acetate + *n*-heptane)

Results

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

$$H_{\mathrm{ij}}^{\mathrm{E}} = x_{\mathrm{i}} x_{\mathrm{j}} \sum_{\mathrm{k}=1}^{\mathrm{k}=3} A_k (x_{\mathrm{i}} - x_{\mathrm{j}})^{\mathrm{k}-1} \tag{1}$$

Table 2 reports values of the parameters A_{k} and the standard deviation σ of the fit, obtained by solving Eq. (1) through a non-linear least-squares treatment. Excess enthalpies of the mixtures (ethyl acetate+*n*-heptane) and (methyl acetate+*n*-heptane), necessary to describe the ternary systems here investigated, were directly taken from Vidal *et al.* [19] and Legido *et al.* [21], respectively, since a few measurements in our laboratory exactly reproduced the data by these authors. As far as we know, no other literature data exist to be compared with binary data measured in present work.

The data of Table 1 show that the interaction of the ester group with an alkane is endothermic and its value gradually decreases as the hydrophobic part of the ester is increased, as already observed by others [21]. Larger effects are in fact noticed with ethyl and methyl acetates (Fig. 3). Smaller endothermic effects are instead displayed by all binary mixtures involving chloroalkanes.

Excess molar enthalpies, H_{123}^{E}, of the ternary mixtures {ClPr(1)+AcOEt(2)+Hep(3)} (set A) and {ClBu(1)+AcOMe(2)+Hep(3)} (set B) are reported in Tables 3 and 4, respectively. Values of the observed pseudobinary excess enthalpies, $H_{\mathrm{obs}}^{\mathrm{E}}$ (see notes to the Tables), are also given for convenience. H_{123}^{E} values were fitted to the polynomial equation:

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

where $H_{\mathrm{ij}}^{\mathrm{E}}$ 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 σ of the fit are reported in Table 5.

A graphical representation of the calculated excess quantities over the whole composition domain is given in Fig. 2. The curves on the triangle base represent contour lines at constant values of H^{E}. It can be observed that the general behaviour of the two systems is very similar, exhibiting always positive values of the excess enthalpies. The main difference consists in the very low interaction enthalpy between ester and chloroalkane displayed by system A.

The experimental H^{E} values of the ternary mixtures were compared with the values calculated through a few empirical procedures which utilize the corresponding information on the parent binary mixtures combined through proper mixing rules. The ternary excess enthalpies were calculated by mixing the binary $H_{\mathrm{ij}}^{\mathrm{E}}$ terms obtained from Eq. (1) according to the methods by Muggianu *et al.* [22], Kohler [23] and Toop [24], chosen as representative of a series of procedures summarized by

Table 1 Excess molar enthalpies, H^{E}/J mol^{-1}, of binary mixtures at 298.15 K^{a}

x_1	H^{E}	x_1	H^{E}	x_1	H^{E}
Ethylpropanoate(1)+*n*-hexane(2)		Methylbutanoate(1)+*n*-hexane(2)		Ethylbutanoate(1)+*n*-hexane(2)	
0.1124	416.6	0.1133	477.3	0.0991	351.7
0.2892	847.9	0.3151	930.8	0.2836	708.9
0.3993	965.8	0.4182	1028.5	0.3822	774.1
0.4992	965.1	0.5016	1033.5	0.4974	792.2
0.6031	912.3	0.6053	962.2	0.5975	765.8
0.6950	789.9	0.6970	846.7	0.6901	679.3
0.9064	317.9	0.9020	357.0	0.8938	307.2
Methylhexanoate(1)+*n*-hexane(2)		Ethylhexanoate(1)+*n*-hexane(2)			
0.1000	331.3	0.1060	283.8		
0.3078	711.0	0.2833	530.7		
0.4001	751.7	0.4157	589.6		
0.5092	749.9	0.4970	595.2		
0.6088	668.8	0.6125	515.8		
0.6897	606.2	0.7034	457.8		
0.9043	216.8	0.8978	187.2		

Table 1 Continued

x_1	H^E	x_1	H^E	x_1	H^E
2-chloropropane(1)+ethylacetate(2)		2-chloropropane(1)+ethylpropanoate(2)		2-chlorobutane(1)+methylacetate(2)	
0.1065	33.2	0.1117	–20.5	0.0966	188.4
0.1065	31.7	0.2010	–25.0	0.1997	356.5
0.2115	69.7	0.2954	–26.1	0.2938	450.6
0.2944	97.0	0.5016	–26.8	0.3958	519.3
0.4014	120.3	0.6044	–25.7	0.4996	538.7
0.4991	127.9	0.7023	–22.3	0.5996	510.9
0.6032	121.6	0.8010	–18.0	0.6919	446.1
0.7071	105.3	0.9042	–12.2	0.8046	325.2
0.8030	82.4			0.8939	182.0
0.8957	42.1				
2-chloropropane(1)+*n*-heptane(2)		2-chlorobutane(1)+*n*-heptane(2)			
0.1384	299.3	0.2008	335.2		
0.1866	374.2	0.2931	431.8		
0.3145	564.0	0.4086	496.8		
0.4009	612.9	0.4795	516.3		
0.4907	621.8	0.5801	506.9		
0.5911	612.8	0.7074	432.7		
0.7067	526.8	0.8056	318.8		
0.8006	408.0	0.8924	189.1		
0.8893	251.7				

[a] Mole fractions were calculated from known volumetric flows and the experimental densities

Table 2 Coefficients A_k/J mol^{-1} of Eq. (1) and standard deviation of the fit, σ/J mol^{-1}

Binary mixture	A_1	A_2	A_3	σ
Ethyl propanoate (1)+*n*-hexane (2)	3907.8	–420.94	–	10.7
Methyl butanoate (1)+*n*-hexane (2)	4121.1	–451.61	421.45	5.3
Ethyl butanoate (1)+*n*-hexane (2)	3192.5	–352.67	658.67	8.7
Methyl hexanoate (1)+*n*-hexane (2)	3004.5	–706.80	209.92	10.8
Ethyl hexanoate (1)+*n*-hexane (2)	2335.9	–560.73	288.88	9.5
2-Chloropropane (1)+ethyl acetate (2)	513.4	69.578	–164.90	2.5
2-Chloropropane (1)+ethyl propanoate (2)	–105.3	32.754	–92.349	1.4
2-Chlorobutane (1)+methyl acetate (2)	2155.7	–126.79	–110.38	4.6
2-Chloropropane (1)+*n*-heptane (2)	2537.6	–	–	8.6
2-Chlorobutane (1)+*n*-heptane (2)	2069.7	–	–	5.0
Methyl acetate (1)+*n*-heptane (2)[a]	7134.1	776.38	256.53	10.8
Ethyl acetate (1)+*n*-heptane (2)[b]	6043.2	–80.142	337.95	10.2

[a] R. [21]; [b] R. [19]

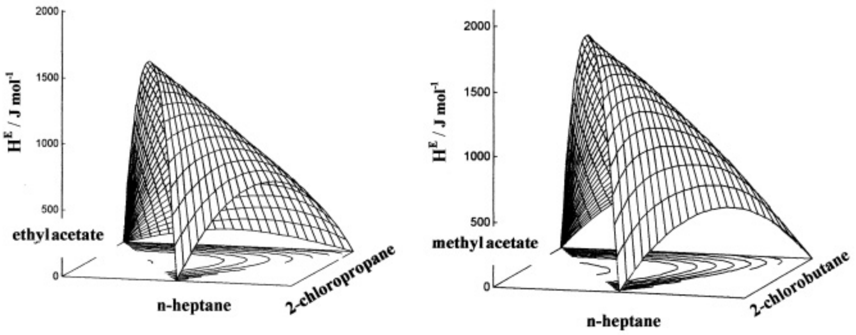

Fig. 2 Molar excess enthalpies for ternary systems A and B. H^{E} surfaces were calculated through Eq. (2) using parameters of Tables 2 and 5

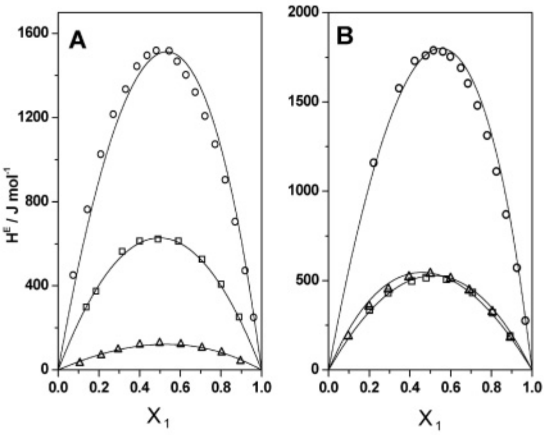

Fig. 3 Comparison between experimental excess enthalpies and values calculated through group contributions — for binary mixtures relevant to ternary systems A and B: △ – {2-chloroalkane(1)+ester(2)}; □ – {2-chloroalkane(1)+ alkane(2)}; ○ – {ester(1) + alkane(2)}

Lopez *et al.* [25]. The H^{E}_{123} values thus calculated reproduced the experimental data of ternary mixtures with a root mean square deviation (*rmsd*) of 35 J mol^{-1} for ternary A and 15 J mol^{-1} for ternary B, which is less than 3% of the maximum H^{E}_{123} value in both cases. The Toop method, representative of asymmetric type procedures, yielded approximately the same result independently of the numbering of the compounds for case A, while a little difference in case B. This was taken as indication that the symmetric trend of all binary data brings about negligible differences between symmetric and asymmetric procedures. It should be emphasized that the *rmsd* value observed for ternary A practically coincides with the mean deviation (*md*), thus indicating a systematic, though small, displacement of the calculated H^{E}_{123} values.

Table 3 Experimental pseudobinary molar enthalpies, $H^{\mathrm{E}}_{\mathrm{obs}}$ /J mol^{-1}, and excess molar enthalpies, H^{E}_{123} /J mol^{-1}, of the ternary system 2-chloropropane (1)+ethyl acetate (2)+*n*-heptane (3) at 298.15 K[a]

x_1	x_2	$H^{\mathrm{E}}_{\mathrm{obs}}$ [b]	H^{E}_{123}	x_1	x_2	$H^{\mathrm{E}}_{\mathrm{obs}}$ [b]	H^{E}_{123}
	x_2=0.2000 H^{E}_{23}=994.1 V^{E}_{23}=0.778				x_2=0.4126 H^{E}_{23}=1470.4 V^{E}_{23}=1.116		
0.3011	0.1398	250.0	944.7	0.2077	0.3269	64.6	1229.6
0.3926	0.1215	284.3	888.1	0.3008	0.2885	88.8	1116.9
0.3926	0.1215	278.5	882.3	0.4997	0.2064	115.6	851.3
0.5013	0.0997	300.7	796.4	0.6084	0.1616	112.3	688.1
0.6013	0.0797	295.9	692.3	0.6998	0.1239	100.6	542.0
0.7904	0.0419	218.8	427.2	0.7966	0.0839	76.0	375.1
				0.8935	0.0439	45.1	201.7
	x_2=0.5195 H^{E}_{23}=1509.8 V^{E}_{23}=1.129				x_2=0.7100 H^{E}_{23}=1249.6 V^{E}_{23}=0.918		
0.1183	0.4580	17.4	1348.6	0.1025	0.6372	–5.9	1115.6
0.1827	0.4246	28.3	1262.2	0.3104	0.4896	3.2	864.9
0.2954	0.3660	40.0	1103.8	0.5077	0.3495	10.6	625.8
0.4015	0.3109	48.1	951.7	0.5976	0.2857	11.1	514.0
0.5015	0.2590	52.5	805.1	0.8049	0.1385	6.1	249.9
0.5924	0.2118	56.3	671.7				
0.7071	0.1522	49.5	491.8				
0.7917	0.1082	34.5	349.0				
0.8994	0.0523	15.9	167.8				

Table 3 Continued

x_1	x_2	$H^{E\ b}_{obs}$	H^{E}_{123}	x_1	x_2	$H^{E\ b}_{obs}$	H^{E}_{123}
	x_2=0.8059 H^{E}_{23}=957.4 V^{E}_{23} =0.698				x_2=0.8467 H^{E}_{23}=798.3 V^{E}_{23} =0.581		
0.1028	0.7231	–7.8	851.2	0.0955	0.7658	–1.6	720.5
0.1353	0.6969	–5.1	822.8	0.2051	0.6730	11.5	646.1
0.1798	0.6610	0.2	785.4	0.4058	0.5031	26.4	500.7
0.2844	0.5767	11.8	696.9	0.4917	0.4304	31.1	436.8
0.4312	0.4584	19.9	564.5	0.6075	0.3323	29.8	343.2
0.4970	0.4054	20.3	501.9	0.6990	0.2549	25.7	266.0
0.7031	0.2393	18.0	302.3	0.8904	0.0928	7.3	94.8
0.8056	0.1567	11.4	197.5				

[a] Measurements performed by successive additions of pure 2-chloropropane to a binary (ethyl acetate+*n*-C_7). For each set of data the composition, excess molar enthalpy (J mol^{-1}) and excess molar volume (cm^3 mol^{-1}, taken from [19] of the starting binary is given

[b] Experimentally observed pseudobinary molar enthalpy ($H^{E}_{23} = 0$)

Table 4 Experimental pseudobinary molar enthalpies, $H^{\mathrm{E}}_{\mathrm{obs}}$ /J mol^{-1}, and excess molar enthalpies, H^{E} /J mol^{-1}, of the ternary system 2-chlorobutane (1)+methyl-acetate (2)+*n*-heptane (3) at 298.15 K[a]

x_1	x_2	$H^{\mathrm{E}}_{\mathrm{obs}}$ [b]	H^{E}_{123}	x_1	x_2	$H^{\mathrm{E}}_{\mathrm{obs}}$ [b]	H^{E}_{123}
	x_2=0.2699 H^{E}_{23}=1346.4 V^{E}_{23}=1.195				x_2=0.3081 H^{E}_{23}=1465.1 V^{E}_{23}=1.275		
0.1279	0.2354	71.3	1245.4	0.1423	0.2643	66.0	1322.6
0.1964	0.2169	126.6	1208.5	0.2103	0.2433	98.8	1255.8
0.3143	0.1851	165.4	1088.6	0.3900	0.1879	145.9	1039.6
0.3946	0.1634	184.1	999.2	0.4895	0.1573	165.2	913.2
0.4782	0.1408	191.7	894.3	0.5997	0.1233	151.8	738.3
0.6044	0.1068	173.7	706.3	0.7057	0.0907	136.4	567.5
0.7097	0.0784	139.4	530.2	0.8075	0.0593	110.5	392.5
0.8029	0.0532	110.3	375.6	0.8570	0.0441	84.8	294.3
0.8800	0.0324	69.4	231.0				
	x_2=0.4844 H^{E}_{23}=1775.8 V^{E}_{23}=1.428				x_2=0.6608 H^{E}_{23}=1661.2 V^{E}_{23}=1.267		
0.1028	0.4346	37.6	1630.8	0.1029	0.5928	58.4	1548.6
0.2008	0.3871	59.4	1478.6	0.2101	0.5220	101.9	1414.1
0.2836	0.3470	85.0	1357.2	0.2948	0.4660	127.6	1299.1
0.4049	0.2883	94.3	1151.0	0.3940	0.4004	136.8	1143.5
0.4949	0.2447	96.0	993.0	0.4938	0.3345	145.1	986.0
0.6852	0.1525	81.0	640.0	0.5940	0.2683	122.9	797.4
0.7921	0.1007	56.6	425.8	0.7092	0.1922	111.0	594.1
0.9118	0.0427	27.4	184.0	0.8977	0.0676	35.1	205.1

Table 4 Continued

x_1	x_2	H^{E}_{obs} [b]	H^{E}_{123}	x_1	x_2	H^{E}_{obs} [b]	H^{E}_{123}
x_2=0.8187 H^{E}_{23}=1147.8 V^{E}_{23}=0.855				x_2=0.9113 H^{E}_{23}=642.3 V^{E}_{23}=0.477			
0.1994	0.6555	145.2	1064.2	0.1954	0.7332	225.9	742.7
0.3035	0.5702	205.6	1005.0	0.2881	0.6488	307.5	764.7
0.4108	0.4824	232.9	909.2	0.3930	0.5532	335.2	725.1
0.5112	0.4002	240.3	801.3	0.4735	0.4798	344.4	682.6
0.5923	0.3338	228.4	696.4	0.5930	0.3709	337.6	599.0
0.6854	0.2576	201.1	562.1	0.7083	0.2658	296.3	483.7
0.7968	0.1664	158.7	391.9	0.8018	0.1806	221.9	349.2
0.8592	0.1153	109.2	270.8				

[a] Measurements performed by successive additions of pure 2-chlorobutane to a binary (methyl-acetate+n-C_7). For each set of data the composition, excess molar enthalpy (J mol^{-1}) and excess molar volume (cm^{3} mol^{-1}, taken from [20]) of the starting binary is given

[b] Experimentally observed pseudobinary molar enthalpy (H^{E}_{23}=0)

Table 5 Ternary coefficients $B_{mn}\cdot 10^{-4}$ /J mol^{-1} of Eq. (2)

	A ClPr(1) + AcOEt(2) + Hep(3)	*B* ClBu(1) + AcOMe(2) + Hep(3)
B_{00}	0.57403	1.2833
B_{10}	–3.5458	–4.6443
B_{11}	–1.6030	–9.8811
B_{20}	5.7135	3.7879
B_{21}	10.701	27.633
B_{22}	1.0809	19.916
B_{30}	–1.6836	–
B_{31}	–10.459	–15.627
B_{32}	–5.9033	–28.929
B_{33}	–	–11.586
σ/J mol^{-1}	3.0	8.3

The group contribution model

A group contribution procedure allows to calculate the enthalpy of mixing of macromolecules through a limited number of binary parameters, δ_{ij}, which measure the pair interactions between the molecular segments (groups) chosen to construct the structure of the polymers. It has the clear advantage, compared with analog calorimetry, of allowing to simulate the exact structure of the macromolecules, thus overcoming the possibly arbitrary choice of the model compounds.

In our procedure we calculated the enthalpy of a mixture of conventional groups by following the same procedure used for deriving the UNIFAC model for Gibbs energy [26]. We made use of the following form of the UNIQUAC equation for a mixture containing *c* compounds and *n* groups:

$$\frac{\Delta H_{\mathrm{mix}}}{R}=\sum_{j=1}^{n}Q_j x_j\left[\frac{\sum_{i=1}^{m}Q_i x_i\delta_{ij}\exp\left(\frac{-\alpha_{ij}\delta_{ij}}{T}\right)}{\sum_{i=1}^{m}Q_i x_i\exp\left(\frac{-\alpha_{ij}\delta_{ij}}{\mathrm{T}}\right)}\right]-\sum_{k=1}^{c}x_k\sum_{j=1}^{n}\delta x_j^{(k)}\left[\frac{\sum_{i=1}^{m}\mathrm{Q}_i x_j^{(k)}\delta_{ij}\exp\left(\frac{-\alpha_{ij}\delta_{ij}}{T}\right)}{\sum_{i=1}^{m}\delta_i x_j^{(k)}\exp\left(\frac{-\alpha_{ij}\delta_{ij}}{T}\right)}\right] \tag{3}$$

where Q_i and x_i are the conventional surface area and mole fraction 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. 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.

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

$$x_i = \frac{\sum_k x_k \nu_{i,k}}{\sum_k x_k \sum_m \nu_{m,k}} \qquad x_i^{(k)} = \frac{\nu_{k,i}}{\sum_i \nu_{k,i}} \tag{4}$$

where $\nu_{I,k}$ is the number of *i* groups in the compound *k*. The second term on the right hand side of Eq. (3) is necessary to fulfil the condition of a null ΔH_{mix} value for all pure compounds.

The structure of the groups which should build up the repeat units of the polymers was chosen in accordance to UNIFAC tables. A rational criterion for the identification of their best structure was proposed by Wu and Sandler [27] on the basis of quantum mechanical calculations of charge densities. This criterion has been recently applied also to macromolecules [28]. The larger number of adjustable parameters there involved seemed not consistent with the limited number of structures considered in our work.

Table 6 Literature excess enthalpy data used for the calculation of UNIQUAC group contributions[a]

Binary mixture	H^E_{max}/J mol^{-1}	Ref.
Methyl acetate+*n*-hexane	1640	[29]
Ethyl acetate+*n*-dodecane	1768	[30]
Ethyl propanoate+*n*-pentane	964	[19]
Ethyl propanoate+*n*-heptane	1180	[19]
Ethyl propanoate+*n*-nonane	1282	[19]
Ethyl butanoate+*n*-nonane	930	[19]
Ethyl butanoate+*n*-heptane	1432	[19]
Ethyl butanoate+*n*-pentane	1205	[19]
Methyl *i*-butanoate+*n*-heptane	1059	[18]
Methyl *i*-butanoate+*n*-dodecane	1329	[18]
Ethyl octanoate+*n*-pentane	264	[31]
Ethyl octanoate+*n*-heptane	439	[31]
Ethyl nonanoate+*n*-pentane	220	[31]
Ethyl nonanoate+*n*-heptane	365	[31]
Ethyl nonanoate+*n*-nonane	443	[31]
Ethyl decanoate+*n*-heptane	304	[31]
Ethyl dodecanoate+*n*-heptane	255	[31]
Ethyl tetradecanoate+*n*-heptane	249	[31]
Ethyl hexadecanoate+*n*-heptane	234	[31]

[a] Data from these sources were used, together with data of binary mixtures of Table 2, to calculate group contributions of Table 7

Table 7 Values of group contributions, δ_{ij}, (K), for use in Eq. (3)

Groups	Q_i	CH_x	CH_3COO CH_2COO	CH–Cl
CH_3	0.848	0	437	500
CH_2	0.540			
CH	0.228			
α^a			0.33	
CH_3COO	1.728	1109	0	42
CH_2COO	1.420			
α^a		0.33		
CH–Cl	0.952	100	–31	0

[a] $\alpha = \alpha_{ij} = \alpha_{ji}$ Eq.(3). Quoted values are to be used only when the CH_x group belongs to a paraffin. In all other cases $\alpha = 1$

Values of relevant group contributions, δ_{ij}, were calculated through a least-square procedure which utilized a set of enthalpy data made up with ten binary systems studied in this work plus twenty-one binary systems taken from the literature. The literature systems are listed in Table 6. Table 7 reports all the δ_{ij} parameters thus calculated, relevant to the polymeric structures examined in this work. The capability of these parameters to reproduce the enthalpy data of the mixtures they were calculated from is more than acceptable. Figure 3 shows this agreement for the binary mixtures pertinent to the two ternaries here investigated. A slight asymmetry in the predicted H^E values is only noticed for the binaries (alkyl acetate+heptane). An acceptable agreement is also observed when these δ_{ij} parameters are used for the prediction of the ternary mixtures A and B.

Discussion

The experimental excess enthalpies of pseudobinaries of the chloroalkane plus preformed mixtures (alkyl acetate+heptane) are all positive, except for a few mixtures of ternary A in the ester rich region (Table 3). The same result can be consistently obtained from the smoothing equation (Eq. (2)), which describes the excess enthalpy of the ternary mixtures over the whole composition range. In effect, if one cuts the spatial surfaces of Fig. 2 with perpendicular planes passing through the chloroalkane and selected compositions of the opposite binary mixture (ester+heptane), and subtracts from the intersecting functions the enthalpic contributions due to the latter binary, one obtains the excess enthalpies of the above pseudobinary mixtures ($H^E_{23}=0$). The observed small positive values of the pseudobinary excess enthalpies, in the limits of assuming the above ternary mixtures as possible models for PVC–EVA interactions, would suggest no miscibilty of EVA with PVC. However, when one applies the above intersecting procedure to the excess enthalpies of ternary A calculated as a combination of binary data (f.i. through the Muggianu's method), the resulting

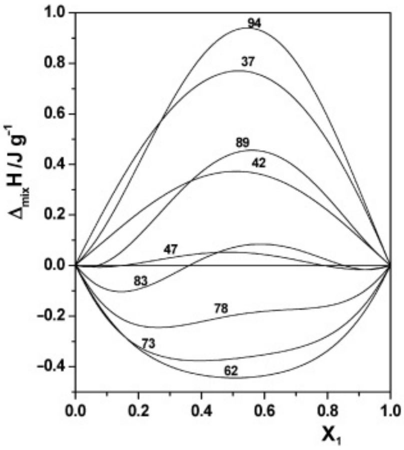

Fig. 4 Pseudobinary excess enthalpies calculated for the mixing of 2-chloropropane (1) with preformed mixtures (ethyl acetate+*n*-heptane) at different acetate mass percent (quoted numbers)

pseudobinary curves display a different trend. A few such curves are represented in Fig. 4. The figure shows that negative mixing heats are exhibited for a selected range of vinyl acetate content in EVA. This is due to the small magnitude of calculated mixing enthalpies, whose sign can be easily changed when including the contribution coming from the B_{mn} coefficients of Eq. (2). The analogous curves calculated for ternary system B display no exothermic mixing heats, thus indicating that model system B would predict no blend formation between EVA and PVC.

In our opinion the interaction enthalpies of a homopolymer with a copolymer, when simulated by ternary mixtures of small molecules modelling the three monomeric units, are probably better approximated by excess properties calculated as a simple combination of only binary data. As a matter of fact, the contribution to by the first term of the right hand side of Eq. (2) probably reflects specific local interactions which are hardly involved in the PVC–EVA blends, owing to the fixed position of the two monomeric units in the copolymer. In other words, the actual thermodynamic behaviour of the ternary mixtures of model molecules probably differs from the behaviour of the polymeric mixtures even more than does the predicted system.

Recently some authors [32, 33] emphasized that the transfer of properties of small molecules to the repeat units of macromolecules may cause an overestimate of the interaction energies of polymeric blends. Indeed, the connectivity of the long and flexible macromolecular chains provokes the *intramolecular screening* phenomenon consisting in a not negligible fraction of intramolecular contacts which reduce the intermolecular interactions in the polymeric mixture. Particularly Indrakanti *et al.* [33] have shown that the fraction of intramolecular contacts, for sufficiently long chains, results approximately 20% of the total. These studies, however, dealt with homopolymers consisting prevailingly of hydrocarbon chains [33] or involved in hydrogen bonds [32]. Application of the above arguments to the mixtures here examined, where one component is a copolymer (EVA) involving strong intramolecular repulsion, does not appear straightforward.

Taking advantage of the fact that the values of both ternary mixtures A and B are nicely reproduced by simple combination of the corresponding binaries, we checked the possible prediction of the formation of the above blends by taking into consideration the two more ternary mixtures (ClPr+AcOME+Hep) (C) and (ClBu+AcOEt+Hep) (D) which can be realized through different combinations of the chosen model compounds. The excess enthalpies of the latter mixtures were calculated by combination of the data of the relevant binary mixtures. The unavailability of experimental data relative to the two binaries (chloropropane+methyl acetate) and (chlorobutane+ethyl acetate) was overcome by computing these data through the UNIQUAC group contributions discussed above. This procedure, though approximate, seems justified by the fact that group contributions of Table 7 are able to reproduce with a nice agreement the data of a large number of binary mixtures (f.i. Fig. 3).

The calculated data of all four ternary systems A, B, C and D were used to compute pseudobinary curves of the type shown in Fig. 4, in order to mimic PVC–EVA blends for all possible compositions of the EVA copolymer. This allowed to identify the occurrence of exothermic mixing heats, and thus the miscibility window of these blends, as they result according to the different model systems. Figure 5 shows the enthalpy of formation of the blends, at 1 to 1 ratio of the polymers, as a function of the vinyl acetate (VA) mass percent in EVA, according to the above ternary systems. The calculated miscibility windows, identified as regions of negative enthalpies, are finally reported in Table 8.

We would like to notice that the miscibility of PVC–EVA blends based on the above analog calorimetry approach might also be inferred by utilizing the simple Z^*

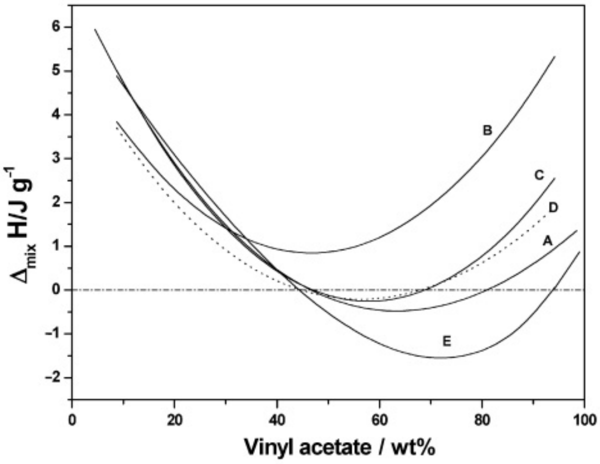

Fig. 5 Mixing enthalpies of PVC–EVA blends simulated by different procedures: A, B, C, D curves from pseudobinary excess enthalpies of the ternary systems A, B, C and D; curve E from UNIQUAC-based group contributions of Table 7

test [18], which provides the approximate miscibility window when one knows only one enthalpy datum relative to each of the pertinent binary mixtures. This test, which can be fruitfully applied when the excess enthalpies of the ternary mixtures can be reasonably simulated by the nearly symmetrical $H_{\mathrm{ij}}^{\mathrm{E}}$ data of the relevant binaries, is expressed by the relationship

$$Z^{*}=\left(H_{12}^{\mathrm{E}^{*}}+\frac{x_{3}^{\mathrm{b}}}{1-x_{3}^{\mathrm{b}}}H_{13}^{\mathrm{E}^{*}}\right)-x_{3}^{\mathrm{b}}H_{23}^{\mathrm{E}^{*}}<0 \qquad (5)$$

where $H_{\mathrm{ij}}^{\mathrm{E}}$ are the values of the excess enthalpies of binaries *i–j* at $x_{\mathrm{i}}=0.5$ and the binary 2–3, with x_{3}^{b} the molar fraction of component 3 in this binary, is chosen to simulate the copolymer structure. When this empirical rule is applied to set A, the miscibility window of the system PVC–EVA is calculated as $47.3<\text{mass \% VA}<80.8$, which fairly matches the result derived from analysis of the complete ternary system (Table 8).

Table 8 Miscibility window of PVC–EVA blends

Method		Mass/% of vinyl acetate units		Ref.
		lower limit	upper limit	
Experimental				
phase equilibria		45	85	[15]
Predicted				
model compounds		46–63	86–90	[9]
Model compounds	set A	46.6	80.3	this work
	set B	–	–	this work
	set C	47.3	69.3	this work
	set D	44.5	67.7	this work
Binary interaction		57–62	70–81	this work
Group contributions		44.5	93.8	this work

The miscibility of PVC with EVA was also evaluated on the basis of the binary interaction model [14]. Pair interaction energy densities, B_{ij} (J cm^{-3}), were calculated for all binary mixtures of the model compounds chosen in present work. These data, which can be interpreted as the pair interaction energies of the segmental units of vinyl chloride (unit 1) in PVC and acetate (unit 2) and ethylene (unit 3) in the EVA copolymer, can be properly combined as

$$B=B_{12}\phi_{2}+B_{13}\phi_{3}-B_{23}\phi_{2}\phi_{3} \qquad (6)$$

to give the interaction energy density *B* of PVC with EVA, as a function of the volume fractions of units 2 and 3 in the copolymer. This calculation was performed for all possible combinations (sets A through D) of the model molecules, and the results are shown in Fig. 6. Interaction energy densities were found always positive when

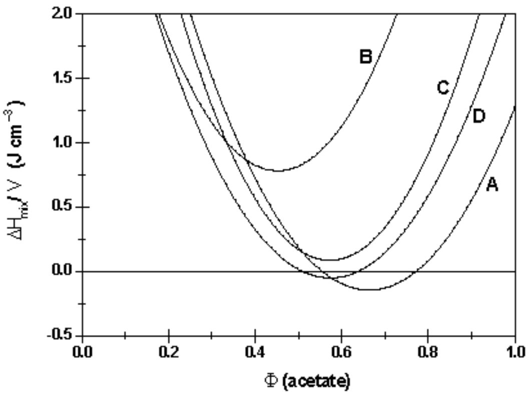

Fig. 6 Interaction energy density of PVC with EVA calculated from the binary interaction model; Φ(acetate)=acetate volume fraction

calculated from B and C ternaries. The average miscibility range calculated from ternaries A and D, identified by negative *B* values at different compositions of the copolymer, were 62< mass % VA<81 and 57< mass % VA<70, respectively.

We finally calculated the mixing enthalpies of PVC–EVA blends by using directly the group contributions of Table 7. These data, as a function of EVA composition, are compared with other predictions in Fig. 5. The miscibility window thus calculated, 44.5< mass % VA<93.8, matches rather closely the experimental datum 45< mass % VA<85 [10]. The miscibility windows calculated through all the above procedures are reported in Table 8 and compared with experimental data and previous literature estimates.

Conclusions

Data of Table 8 show that the experimental miscibility range is qualitatively predicted by different sets of model compounds. As a general observation, model molecules chosen by Cruz-Ramos and Paul [9] provide a fair simulation of the upper limit of the experimental miscibility window while our model systems better simulate the lower limit. However, this comparison should not too much stressed in view of the fact that the experimental datum was obtained from miscibility data at 150°C [10]. We would rather note that when facing the problem of simulating the enthalpy of formation of some new blend, one can never be sure in advance which are the best mimicking model molecules, and thus a procedure which makes such choice unnecessary should possibly be preferred. Moreover, we notice that by treating the experimental data of present work under the frame of different models, slightly different miscibility limits are obtained. In our opinion these uncertainties find a reasonable answer in a group contribution model, since this latter (i) yields a measure of pair interaction energies averaged over a very large set of mixtures of model compounds and (ii) with a proper choice of groups it allows to build up the exact molecular structure of the repeat units of the polymers, thus probably accounting more closely for the actual polymeric interactions.

In conclusion, we deem that the group contribution approach represents a sort of balanced route to the calculation of the enthalpy of formation of polymeric blends, certainly less arbitrary than using simple model molecules. The problem which remains to be solved is the unfit association of group contributions values derived from freely interacting small molecules to macromolecular segments and attached pendant groups, certainly provided with a limited interacting capability. Previous calculations on the PMMA–SAN system [18] did in effect indicate a clear difference between the interactions of the two types of molecules. The fair calculation of the miscibility window of the present case is probably to be ascribed to the fact that the ethylene repeat unit in the EVA copolymer is located on the main chain and possesses practically the same structure as the hydrocarbon portion of the ester unit. Therefore, the fixed position of the two units in the macromolecular chain does not cause an appreciable increase of the repulsive interactions already present in the separate molecules.

It would be interesting to check whether the direct calorimetric determination of the blend formation enthalpies yields results comparable with those obtained from present simulation. The experimental measurements of these heats through a proper Hess cycle [18], which utilizes solution enthalpies of the polymers and their blends in the same solvent, are under way.

* * *

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