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Analogue calorimetry of polymer blends: poly(styrene-*co*-acrylonitrile) and poly(phenyl acrylate) or poly(vinyl benzoate)

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Unlike poly(phenyl acrylate) (PPA), its isomer poly(vinyl benzoate) (PVBZ) is immiscible with poly(styrene-*co*-acrylonitrile) (SAN). The difference in miscibility behaviour of PPA and PVBZ towards SAN is also reflected in the heats of mixing (ΔH_m) of the low-molecular-weight analogues of the respective blend components at compositions corresponding to $\phi_{SAN} = 0.92$ in the blend. It turns out that propionitrile, the hydrogenated monomer of polyacrylonitrile (PAN), is very unsuitable as an analogue of the latter. In contrast, acetonitrile, having a solubility parameter closer to PAN, is a fairly acceptable analogue of PAN as far as miscibility of the latter with PPA is concerned in the PAN-rich region, $\phi_{PAN} > 0.7$. Copyright © 1996 Elsevier Science Ltd.

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INTRODUCTION

The entropy of mixing per unit volume of polymer mixtures is very small compared to that for mixtures of small molecules, since a very small number of molecules are involved in the former systems compared to that in the latter. As a result, homogeneous polymer blends result essentially for systems with exothermic heat of mixing ($\Delta H_m < 0$)[1]. For a homopolymer–copolymer or a copolymer–copolymer blend system, the net heat of mixing may turn out to be negative even though none of the binary interactions are exothermic[2–4]. Unfortunately, direct experimental determination of the heat of mixing is difficult owing to the high viscosity of polymers. Cruz *et al.*[5] suggested that low-molecular-weight analogues of the polymers can be used to estimate the heat of mixing of the corresponding polymers. They showed that, for polyester–polycarbonate blend systems, miscibility can be reasonably well correlated with the heat of mixing of low-molecular-weight analogues. Generally speaking, pairs of polymers whose analogues exhibit a negative heat of mixing are miscible, whereas those for which the analogues exhibit a positive heat of mixing are immiscible. Exceptions do indeed exist. Thus, although diphenyl carbonate (DPC), an analogue of polycarbonate (PC), exhibits a small exotherm on mixing either with ethyl benzoate or with dimethyl orthophthalate, which are analogues of poly(ethylene terephthalate) (PET), PC and PET are only partially miscible. Similarly, when DPC is mixed with diethyl orthophthalate, an analogue of poly(ethylene orthophthalate) (PEOP), a large negative heat of mixing is observed, which predicts that PC would be miscible with PEOP. The prediction, however, is belied, as experiments show that PC is only partially miscible with PEOP. Exceptions notwithstanding, analogue calorimetry finds general acceptance as a means of estimating the enthalpy of polymer–polymer mixing[5–22]. However, the low-molecular-weight analogues must be chosen very carefully in order to get meaningful analogue calorimetry results. For example, Kim *et al.*[13] found that, although polystyrene (PS) and poly(vinyl chloride) (PVC) are immiscible with each other, 1,3-dichlorobutane (DCB), the analogue of PVC, exhibits exothermic mixing with toluene, ethylbenzene and cumene, which may be considered as analogues of PS. On the other hand, when they used styrene oligomers that contain two to four styrene units as analogues of PS, the mixing becomes endothermic. For the analogue calorimetry of poly(vinyl chloride)–poly(styrene-*co*-acrylonitrile) (PVC–SAN) blend systems, these workers used premixtures of styrene trimer and isobutyronitrile (iBuN) in various proportions as analogues for SAN of different copolymer compositions, while DCB was chosen as the analogue for PVC. However, it was found that, although PVC is miscible with SAN only over a small range of copolymer compositions, viz. 11.5 to 26 wt% acrylonitrile (AN), analogue calorimetry reveals exothermic mixing of DCB with the premixture over a much greater range of iBuN concentrations, viz. 5–60 vol% iBuN. Thus, the miscibility window predicted from analogue calorimetry is much broader than that actually observed. They concluded that analogue calorimetry results fail to predict quantitatively the right width of the miscibility window.

Earlier, we reported that SAN forms miscible blends with poly(phenyl acrylate) (PPA) over the copolymer

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Polymer repeat test	Analogues tested		
$-CH_2-CH(COOC_6H_5)-$ PPA	$CH_3-COOC_6H_5$ PhAc	$CH_3-CH_2-COOC_6H_5$ PhPr	
$-CH_2-CH(OCOC_6H_5)-$ PVBZ	$CH_3-OCOC_6H_5$ MeBz	$CH_3-CH_2OCOC_6H_5$ EtBz	
$-CH_2-CH(C_6H_5)-$ PS	$CH_3-C_6H_5$ TE	$CH_3-CH_2-C_6H_5$ EB	
$-CH_2-CH(CN)-$ PAN	CH_3-CN AcN	CH_3-CH_2-CN PrN	$CH_3-CH(CH_3)CN$ iBuN

Figure 1 Structural formula for the polymers and analogues used in this work

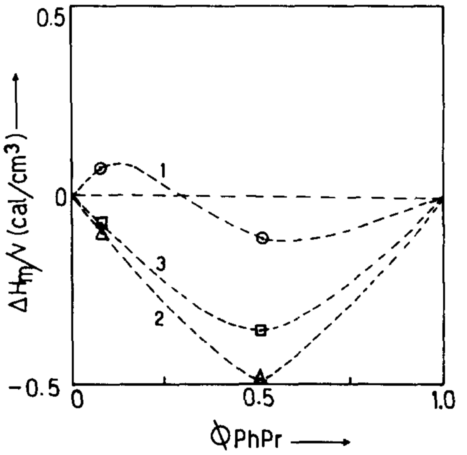

Figure 2 Heat of mixing per unit volume $\Delta H_m/V$ (cal cm^{-3}) of phenyl propionate with aliphatic nitrile vs. volume fraction of phenyl propionate ϕ_{PhPr}: curve 1 (○) for AcN, curve 2 (△) for PrN and curve 3 (□) for iBuN

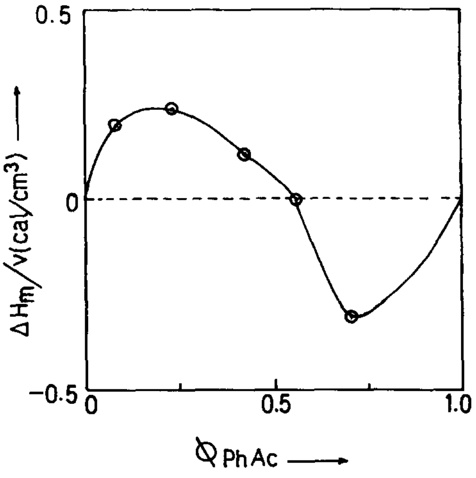

Figure 3 Heat of mixing per unit volume $\Delta H_m/V$ (cal cm^{-3}) of phenyl acetate with acetonitrile vs. volume fraction of phenyl acetate ϕ_{PhAc}

composition range 11.5 to 32 wt% AN at 200°C but SAN is immiscible with poly(vinyl benzoate) (PVBZ), which differs from PPA only in the orientation of the COO group in the repeat units[23,24]. In fact, the similarity of these two polymers (viz. PPA and PVBZ) in respect of both physical and chemical properties is so great that they themselves are miscible with each other[25]. It is of interest to examine if the heats of mixing of polymer-analogous low-molecular-weight compounds parallel with these blend miscibility results, i.e. ΔH_m positive for immiscible blends and negative for miscible blends. For the analogue calorimetry work, the analogues used here are: methyl benzoate (MeBz) and ethyl benzoate (EtBz) for PVBZ; phenyl acetate (PhAc) and phenyl propionate (PhPr) for PPA; toluene (TE) and ethylbenzene (EB) for polystyrene (PS); and acetonitrile (AcN), propionitrile (PrN) or isobutyronitrile (iBuN) for polyacrylonitrile (PAN). SAN is simulated with a mixture of TE and AcN at the same volume ratio as that which exists between styrene and acrylonitrile in the SAN copolymers of varying compositions.

EXPERIMENTAL

Analytical-reagent-grade toluene (E. Merck, India), ethylbenzene (Fluka Chemika, Germany), acetonitrile (E. Merck, India), propionitrile (Fluka AG, Switzerland) and isobutyronitrile (E. Merck, India) were dried and fractionally distilled using a 1 m long fractionating column packed with 3 mm porcelain rings. Methyl benzoate (Burgoyne, India) and ethyl benzoate (BDH, England) were purified by distillation under reduced pressure. Phenyl acetate and phenyl propionate were prepared from phenol with acetic anhydride and from phenol with propionic anhydride, respectively, dried and distilled under reduced pressure. The esters PhAc, PhPr, MeBz and EtBz gave single peaks in g.l.c. on silicone columns.

The heats of mixing were measured using an Isoperibol titration calorimeter (Tronac 458, USA) at 30 ± 0.0002°C. The instrument was calibrated by measuring the heat of reaction of hydrochloric acid and sodium hydroxide. The accuracy of the calorimeter was 0.5% on 2 cal. The reaction vessel was filled up with 20 cm^3 of the titrant, which was either one analogue (for PPA or PVBZ) or premixtures of two analogues (for SAN) at different volume ratios. The whole system was immersed in a 60 dm^3 capacity water bath maintained at a temperature of 30 ± 0.0002°C by a Tronac PTC probe. When thermal equilibrium was reached, 1.7325 cm^3 of the other liquid (titre) was delivered from

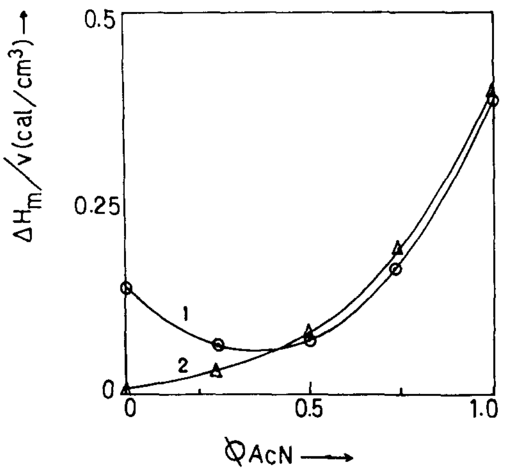

Figure 4 Heat of mixing per unit volume $\Delta H_m/V$ (cal cm^{-3}) of 1 volume of methyl benzoate or ethyl benzoate with 11.54 volumes of premixtures of acetonitrile and toluene plotted against volume fraction of acetonitrile ϕ_{AcN} in the premixture: curve 1 (○) for methyl benzoate and curve 2 (△) for ethyl benzoate

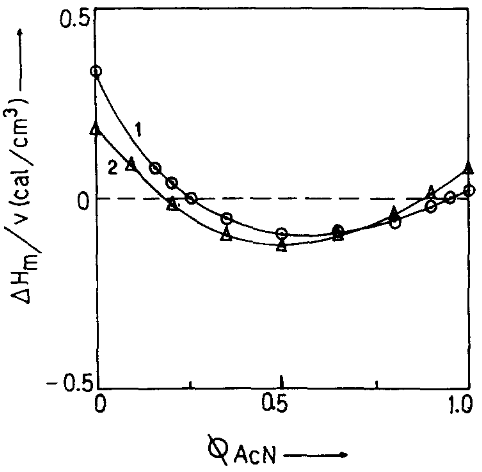

Figure 5 Heat of mixing per unit volume $\Delta H_m/V$ (cal cm^{-3}) of 1 volume of phenyl acetate or phenyl propionate with 11.54 volumes of premixtures of acetonitrile and toluene plotted against volume fraction of acetonitrile ϕ_{AcN} in the premixture: curve 1 (○) for phenyl acetate and curve 2 (△) for phenyl propionate

a burette into the titrant under constant stirring. The heat change was recorded in millivolts on a Houston Instrument Omniscribe D500 strip chart recorder. The heats of mixing were calculated from the thermograms. The calorimeter allows heat of mixing measurements at 1:11.54 volume ratios. For other volume ratios, a home-made flow calorimeter was used[26].

RESULTS

The structural formulae of the low-molecular-weight compounds examined for polymer analogues are shown in *Figure 1*. In selecting the analogues we were guided by our work on the thermodynamic studies of polymer blends using inverse gas chromatography (i.g.c.), wherein we found that hydrogenated monomers are reasonably good analogues for the corresponding vinyl ester or acrylate polymers[27–29]. In order to check whether this generalization will apply for polyacrylonitrile, we measured the heats of mixing of propionitrile (hydrogenated monomer of PAN) and phenyl propionate (hydrogenated monomer of PPA). *Figure 2* (curve 2) shows that the mixing of these two liquids is exothermic. On the other hand, the two corresponding polymers are immiscible with each other. Thus, propionitrile cannot be used as an analogue of PAN. We then checked the results using acetonitrile and isobutyronitrile in place of propionitrile. *Figure 2* (curves 1 and 3) shows that, while mixing of iBuN with PhPr is exothermic, there exists a range of composition rich in AcN ($\phi_{AcN} > 0.7$) where mixing of AcN and PhPr is endothermic. This latter result suggests that AcN may be used as an analogue of PAN for PPA + PAN blends rich in it, viz. $\phi_{PAN} > 0.7$. *Figure 3* shows that mixing of AcN with the immediately lower homologue of PhPr, viz. PhAc, is also endothermic over a broader range of composition ($\phi_{AcN} > 0.44$) than that found for the PhPr + AcN system. In the work that follows we have simulated SAN with premixtures of AcN and toluene, the latter being used as the analogue of the styrene and the former of the acrylonitrile residue in the copolymer. For the homopolymers, PPA and PVBZ, the analogues used are the hydrogenated monomers and their immediately lower homologues. Furthermore, in line with the results shown in *Figures 2* and *3* and discussed above, the volume ratio for mixing has been selected from within the endothermic region of the two figures. As stated in the 'Experimental' section the Isoperibol titration calorimeter handles a mixing volume ratio of 1:11.54 of two liquids. *Figures 2* and *3* show that at this volume ratio of PhPr:AcN or PhAc:AcN the heats of mixing are positive, which is commensurate with the immiscibility of PPA and PAN.

Figure 4 gives the analogue calorimetry results with respect to blends of PVBZ + PS, PVBZ + PAN and PVBZ + SAN. The heats of mixing per unit volume for the pair of liquids involving one volume of EtBz or MeBz (analogues of PVBZ) with 11.54 volumes of toluene (analogue of PS), AcN (analogue of PAN) and various premixtures of toluene and AcN of varying proportions (analogue of SAN) are shown in the figure. The heats of mixing are positive (endothermic) for all the binary mixtures referred to above. This result is thus commensurate with the immiscibility of PVBZ not only with the homopolymers PS and PAN but also with the copolymer SAN. *Figure 5*, on the other hand, shows the analogue calorimetry results with respect to blends of PPA + PS, PPA + PAN and PPA + SAN. The heats of mixing per unit volume for the pairs of liquids involving one volume of PhAc or PhPr (analogue of PPA) with 11.54 volumes of toluene, AcN and various premixtures of toluene and AcN (as detailed above) is shown in the figure. Positive ΔH_m is observed for mixing of PhAc/PhPr with AcN or toluene. This result is commensurate with the observation that PPA is miscible neither with PS nor with PAN. *Figure 5* also shows that certain mixtures of toluene and AcN give negative ΔH_m on mixing with PhAc or PhPr. These results predict that PPA would be miscible with SAN over the composition range $\phi_{AN} = 0.25$ to 0.90 (based on PhAc as analogue for PPA) or $\phi_{AN} = 0.20$ to 0.85 (based on PhPr as analogue for PPA). The predicted miscibility window, however, is shifted to higher acrylonitrile region from that experimentally observed[23], viz. $\phi_{AN} = 0.103$ to 0.294. Considering the poor representation of PAN by AcN and consequently

Table 1 Binary interaction energy densities B_{ij} (cal cm^{-3}) at 30°C. Volume ratio of liquid 1 : liquid 2 = 1 : 11.54

	Liquid 1					
Liquid 2	MeBz	EtBz	PhAc	PhPr	TE	EB
TE	1.949	0.051	4.695	2.557	–	–
EB	4.406	0.297	5.098	3.136	–	–
AcN	5.288	5.280	0.258	0.974	8.437	–
PrN	1.774	2.443	−1.670	−0.921	–	4.668
iBuN	1.241	1.505	−0.968	−0.893	–	–

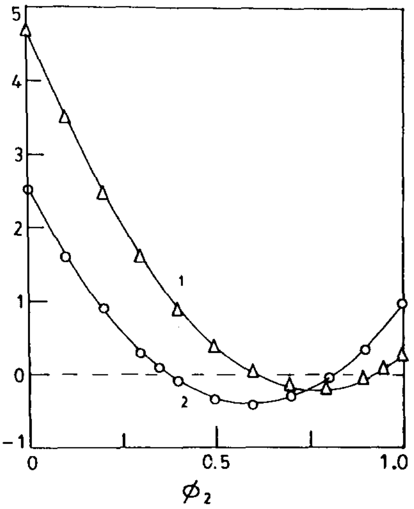

Figure 6 Plot of B_{net} vs. ϕ_2 calculated from equation (2) using B_{ij} data of *Table 1* for the PPA + SAN blend pair, $\phi_{\text{PPA}} : \phi_{\text{SAN}} = 1 : 11.54$. A mixture of toluene and AcN has been used as the analogue of SAN. Curve 1 (Δ) for phenyl acetate and curve 2 (O) for phenyl propionate

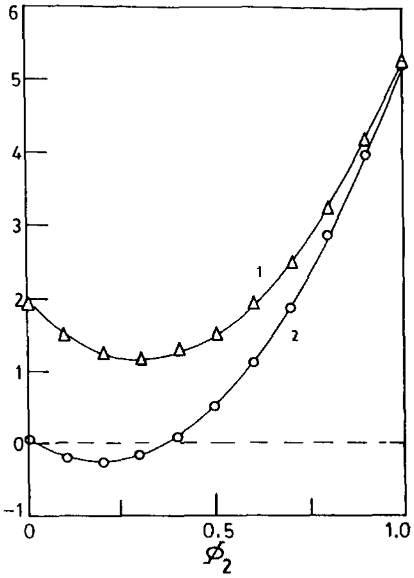

Figure 7 Plot of B_{net} vs. ϕ_2 calculated from equation (2) using B_{ij} data of *Table 1* for the PVBZ + SAN blend pair, $\phi_{\text{PVBZ}} : \phi_{\text{SAN}} = 1 : 11.54$. A mixture of toluene and AcN has been used as the analogue of SAN. Curve 1 (Δ) for methyl benzoate and curve 2 (O) for ethyl benzoate

of SAN by premixtures of AcN and toluene, the prediction is expected to be far from quantitative.

DISCUSSION

This study establishes that of the three nitriles (viz. AcN, PrN and iBuN) only AcN may be used as an analogue of PAN and of mixtures rich with it. PrN, which is the hydrogenated monomer of PAN, is very unsuitable. The basis of selecting the hydrogenated monomer as the analogue is that it has the same ($CH_3 + CH_2$)/X ratio (X = functional group) as the polymer. However, this guideline is not adequate in the case of PAN. In order to arrive at a better selection criterion for the analogue than the hydrogenated monomer guideline, we compared the solubility parameter (δ) values of the compounds concerned. The values are[30] $\delta_{\text{PAN}} = 12.75$, $\delta_{\text{AcN}} = 11.9$, $\delta_{\text{PrN}} = 10.8$ and $\delta_{\text{iBuN}} = 9.8$ (cal cm^{-3})$^{1/2}$. Thus of the three nitriles the δ value for AcN is closest to that of PAN. We are therefore led to conclude that for polar polymers the closeness of solubility parameters between the analogue and the polymer should also be given due consideration in selecting the former from compounds having the same functional group (X) as the latter.

The binary segmental interaction energy densities (B_{ij}) were calculated from the heat-of-mixing data of the pure liquids, using equation (1):

$$\Delta H_m / V = B_{ij} \phi_i \phi_j \qquad (1)$$

where ϕ_i represents the volume fraction of component i and V is the total volume of the mixture. The B_{ij} values so calculated are given in *Table 1*. The B_{ij} values for toluene–acetonitrile[16] agree well with the literature value of 8.35 cal cm^{-3}.

The B_{ij} data have been used to calculate the net interaction energy density (B_{net}) for the homopolymer–copolymer blend systems under investigation. According to the mean-field model B_{net} between a copolymer (1–2) and a homopolymer (3) system can be expressed as follows[2–4]:

$$B_{\text{net}} = B_{13}\phi_1 + B_{23}(1 - \phi_1) - B_{12}\phi_1(1 - \phi_1) \qquad (2)$$

where each B_{ij} corresponds to the interaction energy densities between various kinds of segments present in the blend and ϕ_1 is the volume fraction of component 1 in the copolymer. In order to be miscible B_{net} should be negative. For the two blend systems under study here, viz. SAN + PPA and SAN + PVBZ, B_{12} is common for both, 1 being styrene residue and 2 the acrylonitrile residue in the copolymer. The calculated B_{net} values residue in the copolymer. The calculated B_{net} values for PPA–SAN and PVBZ–SAN blends are shown in *Figures 6* and *7* respectively. For the PPA–SAN blend the miscibility window appears at $\phi_{AN} = 0.6$ to 0.9 and $\phi_{AN} = 0.4$ to 0.8 in SAN using PhAc and PhPr respectively as analogues for PPA. The compositions of the window do not agree with the experimental analogue calorimetry result shown in *Figure 5* obtained using the same analogues. This discrepancy may originate from the composition dependence of the B_{ij} parameters used in equation (2). In particular, the $\Delta H_m / V$ values shown in *Figure 1* (curve 1) and *Figure 2* for the mixing of AcN with PhPr and PhAc respectively establish that B_{23} in equation (2) is strongly composition-dependent. The discrepancy becomes more glaring for the miscibility window calculated for the PVBZ + SAN system using the B_{ij} data in *Table 1* along with the mean-field model (equation (2)), when EtBz is used as the analogue for PVBZ. The calculated result shown in *Figure 7* predicts a miscibility window at $\phi_{AN} = 0.05$ to 0.35, while the experimental calorimetry result shown in *Figure 4* shows correctly that there is no miscibility window for this homopolymer–copolymer blend pair. On the other hand, using MeBz as the analogue for PVBZ, correct predictions on the miscibility of SAN and PVBZ are obtained. The discrepancy in the results using EtBz as the analogue for PVBZ (shown in *Figure 7*) may again be traced to the strong composition dependence of B_{23}.

The present work thus shows that of the three nitriles tested (viz. AcN, PrN and iBuN) only AcN may be used as an analogue, albeit a poor one, for PAN and that too at high volume fraction of AcN, $\phi_{AcN} > 0.7$. The analogue calorimetry for SAN + PPA blends at $\phi_{SAN} = 0.92$ predicts a miscibility window that is far removed from the experimentally determined one. On the other hand, the analogue calorimetry correctly predicts the absence of any miscibility window for the SAN + PVBZ pair.

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