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Analogue Calorimetric Studies of Blends of Poly(vinyl ester)s and Polyacrylates

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ABSTRACT: Analogue calorimetry for blends of poly(vinyl ester)s and polyacrylates has been studied. Hydrogenated monomers were used as analogues of the corresponding polymers. It is found that isomeric esters differing only in the orientation of the COO group mix with only small heat change, which can be positive or negative. The values of the interaction energy density, B_{12} (in cal/cm^3), are −0.045, 0.031, and −0.076, respectively, for the following binary mixtures; ethyl acetate + methyl propionate, *n*-propyl propionate + ethyl butyrate, and phenyl propionate + ethyl benzoate. The negative heat of mixing for the two pairs of very similar liquids, although unexpected, explains why the corresponding polymers are miscible. The small positive heat of mixing for the other pair is sufficient to predict demixing of the corresponding polymers, viz., poly(*n*-propyl acrylate) and poly(vinyl butyrate), which contradicts the observation of their homogeneous mixing. This suggests that hydrogenated monomers are not always the proper analogues for vinyl polymers for the prediction of the interaction energy. A novel flow calorimeter is also described. H^E and V^E data for binary mixtures of the above esters are presented.

Introduction

Miscibility in polymer−polymer systems is principally governed by the heat of mixing because of a vanishingly small gain in combinatorial entropy in high polymer mixtures. An exothermic mixing outweighs the unfavorable equation-of-state effect on the thermodynamics of mixing.[1] Miscible polymer blends are therefore usually encountered when there exist specific interactions between the components. There are, however, some miscible polymer blends reported in the literature for which specific interactions are neither apparent nor proved.[2−20] It has been presumed that for such mixtures the like and unlike contact energies are nearly equivalent so that the van der Waals interaction energy and the heat of mixing are negligible. The very close similarity in chemical structure between the components also ensures that the equation-of-state effect would be small so that it is outweighed by the combinatorial entropy.[7,8,12−14,15−19]

However, for some similar polymer blends, e.g., polyisoprene (7−15% 3,4 linkage) + polybutadiene (12−28% 1,2 linkage)[21,22] and *cis*-1,4-polyisoprene (PIP) + poly(vinylethylene) (PVE),[23] SANS study revealed that $\chi < 0$. For the former system, the result was attributed to a subtle balance of intramolecular and intermolecular interactions as in copolymer blends. For the latter system, cross-polarization solid state NMR study revealed a closer spatial contact between the components which strengthens the van der Waals dispersion interaction resulting in exothermic mixing.[24] More recently, a two-dimensional nuclear Overhauser effect spectroscopic study suggested that the component moieties are orientationally ordered such that the methyl group in PIP is closest to the vinyl side chain of PVE, which reflects some weak specific interaction between the two groups.[25]

With regard to the miscibility of similar polymer pairs comprising poly(vinyl ester)s and polyacrylates, miscible blends are obtained only if their repeating units are isomeric differing only in the orientation of the COO group.[2−4,15−19] The following polymer pairs were proved to form miscible blends: poly(methyl acrylate) (PMA) + poly(vinyl acetate) (PVAc); poly(ethyl acrylate) (PEA) + poly(vinyl propionate) (PVPr); poly(*n*-propyl acrylate) (PPrA) + poly(vinyl butyrate) (PVBu); poly(phenyl acrylate) (PPA) + poly(vinyl benzoate) (PVBz). However, if the repeating units differ by only one CH_2 group, the respective polymers become immiscible. For example, PEA is immiscible with PVAc, PMA with PVPr or PEA, and PVAc with PVPr. It was suggested that for the isomeric polymer pairs the heat of mixing as well as the equation-of-state effect is vanishingly small.[15−19] However, in view of the exothermicity of the similar polymer blends discussed above it is of interest to have some estimate of the heats of the mixing of the present systems. This paper represents an attempt in that direction.

Cruz et al.[26] suggested that polymer blend miscibility can be reasonably well correlated with the heat of mixing of analogous small molecular weight compounds. They showed that polyester−polycarbonate blends whose small molecular weight analogues exhibit exothermic mixing are miscible whereas those whose analogues exhibit endothermic 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, analogues of poly(ethylene terephthalate) (PET), PC and PET are only partially miscible. Exceptions not withstanding, analogue calorimetry finds general acceptance as a means of estimating the enthalpy of polymer−polymer mixing.[26−38]

The heat of mixing of the small molecular weight analogues of similar polymers is expected to be very small. To measure such small heats of mixing, elimination of vapor space is necessary. To this end, we designed and fabricated a flow calorimeter in which differential change of temperature is measured by a Hewlett-Packard quartz thermometer probe. In this work, we describe the calorimeter and present the results of analogue calorimetry for the blends of poly(vinyl ester)s and polyacrylates.

Experimental Section

Materials. Analytical reagent grade benzene (BE) (E. Merck), toluene (TE) (E. Merck), ethyl acetate (EtAc) (SD)

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ethyl propionate (EtPr) (E. Merck), and ethyl benzoate (EtBz) (BDH) were dried and fractionally distilled using a 1 m long fractionating column packed with 3 mm porcelain rings. Methyl propionate (MePr), propyl propionate (PrPr), ethyl butyrate (EtBu), and phenyl propionate (PhPr) were prepared in the laboratory by following standard procedures. The products were dried and fractionally distilled.

Material Characterization. All esters were characterized by GLC and ^{1}H NMR spectra recorded using a Varian T-60 instrument at room temperature. The GLC (Hewlett-Packard 5730A) analysis showed that all the esters are more than 99.5% pure. The liquids were also characterized by measuring their densities using a Picker dynamic flow densimeter (Model 03D, Sodev Inc.) calibrated with dry nitrogen and double-distilled water at 25 °C. The accuracy of the densimeter was ±0.1%. The densities of BE, TE, AN, MePr, EtAc, EtPr, EtBu, PrPr, EtBz, and PhPr were measured to be 0.8731, 0.8620, 0.7763, 0.9099, 0.8945, 0.8843, 0.8737, 0.8767, 1.0420, and 1.0438 gm/cm^3 at 25 °C, respectively. The excess volumes of the mixtures were calculated from density measurements with a Picker flow dynamic densimeter at 25 °C. The measurement has an accuracy better than four decimal places.

Fabrication of a Flow Calorimeter. A simple flow calorimeter was designed and fabricated to measure the enthalpies of mixing. The calorimeter is of the isothermal twin differential type, and the temperature difference between the mixing cell and reference cell is measured with a 1×10^{-4} °C accuracy by incorporating two probes of a Hewlett-Packard quartz thermometer (Model 2804A) in the two cells. Both the cells are identical glass tubes 8 cm long and having a 1.8 cm i.d. Each is a part of a unsilvered Dewar vessel and contains two thin-walled flow tubes (stainless steel tube) leading to a small mixing vessel where walls are corrugated to accomplish vortex mixing. The mixture comes out of a third thin-walled tube and spirals around the thermometer probe to exchange the heat produced to the highly conducting thermometric fluid, mercury, kept in the cell and comes out as waste. A calibrating heater of 7.5 Ω resistance and made of manganin wire is wrapped around the probe. Power is supplied to the heater from a stabilized variable-power supply, and the current and voltages are measured by a $4^1/_2$ digit digital multimeter. The twin calorimeter is suspended from the brass lid, which is especially made to fit the lower part of a thick-walled glass bottle of 1000 cm^3 capacity. The bottle is filled with mercury, which acts as a constant-temperature bath without any stirring. The bottle in turn is kept in a cardboard box lined with polystyrene foam. In this form, the calorimeter is always at ambient temperature, which can be monitored before and after an experiment and is always ready for measurement. Alternatively, the bottle can be kept inside a constant-temperature bath.

The liquids are pumped by a bent axis peristaltic pump (Model P-DB, Sodev Inc.) which contains two pairs of programmable pumps. One of the liquids is mixed with itself in the reference cell with one pair of pumps while two different liquids are mixed in the mixing cell with the other pair. The liquids are sent to the calorimeter through 1.65 mm o.d. Teflon tubes and then through a 1 m long thin-walled stainless steel tube of similar outer diameter immersed in the mercury pool in order to attain the temperature of the calorimeter. A schematic diagram of the flow calorimeter is shown in Figure 1.

Calibration of the Flow Calorimeter. A standard system, benzene + toluene, is used to calibrate the calorimeter. A base line I is obtained when one of the liquids is mixed with itself in the mixing cell, as shown in Figure 2. When the base line is established, one of the inputs is replaced by the other liquid to obtain a constant deflection (base line II). The difference, II−I = ΔX, represents the heat of mixing at that composition. A known amount of heat per second is then generated by the heater and added to the mixing cell with the liquids still flowing. This produces a third baes line, base line III (as shown by the ΔT(K), $T_{\text{reference cell}} - T_{\text{mixing cell}}$, vs time plot in Figure 2). The difference III−II = ΔY represents the known amount of power delivered by the heater. From this value the heat evolved per second per cubic centimeter during mixing can be estimated, yielding the heat of mixing per mole of the mixture if the flow rate and densities are known. The flow rates are measured during each experiment by measuring the time taken by the liquids to fill a calibrated volume. The densities of the mixtures were measured by a Picker flow densimeter (Model 03D, Sodev Inc.) with an accuracy better than four decimal places.

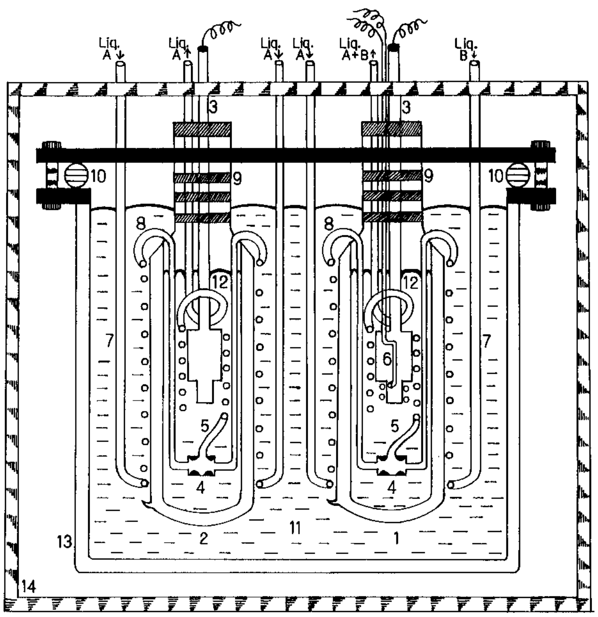

Figure 1. Schematic diagram of the flow calorimeter: 1, Dewar vessel for mixing cell; 2, Dewar vessel for reference cell; 3, Hewlett-Packard quartz thermometer probe; 4, vortex mixing chamber; 5, spiral steel tube; 6, heater; 7, thin-walled steel tube; 8, Teflon tubes; 9, Teflon rings; 10, rubber O-rings; 11, thermometric fluid mercury; 12, mercury inside the cell; 13, thick-walled glass vessel; 14, cardboard box with PS foam.

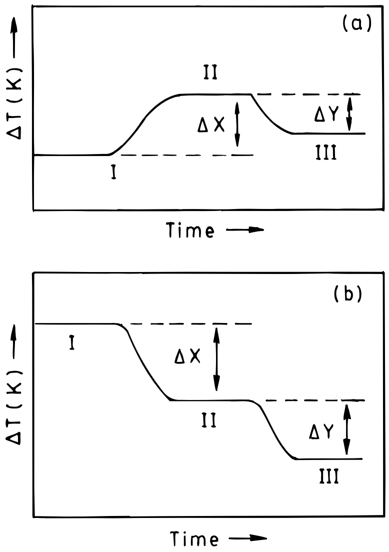

Figure 2. Change of temperature vs time plot during heat of mixing measurement by flow calorimeter: (a) endothermic system; (b) exothermic system.

We find that heats of mixing of benzene + toluene measured in this way are always smaller than the standard literature value by a certain factor.[39] This factor, an instrument calibration factor (K) is the ratio between the actual and measured heats of mixing. It is subsequently used to correct the heats of mixing of other systems. The necessity of the factor (K) arises because the calibrating heater is too large to be placed into the flowing liquids inside the tiny mixing chamber. We measured the heat of mixing of toluene + acetonitrile at various compositions, compared the results with those obtained by Orye and Prausnitz[40] at 30 °C, and obtained agreement

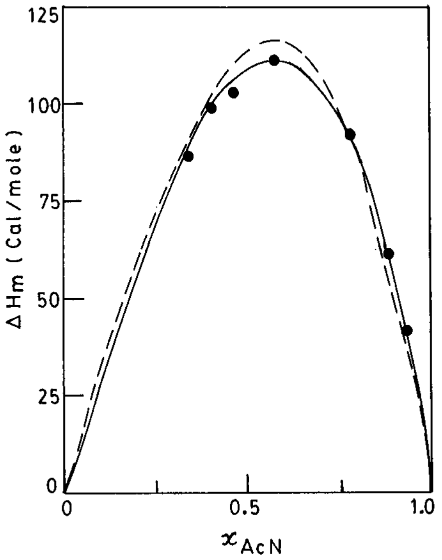

Figure 3. Heat of mixing of toluene and acetonitrile vs mole fraction of acetonitrile. The solid curve represents flow calorimeter experimental data. The dashed curve represents the calculated ΔH_m data of Orye and Prausnitz[40] at 30 °C.

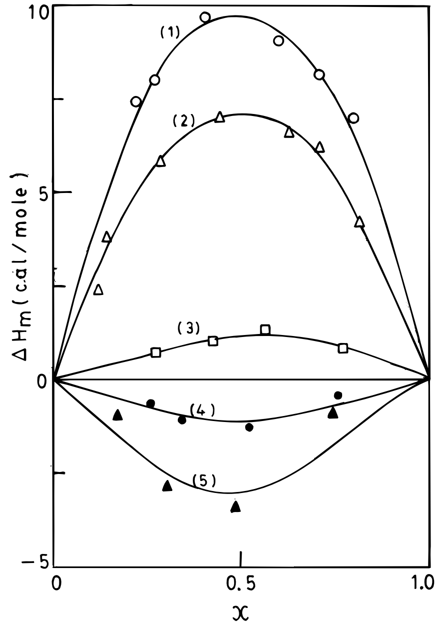

Figure 4. Heat of mixing for (1) ethyl propionate + ethyl acetate vs x_{EtPr}, (2) ethyl propionate + methyl propionate vs x_{EtPr}, (3) propyl propionate + ethyl butyrate vs x_{PrPr}, (4) methyl propionate + ethyl acetate vs x_{MePr}, and (5) phenyl propionate + ethyl benzoate vs x_{PhPr}.

within 4% as shown in Figure 3. Repeated experiments at fixed conditions showed that the heat of mixing (ΔH_m), i.e., excess enthalpies of mixing (H^E), data were reproducible within ±1%.

Results

The results of the heats of mixing for the various binary mixtures are shown in Figure 4. With regard to the PMA–PVAc blend, their hydrogenated monomers, MePr and EtAc, yield a small negative heat of mixing over the entire composition range. Since the hydrogenated monomers for both PEA and PVPr are identical, i.e., EtPr, the heat of mixing of their hydrogenated monomers is zero. For the PPrA and PVBu blend system, the hydrogenated monomers, PrPr and EtBu, yield positive (although small) heats of mixing over the entire range of composition. Similarly, as regards the PPA and PVBz blend system, the hydrogenated monomers, viz., PhPr and EtBz, yield a small negative heat of mixing over the entire range of composition. Thus, the ΔH_m values for the binary mixtures of the hydrogenated monomers corresponding to the three miscible blend systems discussed above, PMA + PVAc, PPrA + PVBu, and PPA + PVBz, are small negative or small positive.

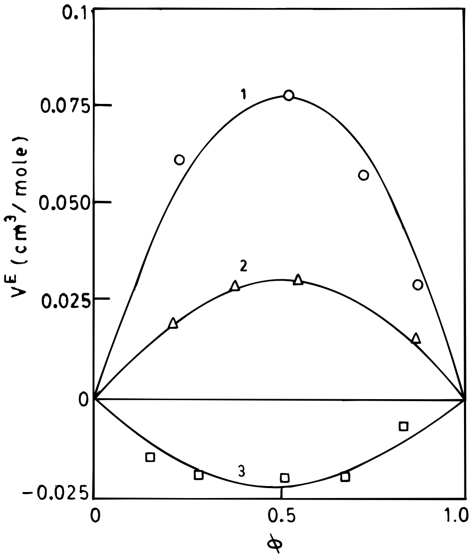

Figure 5. Excess volume for (1) phenyl propionate + ethyl benzoate vs ϕ_{PhPr}, (2) propyl propionate + ethyl butyrate vs ϕ_{PrPr}, and (3) methyl propionate + ethyl acetate vs ϕ_{MePr}.

Table 1. Binary Interaction Energy Densities (B_{12}) Calculated from Calorimetric Data

entry	liquid pairs	B_{12} (cal/cm^3)
1	MePr + EtAc	−0.45 ± 0.001
2	PrPr + EtBu	0.031 ± 0.001
3	PhPr + EtBz	−0.076 ± 0.001
4	MePr + EtPr	0.276 ± 0.005
5	EtAc + EtPr	0.378 ± 0.008

The hydrogenated monomers of the immiscible polymer pairs PMA + PVPr, PMA + PEA, PVAc + PEA, and PVAc + PVPr are MePr and EtPr for the first two pairs and EtAc and EtPr for the last two. Both the above pairs of hydrogenated monomers mix with positive heats of mixing which are much larger than for the mixtures of isomeric esters discussed above. Thus, for these four immiscible blend systems, the analogue calorimetry results agree with the miscibility results.

The excess volumes (V^E) for the mixtures of isomeric esters MePr + EtAc, PrPr + EtBu, and PhPr + EtBz are shown in Figure 5. For MePr + EtAc, V^E is negative over the entire range of composition. However, for the other two other mixtures, EtBu + PrPr and PhPr + EtBz, V^E is positive over the entire range of composition.

The binary interaction energy densities (B_{12}) were calculated from theheat of mixing of the esters, using

$$\Delta H_m/V = B_{12}\phi_1\phi_2 \qquad (1)$$

where ϕ_i represents the volume fraction of the component i and V is the volume fraction average molar volume of the mixture. Thus, plotting $\Delta H_m/V$ as a function of ϕ_1 and obtaining the best fit curve by least-squares treatment, B_{12} values are obtained and given in Table 1.

Table 2. Values of Free Energy of Mixing Parameters[a]

blend systems	X_{12} (J/cm^3)	$\frac{\chi^*_{12,\mathrm{Int}}}{V^*_1}$ (mol/cm^3)	$\frac{\chi^*_{12,\mathrm{FV}}}{V^*_1}$ (mol/cm^3)	$\frac{\chi^*_{12}}{V^*_1}$ (mol/cm^3)	$\frac{\chi^*_{12,\mathrm{Crit}}}{V^*_1}$ (mol/cm^3)
PMA−PVAc[b]	−0.188	-6.44×10^{-5}	9.1×10^{-6}	-5.53×10^{-5}	1.045×10^{-5}
PPrA−PVBu	0.130	4.45×10^{-5}			1.102×10^{-5}

[a] Component 1 is poly(vinyl ester), and component 2 is polyacrylate. [b] Equation-of-state parameters for this system were obtained from ref 16.

In the following part, we have examined how good the analogues are in supporting the miscibility results of their corresponding polymers. In doing so, we have calculated the interaction parameter, χ^*_{12}, as defined by Flory−Prigogine−Patterson.[41−46] The modified form of the corresponding states theory of Patterson and Delmas[45] is given as

$$\chi^*_{12} = \chi^*_{12,\mathrm{Int}} + \chi^*_{12,\mathrm{FV}} \tag{2}$$

$$\frac{\chi^*_{12}}{V^*_1} = \frac{X_{12}}{\tilde{V}_2 RT} + \frac{P^*_1}{RT}\left[\frac{1}{\tilde{V}_1} - \frac{1}{\tilde{V}_2} + 3\tilde{T}_1 \ln \frac{\tilde{V}_1^{1/3} - 1}{\tilde{V}_2^{1/3} - 1}\right] \tag{3}$$

Where V^*_1 is the molar core volume of component 1, X_{12} is the exchange interaction parameter, $\tilde{V}_1$ and $\tilde{T}_1$ are the reduced volume and reduced temperature of component 1, respectively, $\tilde{V}^{1/3} = 1 + \alpha T/3(1 + \alpha T)$, and $\tilde{T} = (\tilde{V}^{1/3} - 1)\tilde{V}^{-4/3}$, where α is the coefficient of cubic expansion. Equation 2 shows that χ^*_{12} consists of two terms: (i) interactional ($\chi^*_{12,\mathrm{Int}}$) and (ii) free volume ($\chi^*_{12,\mathrm{FV}}$). For miscible polymer blends, χ^*_{12} must be lower than $\chi^*_{12,\mathrm{Crit}}$, which is defined by[1]

$$\frac{\chi^*_{12,\mathrm{Crit}}}{V^*_1} = \frac{1}{2}\left[\frac{1}{V_1^{*1/2}} + \frac{1}{V_2^{*1/2}}\right]^2 \tag{4}$$

In calculating the χ^*_{12} values from eq 3, we have taken the value of the X_{12} parameter equal to that of the interaction energy density, B_{12}, of polymer analogues. The values of the latter are given in Table 1.

The data for the characteristic equation-of-state parameters P^*, V^*, and T^* for the polymer pairs under investigation are not available in the literature. Hence, χ^*_{12} for all the polymer pairs could not be calculated. The calculated values are given in Table 2.

The results show that $\chi^*_{12,\mathrm{Int}}$ for PMA−PVAc blend is negative and this added to $\chi^*_{12,\mathrm{FV}}$ is less than $\chi^*_{12,\mathrm{Crit}}$. The case for PPA−PVBz blend should be similar, where $\chi^*_{12,\mathrm{Int}}$ is negative. For this system, however, χ^*_{12} could not be calculated using eq 3 because of the nonavailability of the P^* and V^* data for the polymers concerned. On the other hand, for the PPrA−PVBu blend, $\chi^*_{12,\mathrm{Int}}$ is positive and it alone is greater than the $\chi^*_{12,\mathrm{Crit}}$. The analogue calorimetry results for this blend suggests that the heat of mixing of the polymers has a small positive, value, sufficient to make the system immiscible. This contradicts the miscibility found experimentally. Thus, hydrogenated monomers are not always proper analogues for the corresponding vinyl polymers.

Discussion

The analogues used here are all esters. For the aliphatic esters, there exists no specific interactions. For the two aromatic esters PhPr and EtBz, however, one can recognize sites of specific interactions, e.g., between the π electrons of the benzene ring acting as the donor and C=O group acting as the acceptor.[47,48] The two binary mixtures of isomeric aliphatic esters, MePr + EtAc and PrPr + EtBu, represent van der Waals mixtures and their heat of mixing should therefore be positive.[49−52] The magnitude of the heat change should be small in view of the close similarity in the chemical structure of the components. This is reflected in their solubility parameters[53] [$\delta_{\mathrm{MePr}} = 8.9$, $\delta_{\mathrm{EtAc}} = 9.1$, $\delta_{\mathrm{PrPr}} = 8.5$, $\delta_{\mathrm{EtBu}} = 8.5$] (in (cal/cm^3)$^{1/2}$), which are very close for the isomeric esters. The negative ΔH_{m} for MePr + EtAc is quite unexpected for a van der Waals mixture.[49−52] However, Tomlin and Roland[23] suggested that van der Waals mixtures with nearly equivalent like and unlike contact energies can give rise to exothermic mixing if the unlike contacts are more closely spaced. In conformity with this hypothesis, the mixtures of MePr + EtAc have been found to have a negative V^{E}.

For the mixture of the two isomeric aromatic esters PhPr + EtBz, the specific interaction between the unlike molecules may be stronger than between the like molecules leading to exothermic mixing.

The large positive ΔH_{m} for mixtures of nonisomeric esters are quite expected for van der Waals mixtures with components differing substantially in their intermolecular energies, as evident from their solubility parameters [$\delta_{\mathrm{MePr}} = 8.9$, $\delta_{\mathrm{EtPr}} = 8.4$, $\delta_{\mathrm{EtAc}} = 9.1$] for the combinations MePr + EtPr and EtPr + EtAc.

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