Binary Interactions in Dimethyl Terephthalate/bis(2-ethylhexyl)adipate/Poly(vinyl chloride) Blends Studied by Melting Point Depression Method

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SYNOPSIS

A novel approach is developed to estimate the interaction energy density, B, of polymer solutions by the melting point depression method using a crystallizable molecule as the probe. It rests on the classical Flory–Huggins lattice model of polymer solutions, and considers the polymer–solvent interaction parameter to be concentration dependent. The ternary system dimethyl terephthalate (DMT)/bis(2-ethylhexyl)adipate (DOA)/poly(vinyl chloride) (PVC) is chosen for the present study. The data of B for the three possible binary interactions are reported as the functions of composition at elevated temperatures. For a plasticized PVC resin containing 20 vol % DOA, the B is estimated to be 6 MJ m^{-3}, which is approximately 2 MJ m^{-3} higher than the B value cited in the literature for the PVC mixed with almost 100% DOA. The thermodynamic stability of the ternary system is discussed. © 1996 John Wiley & Sons, Inc.

INTRODUCTION

Despite the advances of the contemporary theories of polymer solutions,[1-3] such as the Flory–Prigogine equation-of-state theory, the classical Flory–Huggins (FH) lattice model[4] is still prevalent. Perhaps one of the most noteworthy features of the FH theory is the description of the exchange interaction energy between a solvent molecule and an equivalent polymer segment in solution, in terms of a single physical factor known as the polymer–solvent or FH interaction parameter designated by χ. This particular parameter is accessible by various methods as reviewed by Orwoll[5] and Bonner.[6]

The compatibility of a plasticizer with poly(vinyl chloride) (PVC) may depend considerably on the intensity of interactions between the two components.[7] As such it is informative to know the values of χ for some relevant systems. Doty and Zable[8] resorted to the equilibrium swelling method to investigate the compatibility of a series of dialkyl phthal-

ates with PVC. On the basis of the FH theory of the melting point depression of polymers in the presence of diluent, Anagnostopoulos et al.[9,10] established a simple method to monitor the parameter χ for the plasticized PVC resins. The experimental technique of this particular method was further improved by Bigg[11] who compared the various approaches for the χ determinations. Recently, Chee reported a dilute solution-viscosity method to study the PVC–plasticizer interactions at the intermediate temperatures.[12] A common feature of the foregoing methods is that they only result in information for PVC solutions of infinite dilution. The main objective of the present work is to develop a novel approach to determine the interaction energy density (B), which is related to χ, of PVC–plasticizer blends at various compositions. To the best of our knowledge, this is the first attempt on these measurements, which apparently are unattainable by osmometric pressure, vapor sorption, and other conventional methods, because of the nature of the systems. It is well known that the equilibrium melting processes of semicrystalline polymers are formidable to be realized experimentally due to various morphological defects. On the other hand, a low molecular weight com-

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pound would display a sharp melting point, which is more amenable. In the present study, dimethyl terephthalate (DMT), which exhibits well-defined melting endotherms by differential scanning calorimetry (DSC),[13] is selected as the probe.

METHOD DEVELOPMENT

Consider a ternary system consisting of n_i moles of component i with the number of segments per molecule equal to x_i, where $i = 1, 2, 3$ and $x_3 \gg x_1, x_2$. The free energy of mixing, ΔG_m, at the temperature T is given by the FH theory as[4]

$$\Delta G_m = RT\left[\sum_{i=1}^{3} n_i \ln \phi_i + \sum_{\substack{j>i=1 \\ j\leq 3}}^{2} \chi_{ij} n_i \chi_i \phi_j\right] \quad (1)$$

where χ_{ij} is the FH interaction parameter for components i and j, ϕ_i is the normalized volume fraction of the ith component in the ternary system, and R is the gas constant. Partial differentiation of ΔG_m with respect to n_1 yields the difference between the chemical potential of the component in the solution and that of the pure state at T, $\Delta\mu_1$, that is,

$$\Delta\mu_1 = RT\left[\ln \phi_1 + \phi_2\left(1 - \frac{x_1}{x_2}\right) + \phi_3\left(1 - \frac{x_1}{x_3}\right)\right.$$
$$\left. + (1 - \phi_1)x_1(\phi_2 g_{12} + \phi_3 g_{13}) - \phi_2\phi_3 x_1 \chi_{23}\right] \quad (2)$$

where the concentration-dependent parameters

$$g_{12} = \chi_{12} + \phi_1\partial\chi_{12}/\partial\phi_1 \quad (2a)$$

$$g_{13} = \chi_{13} + \phi_1\partial\chi_{13}/\partial\phi_1. \quad (2b)$$

By setting $\phi_3 = 0$, eq. (2) reduces to the $\Delta\mu_1$ for the binary mixture of components 1 and 2 designated by

$$\Delta\mu_1' = RT\left[\ln \theta_1 + \theta_2\left(1 - \frac{x_1}{x_2}\right) + \theta_2^2 y_{12}\right] \quad (3)$$

where

$$y_{12} = \chi_{12} + \theta_1\partial\chi_{12}/\partial\theta_1 \quad (3a)$$

and θ_1, θ_2 are, respectively, the normalized volume fractions of components 1 and 2 in the solution. Analogously, the binary system consisting of components 1 and 3 with normalized volume fractions

κ_1 and κ_3, respectively, results in the chemical potential difference of the component 1 ($\Delta\mu_1''$) given by

$$\Delta\mu_1'' = RT\left[\ln \kappa_1 + \kappa_3\left(1 - \frac{x_1}{x_3}\right) + \kappa_3^2 y_{13}\right] \quad (4)$$

where

$$y_{13} = \chi_{13} + \kappa_1\partial\chi_{13}/\partial\kappa_1. \quad (4a)$$

Because the parameters χ_{12} and χ_{13} extracted from eqs. (3) and (4) are dependent on θ_1 and κ_1, respectively, we propose to convert eqs. (2a) and (2b) to

$$g_{12} = \chi_{12} + \theta_1\theta_2\partial\chi_{12}/\partial\theta_1 \quad (5)$$

$$g_{13} = \chi_{13} + \kappa_1\kappa_3\partial\chi_{13}/\partial\kappa_1. \quad (6)$$

If component 1 is a crystalline molecule characterized by the molar heat of fusion $\Delta\bar{H}_{m1}^{\circ}$ and equilibrium melting point T_{m1}°, which may be depressed to T_{m1} in a ternary solution of volume fractions ϕ_1, ϕ_2, and ϕ_3, the Flory theory of melting point depression[4] shows

$$\Delta\mu_1 = \Delta\bar{H}_{m1}^{\circ}(T_{m1}/T_{m1}^{\circ} - 1). \quad (7)$$

The interaction energy density B_{ij} of the components i and j is defined by

$$B_{ij} = RT\chi_{ij}/\bar{V}_i \quad (8)$$

where $\bar{V}_i$ is the molar volume of component i, hereafter. In the present analysis, we assume $x_1 = 1$, $x_1/x_2 = \bar{V}_1/\bar{V}_2$, and $x_1/x_3 = \bar{V}_1/\bar{V}_3$. Combining eqs. (2), (7), and (8) yields

$$B_{23} = [\Delta\bar{H}_{m1}^{\circ}(1 - T_{m1}/T_{m1}^{\circ})/\bar{V}_1$$
$$+ RT_{m1}[\ln \phi_1 + \phi_2(1 - \bar{V}_1/\bar{V}_2)$$
$$+ \phi_3(1 - \bar{V}_1/\bar{V}_3)]/\bar{V}_1$$
$$+ (1 - \phi_1)[\phi_2 b_{12} + \phi_3 b_{13}]]\bar{V}_1/\phi_2\phi_3\bar{V}_2 \quad (9)$$

where

$$b_{12} = B_{12} + \theta_1\theta_2\partial B_{12}/\partial\theta_1 \quad (9a)$$

$$b_{13} = B_{13} + \kappa_1\kappa_3\partial B_{13}/\partial\kappa_1. \quad (9b)$$

Analogously, the binary systems defined by eqs. (3) and (4) would lead to

$$y_{12} = [\Delta\bar{H}^{\circ}_{m1}(1/T^{\circ}_{m1} - 1/T'_{m1})/R$$
$$- \ln\theta_1 - \theta_2(1 - \bar{V}_1/\bar{V}_2)]/\theta_2^2 \quad (10)$$

$$y_{13} = [\Delta\bar{H}^{\circ}_{m1}(1/T^{\circ}_{m1} - 1/T''_{m1})/R$$
$$- \ln\kappa_1 - \kappa_3(1 - \bar{V}_1/\bar{V}_3)]/\kappa_3^2 \quad (11)$$

where T'_{m1} and T''_{m1} are the corresponding melting point of component 1. With the aid of eqs. (3a), (4a), and (8), we obtain

$$B_{12} = \left[\int_{\theta'_1}^{\theta_1} z_{12}\, d\theta_1 + \theta'_1 B_{12}(\theta'_1)\right]\Big/\theta_1 \quad (12)$$

$$B_{13} = \left[\int_{\kappa'_1}^{\kappa_1} z_{13}\, d\kappa_1 + \kappa'_1 B_{13}(\kappa'_1)\right]\Big/\kappa_1 \quad (13)$$

where

$$z_{12} = RT'_{m1}y_{12}/\bar{V}_1 \quad (13a)$$

$$z_{13} = RT''_{m1}y_{13}/\bar{V}_1. \quad (13b)$$

Here, θ'_1 and κ'_1 indicate the concentrations under the boundary conditions. Certainly, eqs. (12) and (13) would facilitate the computations of B_{12} and B_{13}, and subsequently the parameter B_{23} via eq. (9).

EXPERIMENTAL

DMT was purchased from Aldrich and purified by means of sublimation at ca. 138°C under vacuum. However, the PVC of medium molecular weight and bis(2-ethylhexyl)adipate (DOA) were used as received from Aldrich and Kasei (Tokyo), respectively.

Appropriate amounts (ca. 3–5 mg) of DMT and DOA were weighed accurately into the high pressure DSC pans, which were encapsulated and annealed in an oven at 160°C for ca. 2 h. Only sample pans ·that did not leak were selected for the DSC runs. For the PVC blends, reagent grade tetrahydrofuran (THF) was used as the solvent to facilitate thorough mixing. The solvent was removed by evaporation at ambient temperature. The samples were finally dried in a vacuum oven at 50°C to constant weight. About 3 mg of each sample was sealed in an aluminum pan as described above for the DSC measurements.

A Perkin–Elmer DSC-7 was employed in the present investigations. The instrument was calibrated against cyclohexane and indium at a heating rate of 10 K/min using nitrogen as the purge gas. All the DSC measurements were performed from 25

to 160°C using the above scanning conditions. The melting point (T_{m1}) of a sample was derived from the peak temperature of the melting endotherm. The reproducibility of T_{m1} was estimated after rescanning the sample at least twice. The heat of fusion of DMT (ΔH°_{m1}) was determined by the area under the sharp melting peak of pure DMT as recorded by the TADs standard program.

Intrinsic viscosity ($[\eta]$) measurement was performed on solutions of the PVC in THF at 25°C.

The linear least squares method was applied for data treatments.

RESULTS AND DISCUSSION

The present analysis designates DMT, DOA, and PVC as components 1, 2, and 3, respectively. The DSC measurements resulted in $T^{\circ}_{m1} = 417.1 \pm 0.2$ K and $\Delta\bar{H}^{\circ}_{m1} = 31.90 \pm 0.10$ kJ mol^{-1}.

The $[\eta]$ of the PVC solution was found to be 0.089 mol^3 kg^{-1}, corresponding to $\bar{M}_v = 7.6 \times 10^4$, where $\bar{M}_v$ is the viscosity-average molecular weight. Hence, we assume $x_1/x_3 \ll 1$ is the ensuing treatment.

With the aid of the following information on density[14] (ρ) for bis(2-ethylhexyl) terephthalate ($\rho = 0.9835$ Mg m^{-3}), dimethyl phthalate ($\rho = 1.190$ Mg m^{-3}), and bis(2-ethylhexyl)phthalate ($\rho = 0.982$ Mg m^{-3}), the ρ of DMT at 25°C was estimated to be 1.194 Mg m^{-3} by the group contribution method.[15] The isothermal expansion coefficient of DMT (α) may be estimated by $\alpha T^{\circ}_{m1} = 0.11$ as proposed by Bondi.[16] It follows that the specific volume ($v = 1/\rho$) of DMT, designated by v_1, is a function of temperature T (K) given by

$$\ln v_1 = -0.2564 + 2.6 \times 10^{-4}T \quad (14)$$

where v_1 is in m^3 Mg^{-1} hereafter. The corresponding equation of v and ρ, respectively, for DOA (v_2) and PVC in the rubbery state (ρ_3) are obtainable from the literature[12,14] and listed as follows:

$$\ln v_2 = -0.1363 + 7.3 \times 10^{-4}T \quad (15)$$

$$\rho_3 = 1.646 - 7.8 \times 10^{-4}T. \quad (16)$$

The foregoing information is essential for the ensuing analysis.

Figures 1 and 2(A) display the typical melting behavior of a binary and a ternary system, respectively. It is striking that the latter exhibits two reproducible melting peaks with the major one defining the T_{m1}. The minor transition may be caused by the
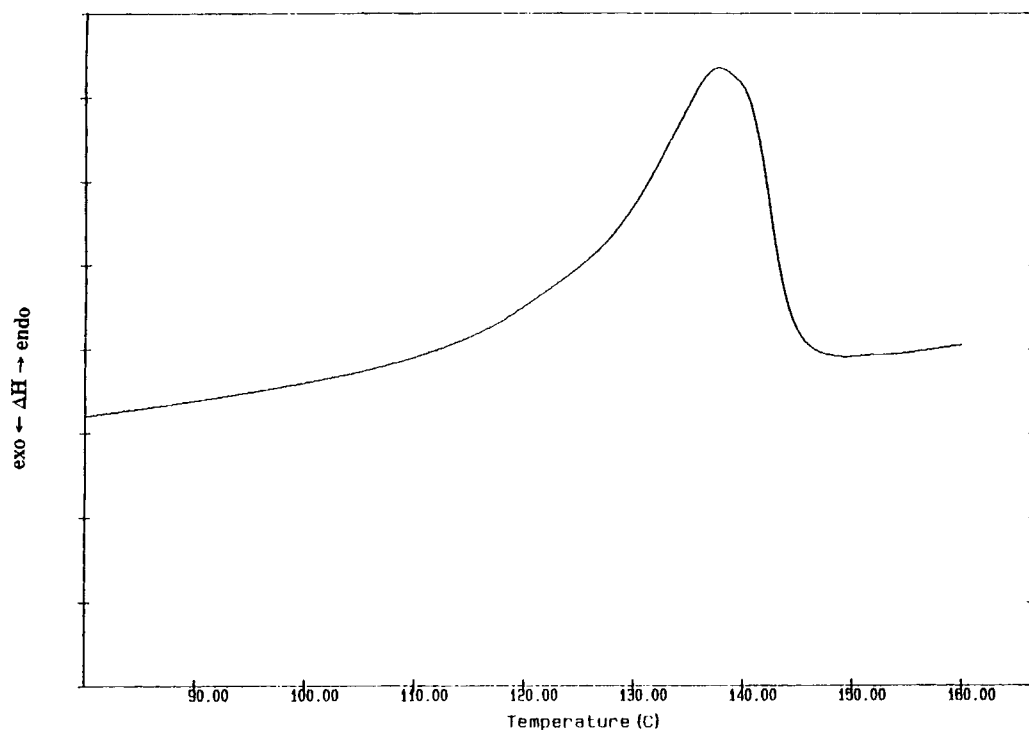
Figure 1 DSC thermogram of DMT/PVC with $w_1 = 0.498$ (Table I), heating rate 10 K/min.
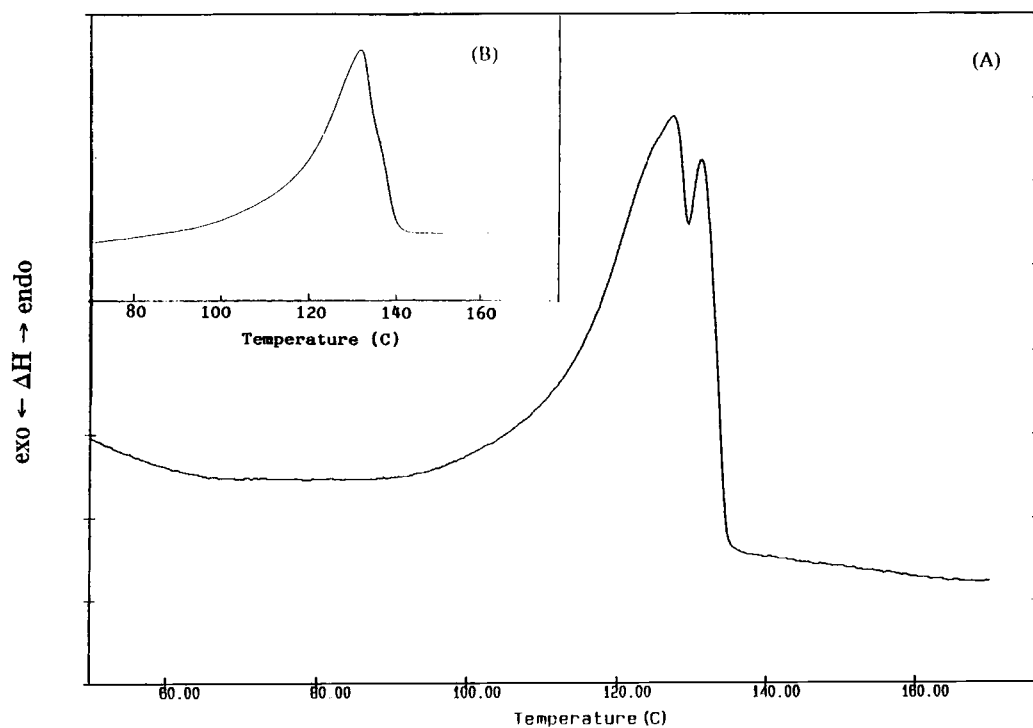

Figure 2 DSC thermograms of DMT/DOA/PVC with $w_1 = 0.4904$, and $w_2 = 0.1215$ (Table I): (A) heating rate 10 K/min, (B) heating rate 40 K/min.

melting of DMT crystallites of different sizes and higher thermal stability, and has no significant effect on T_{m1} and thus the present analysis. On this basis, one would expect the two distinct peaks to merge and form a single melting endotherm at the higher heating rates. Indeed, this is evidenced as in Figure 2(B). However, if this dual melting behavior resulted from the phase separation, the following considerations would be impossible. Hence, it is vital to show that the systems of interest are positively thermally stable. This will be elaborated later.

Table I lists the data of T_{m1} for the systems studied. The weight fraction of DMT (w_1) in the binary solutions varies from approximately 0.40–0.85, whereas that in the ternary system is around 0.50. It is noted that a low w_1 would broaden the melting peak considerably, hence defying the reliable determination of T_{m1}. On the other hand, a solution of high DMT content is equally undesirable due to the high relative precisions in the concentrations of the other components.

For the binary systems DMT/DOA and DMT/PVC, eqs. (10) and (11) yield y_{12} and y_{13}, which are applied to compute z_{12} and z_{13}, respectively. Figure 3 shows that the data of z_{12} (MJ m^{-3}) and z_{13} (MJ m^{-3}) thus obtained, are fitted satisfactorily by the following empirical expressions

$$z_{12} = 12.06 - 22.8\theta_1 \quad \text{for } \theta_1 \le 0.54; \quad (17a)$$

$$z_{12} = 4.594 - 107\theta_1^5 \quad \text{for } \theta_1 > 0.54; \quad (17b)$$

$$z_{13} = 9.168 - 39.9\kappa_1 \quad \text{for } \kappa_1 \le 0.74; \quad (18a)$$

$$z_{13} = -1.315 - 156\kappa_1^7 \quad \text{for } \kappa_1 > 0.74 \quad (18b)$$

with the standard errors of estimate of z_{12} or z_{13} equal to 0.54, 0.88, 0.29, and 1.7 MJ m^{-3}, respectively. Substituting eqs. (17a) and (17b) into (12) and (18a) and (18b) into (13) result in B in MJ m^{-3}, i.e.

$$B_{12} = 12.06 - 11.4\theta_1 \quad \text{for } \theta_1 \le 0.54; \quad (19a)$$

$$B_{12} = 1.15/\theta_1 + 4.59 - 18\theta_1^5$$
$$\text{for } \theta_1 > 0.54; \quad (19b)$$

$$B_{13} = 9.168 - 20\kappa_1 \quad \text{for } \kappa_1 \le 0.74; \quad (20a)$$

$$B_{13} = -1.44/\kappa_1 - 1.315 - 19.5\kappa_1^7$$
$$\text{for } \kappa_1 > 0.74. \quad (20b)$$

The data of B_{12} computed by eqs. (19a) and (19b) are compared with the results on B_{13} from eqs. (20a) and (20b) in Figure 4(A). A common feature of the two curves is the decrease of the gradients $d\,B_{12}/d$

Table I Melting Behavior of DMT in Various Systems

	1	2	3	4	5	6	7	8	9	10	11	12
DMT/DOA												
w_1[a]	0.399	0.431	0.458	0.505	0.543	0.577	0.620	0.640	0.692	0.762	0.804	0.844
T'_{m1}[b] (K)	391.7	393.1	395.1	398.0	398.7	400.9	402.5	403.5	404.8	406.6	408.5	409.9
DMT/PVC												
w_1	0.377	0.453	0.498	0.543	0.600	0.698	0.757	0.779	0.843	0.889		
T''_{m1}[b] (K)	398.5	402.2	404.0	406.2	408.2	412.1	412.9	412.9	414.4	415.2		
DMT/DOA/PVC												
w_1	0.4784	0.4904	0.4992									
w_2[c]	0.0825	0.1215	0.1636									
T'_{m1}[b] (K)	401.2 ± 0.4	400.6 ± 0.3	399.4 ± 0.3									

[a] Weight fraction of DMT.
[b] Melting point of DMT.
[c] Weight fraction of DOA.
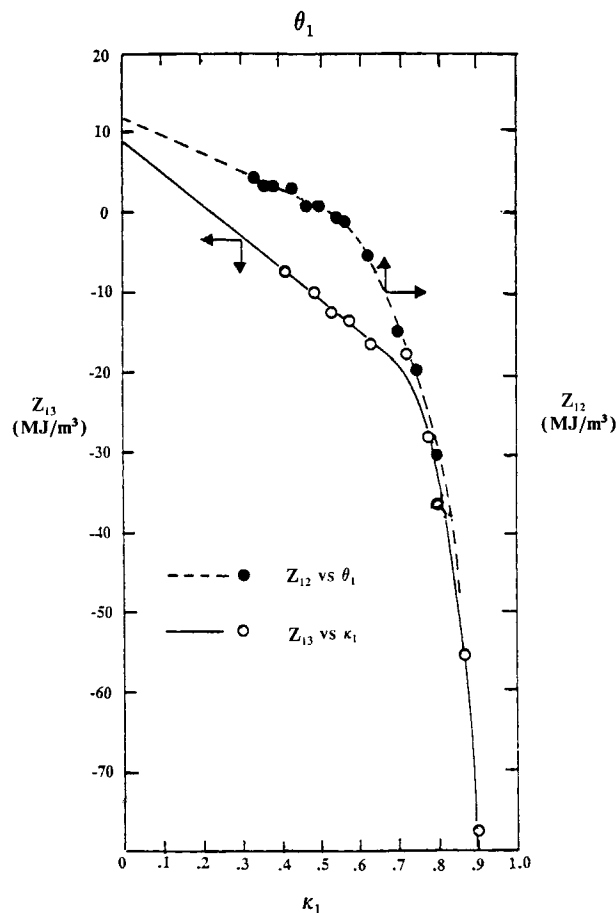
Figure 3 Plots of ($\cdot\cdot\cdot$, $\bullet$) z_{12} against θ_1, and ($-$, $\circ$) z_{13} against κ_1. The data points are based on the DSC melting endotherms, whereas the curves are drawn according to eqs. (17a)-(18b).

θ_2 and $d\,B_{13}/d\,\kappa_3$ with increasing amounts of DOA and PVC, respectively, until the linear portions are realized. Clearly, the thermodynamic interactions between DMT and PVC are more intense than the dispersion and dipolar forces between the ester groups of the DMT and DOA over the whole range of compositions. At the limiting dilutions where κ_3 approaching zero, the B_{13} is equal to -22 MJ m^{-3}, indicating the strong interaction between the carbonyl group of DMT and the α hydrogen of the PVC chain.

The solubility parameter of the ith component (δ_i') may be estimated by the group additivity method. On the basis of the Small's molar-attraction constants,[14] the relevant data in (MJ m^{-3})$^{1/2}$ for DMP, DOA, and PVC are, respectively, found to be 21.5(δ_1'), 17.3(δ_2'), and 19.8(δ_3'). Because $B_{ij} = (\delta_i' - \delta_j')^2$, it follows that $B_{12} > B_{13}$. Indeed, this prediction is in line with the curves shown in Figure

4(A). Equation (9) shows that B_{23} can be obtained from the T_{m1} data listed in Table I for the ternary system DMT/DOA/PVC, because the quantities b_{12} and b_{13} are accessible by combining eqs. (9a) and (9b), and (19a)-(20b). The results are shown in Figure 4(B), which also includes the literature datum of B_{23} at $\delta_3 = 0$.[12] Here, δ_3 is the volume fraction of component 3 in a binary blend of components 2 and 3. Although the data points are somewhat scattered, the linear relationship, represented by the straight line drawn, is indeed valid within the experimental error. The data on δ_2' and δ_3' predict agreeable $B_{23} = 5.8$ MJ m^{-3}. As noted, the change of the intensity of the PVC-ester interactions with concentration is less drastic for the case of DOA than for the aromatic DMT.

The distinct features of the composition profile of the B_{ij} are best examined by the equation-of-state theory,[1-3] which unfortunately is inaccessible for the foregoing systems in the sense that the relevant physical characteristics of the various components are not available.

We are now in the position to estimate the values of the second partial derivatives of molar free energy
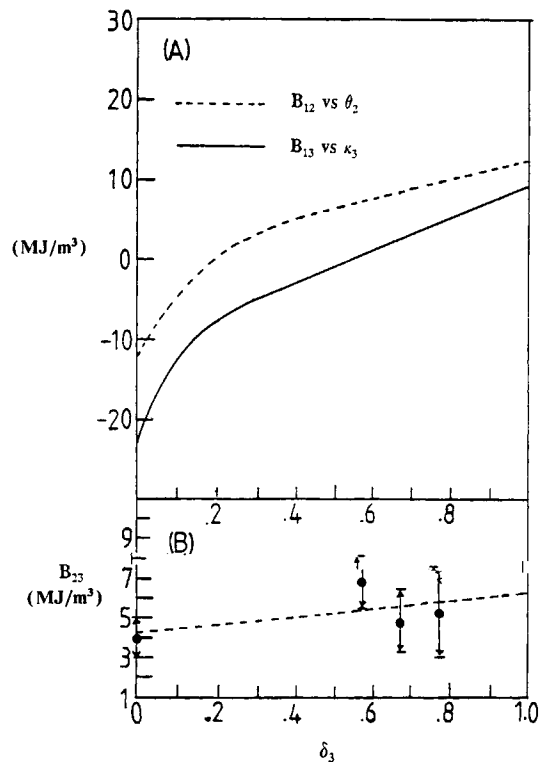

Figure 4 (A) Composition dependence of interaction energy density for ($\cdot\cdot\cdot$) DMT/PVC and ($-$) DMT/DOA as predicted by eqs. (19a)-(20b). (B) Plot of B_{23} against δ_3 for DOA/PVC blends. The error bars are indicated.

Table II Derivatives of Molar Free Energy for DMT/DOA/PVC

No.	$\bar{G}_{11} \times 10^{-3}$ (J/mol)	$\bar{G}_{22} \times 10^{-3}$ (J/mol)	$\bar{G}_{12} \times 10^{-3}$ (J/mol)	$D \times 10^{-7}$ (J/mol)^2
1	8.2	4.2	−1.1	3.3
2	8.3	1.6	−0.27	1.3
3	8.5	0.5	0.33	0.42

($\bar{G}_{ij}$) and factor D as detailed in the Appendix. The results are summarized in Table II, based on the B_{ij}-volume fraction relationships shown in Figure 4(A) and (B). Clearly, $\bar{G}_{11}$ and D are both positive for all three ternary mixtures, thus supporting the foregoing exercise.

In conclusion, the thermodynamic interactions between two amorphous compounds may be studied by the melting point depression method by introducing a third crystallizable component as the probe in the solution. Evidently, this particular technique may be readily adapted to study the miscibility of polymer–polymer blends, which is of growing interest recently, by employing an appropriate probe of high T_m. The present finding reveals that PVC interacts much stronger with the linear aromatic ester DMT than with the linear aliphatic plasticizer DOA at the elevated temperatures and infinite dilution. However, the difference between the two esters is less pronounced in terms of B (i.e., $|B_{23} - B_{13}|$), over the practical range of plasticizer loading (ca. 10–30%) in the PVC plastisols as illustrated by Figure 4(A) and (B).

APPENDIX

Equation (1) can be arranged to yield the molar free energy of mixing, $\Delta\bar{G}_m$,[17] that is,

$$\Delta\bar{G}_m = \Delta G_m / \sum n_i x_i$$

$$= RT\left[\sum_{i=1}^{3} \phi_i \ln \phi_i / x_i + \sum_{\substack{j>i=1 \\ j\leq 3}}^{2} \chi_{ij}\phi_i\phi_j\right]. \quad (A.1)$$

Hence, the second partial derivatives defined as follows can be obtained readily

$$\bar{G}_{11} = \partial^2\Delta\bar{G}_m/\partial\phi_1^2$$

$$= RT\left[\frac{1}{x_1\phi_1} + \frac{1}{x_3\phi_3} + \phi_2(2\chi'_{12}\right.$$

$$+ \phi_1\chi''_{12}) - 2(\chi_{13} + \phi_1\chi'_{13})$$

$$\left. + \phi_3(2\chi'_{13} + \phi_1\chi''_{13})\right] \quad (A.2)$$

$$\bar{G}_{22} = \partial^2\Delta\bar{G}_m/\partial\phi_2^2$$

$$= RT\left[\frac{1}{x_2\phi_2} + \frac{1}{x_3\phi_3} + \phi_2(2\chi^*_{12}\right.$$

$$+ \phi_2\chi^{**}_{12}) - 2(\chi_{23} + \phi_2\chi^*_{23})$$

$$\left. + \phi_3(2\chi^*_{23} + \phi_2\chi^{**}_{23})\right] \quad (A.3)$$

$$\bar{G}_{12} = \partial^2\Delta\bar{G}_m/\partial\phi_1\partial\phi_2$$

$$= RT\left[\frac{1}{x_3\phi_3} + (\chi_{12} + \phi_{12}\chi^*_{12})\right.$$

$$+ \phi_1(\chi'_{12} + \phi_2\chi'^*_{12}) - (\chi_{13} + \phi_1\chi'_{13})$$

$$\left. - (\chi_{23} + \phi_2\chi^*_{23})\right] \quad (A.4)$$

where

$$\chi'_{ij} = \partial\chi_{ij}/\partial\phi_1 \quad (A.5)$$

$$\chi''_{ij} = \partial^2\chi_{ij}/\partial\phi_1^2 \quad (A.6)$$

$$\chi^*_{ij} = \partial\chi_{ij}/\partial\phi_2 \quad (A.7)$$

$$\chi^{**}_{ij} = \partial^2\chi_{ij}/\partial\phi_2^2 \quad (A.8)$$

$$\chi'^*_{ij} = \partial^2\chi_{ij}/\partial\phi_1\partial\phi_2. \quad (A.9)$$

Because the parameter χ_{ij} depends mainly on the volume fraction of component i (or j), we propose to correlate ϕ_i and other concentration units defined for the binary systems by

$$\theta_1 = \phi_1/(\phi_1 + \phi_2) \quad (A.10)$$

$$\kappa_1 = \phi_1/(\phi_1 + \phi_3) \quad (A.11)$$

$$\delta_2 = \phi_2/(\phi_2 + \phi_3). \quad (A.12)$$

Certainly, eqs. (A.5)–(A.12) would facilitate the computations of $\bar{G}_{11}$, $\bar{G}_{22}$, and $\bar{G}_{12}$ via eqs. (A.2)–(A.4). A ternary solution is thermodynamically stable if the factor D defined by

$$D = \bar{G}_{11}\bar{G}_{12} - \bar{G}_{12}^2 \quad (A.13)$$

and $\bar{G}_{11}$ are both positive.[18] This criterion is applied in the present analysis.

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