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Calorimetric and small-angle neutron scattering investigation of an ethylene–vinyl acetate blend

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The enthalpy of mixing at 341.45 K of an ethylene–vinyl acetate copolymer mixed with a docosanyl diester of poly(ethylene glycol) has been determined as a function of composition by mixing calorimetry. Endothermic enthalpies were obtained with values in the range 2 to 15 J mol^{-1}. Small-angle neutron scattering has been used on similar mixtures where the diester was perdeuterated to obtain the effective interaction parameter over the temperature range 353 to 383 K for a volume fraction of ethylene–vinyl acetate copolymer in the mixture from 0.81 to 0.27. The temperature dependence of this effective interaction parameter has been used to obtain the enthalpic contribution. This latter parameter was compared with that obtained from the enthalpy of mixing. Although exact agreement is not obtained, the values are reasonably close and the differences can be attributed to the effect of deuterium labelling on the interaction between the constituents of the polymer blend.

(Keywords: polymer blends; interaction parameter; enthalpic contribution)

INTRODUCTION

A knowledge of the thermodynamics of polymer mixtures and the temperature and composition dependences of the relevant parameters is vital for understanding the behaviour of polymer blends in the tasks for which they may be employed. Chief amongst the thermodynamic parameters is the interaction parameter χ, which was first defined by Flory[1]. In principle, a variety of methods exist to obtain values for χ in polymer blends, e.g. vapour sorption[2], inverse phase gas chromatography[3], melting point depression studies[4], Hess's law type calculations using calorimetric measurements on mixtures with solvents[5]. Direct measurements of the enthalpy of mixing of polymers are rare, primarily due to the small values to be measured and the resistance to mixing due to the high viscosity of polymer melts. However, when the molecular weight is sufficiently low, mixing calorimetry can be successfully used[6]. A popular method of determining the interaction parameter is by the use of small-angle neutron scattering (SANS) on mixtures where one component is deuterated[7,8]. This is a reasonably rapid means of obtaining values of the interaction parameter over a temperature and composition range. However, there are some problems associated with this approach which arise from two sources. First, the interpretation of the SANS data generally relies on the use of the incompressible random phase approximation[9], which in turn relies on additivity of volumes via the assumption of incompressibility. Deviations from these assumptions have been shown to lead to considerable composition dependence of the interaction parameter[10,11]. Second, deuteration of one of the polymers may itself lead to an additional contribution to the interaction parameter due to changes in zero point energy, bond length and polarizability consequent on replacement of protons for deuterons[12–14]. These effects are particularly evident near the first-order phase transition and in high-molecular-weight polymers, although such effects have also been noted in dilute solutions of polystyrene in deuterocyclohexane[15].

We report here the use of both mixing calorimetry and SANS in evaluating the interaction parameter in a blend formed by mixing any ethylene–vinyl acetate copolymer with a docosanyl diester of poly(ethylene glycol). Both polymers are of sufficiently low molecular weight that viscosity does not invalidate the enthalpy of mixing experiments. Attention has been focused on obtaining

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the enthalpic and entropic contributions to the interaction parameter from the SANS data and a comparison is made with the data from direct measurement of the enthalpy of mixing.

THEORY

The Gibbs free energy of mixing of any mixture is expressible as the sum of the enthalpy and entropy of mixing. Non-ideal solutions are generally treated by the Bragg–Williams regular solution theory, where any deviations from ideal behaviour are attributed to a finite enthalpy of mixing. Flory–Huggins lattice theory[1] of polymers dissolved in a low-molecular-weight solvent is one example of the use of such ideas, with some additional modifications included to account for the contiguity of mass elements in a polymer chain. Although the Flory–Huggins theory has failings, it has been applied to the description of the thermodynamics of polymer blends[9,16] since it is easier to manipulate than the more rigorous equation of state theories.

For a mixture of two polymers 1 and 2 consisting of n_1 and n_2 moles of each polymer, with each polymer having m_1 and m_2 segments, the Gibbs free energy of mixing per lattice site of the hypothetical lattice of the polymer mixture is given by

$$\frac{\Delta G_{\text{mix}}}{RT} = \frac{\phi_1}{m_1}\ln\phi_1 + \frac{\phi_2}{m_2}\ln\phi_2 + \phi_1\phi_2\chi \quad (1)$$

where ϕ_i is the volume fraction and χ is the polymer–polymer interaction parameter defined per segment of the two polymers, and is related to the enthalpy of mixing per lattice site by

$$\Delta H_{\text{mix}} = RTn_1\phi_2\chi \quad (2)$$

In equation (1) we implicitly assume that segments 1 and 2 have the same volume.

For two polymers to be miscible, the following criteria need to be fulfilled:

$$\Delta G_{\text{mix}} < 0$$

$$\partial^2\Delta G_{\text{mix}}/\partial\phi_1^2 > 0$$

The first differential of the Gibbs free energy change on mixing defines the coexistence curve when it is equal to zero; the second differential when equated to zero gives the locus of the spinodal curve for the mixture, i.e. the stability limit, and we can define a spinodal value of the interaction parameter as

$$\chi_{\text{Sp}} = \frac{1}{2m_1\phi_1} + \frac{1}{2m_2\phi_2} \quad (3)$$

Equation (2) indicates that the interaction parameter χ has neither concentration nor temperature dependence. However, Flory pointed out that χ has the characteristics of a free energy and contains an entropic component as well as the original enthalpic component. Each of these contributions can be obtained from the temperature dependence of the total interaction parameter, thus the enthalpic interaction parameter χ_{H} is given by

$$\chi_{\text{H}} = -T(\partial\chi/\partial T)_{\text{v}} \quad (4)$$

and the entropic interaction parameter is

$$\chi_{\text{S}} = (\partial(T\chi)/\partial T)_{\text{v}} \quad (5)$$

Mixing calorimetry experiments determine χ_{H} directly, whereas scattering experiments (small-angle X-ray scattering or SANS) on polymer mixtures are able to provide values of the total interaction parameter as long as there is sufficient scattering contrast between the blend components to provide a measurable scattering intensity. Obtaining interaction parameters for bulk polymer mixtures from scattering data relies on the use of the incompressible random phase approximation, which gives the scattering law as[9]

$$\frac{1}{S(Q)} = \frac{1}{m_1\phi_1 g_{\text{D}}(R_{\text{g}1},Q)} + \frac{1}{m_2\phi_2 g_{\text{D}}(R_{\text{g}2},Q)} - 2\chi_{\text{eff}} \quad (6)$$

where $g_{\text{D}}(R_{\text{g}i},Q)$ is the Debye expression for the form factor scattering from a Gaussian coil and Q is the scattering vector defined as $(4\pi/\lambda)\sin\theta$, where λ is the radiation wavelength and 2θ the scattering angle. In equation (6), χ_{eff} is the effective interaction parameter which may be composition and molecular weight dependent and also subsumes any possible differences in segment length between D and H polymers. In the Guinier region ($QR_{\text{g}i} \leq 1$) and defining an average composition fluctuation length ξ in the blend, then, in combination with the definition of the spinodal value of χ (equation (3)), equation (6) may be written in the Ornstein–Zernicke form[17] as

$$S(Q) = \frac{1}{2(\chi_{\text{Sp}} - \chi_{\text{eff}})(1 + Q^2\xi^2)} \quad (7)$$

Rearranging we have

$$\frac{1}{S(Q)} = 2(\chi_{\text{Sp}} - \chi_{\text{eff}}) + 2(\chi_{\text{Sp}} - \chi_{\text{eff}})\xi^2Q^2 \quad (8)$$

In small-angle neutron scattering, the contrast between the two polymers is provided by ensuring that one of the polymers is deuterated. The parameter measured is the differential coherent scattering cross-section, $(\mathrm{d}\Sigma/\mathrm{d}\Omega)_{\text{coh}}$, which is related to $S(Q)$ by[18]

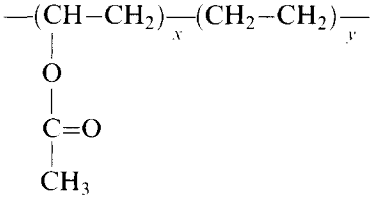
$$\left(\frac{\mathrm{d}\Sigma}{\mathrm{d}\Omega}\right)_{\text{coh}} = (\rho_1 - \rho_2)^2 S(Q) \quad (9)$$

where ρ_i is the coherent scattering length density of polymer segment i. Hence, by obtaining the scattering intensity of a polymer mixture, the total interaction parameter can be obtained from the intercept at $Q = 0$ provided that the coherent scattering lengths are known and χ_{Sp} can be calculated. Additionally, if χ_{eff} is obtained as a function of temperature, the enthalpic and entropic values of χ_{eff} can be obtained and the enthalpic value compared with that calculated from a direct measurement of the heat of mixing.

EXPERIMENTAL

Polymers

A random copolymer of ethylene and vinyl acetate (EVA) was provided by Exxon Chemical Ltd, having the schematic structure



$$\text{—(}\underset{\underset{\underset{\underset{\text{CH}_3}{|}}{\text{C=O}}}{|}}{\underset{\text{O}}{\overset{|}{\text{CH}}}}\text{–CH}_2\text{)}_x\text{—(CH}_2\text{–CH}_2\text{)}_y\text{—}$$

Table 1 Molecular weights of polymers

Polymer	$\bar{M}_w$ (10^3 g mol^{-1})	$\bar{M}_n$ (10^3 g mol^{-1})	$\bar{M}_w/\bar{M}_n$
EVA	6290	2670	2.4
PEG ester	1440	1440	1.0
DPEG ester	1240	1150	1.1

where the average values of x and y calculated from elemental analyses and ^{13}C n.m.r. spectra are 1 and 7, respectively. Molecular weights of this polymer were obtained by size exclusion chromatography using both refractive index and viscosity detection, and polystyrene calibration standards. The molecular weights obtained are given in *Table 1*.

The hydrogenous docosanyl diester of poly(ethylene glycol) (PEG ester) was prepared by esterification of poly(ethylene glycol) with a molecular weight of $\sim$400 g mol^{-1}. Docosanoic acid (11.7 mmol) was mixed with the poly(ethylene glycol) (5.86 mmol) in toluene (60 cm^3) to which was added *p*-toluene sulfonic acid (0.8% w/w). The mixture was refluxed at 413 K for 2 h before the temperature was increased to 443 K over a 3 h period and the toluene/water azeotrope removed. Finally, the temperature was held at 443 K for 30 min to remove the remaining water and toluene. On cooling, a white crystalline solid was obtained which was crushed to a powder and stirred in a large excess of 1 M aqueous sodium hydroxide solution for 30 min before being filtered. The wet powder was washed twice by stirring in distilled water before being filtered and dried under vacuum at 373 K to constant weight. Elemental analysis and ^{13}C n.m.r. spectra were consistent with complete formation of the diester. Size exclusion chromatography in chloroform solution was used to obtain the molecular weights of the polymer and these values are given in *Table 1*.

A fully deuterated docosanyl ester of poly(ethylene glycol) (DPEG ester) was prepared using deuterio ethylene glycol as starting material. Deuterio ethylene glycol (99 atom% D), to which was added 1% w/w iodine, was stirred under a nitrogen atmosphere at 463 K. The polymerization was continued for 96 h with the repeated addition of further aliquots of iodine (1% w/w) at 24 h intervals. During reaction, iodine sublimed out of the solution and water was removed. After 96 h the solution was fractionated at 423 K and 0.025 mbar for 1 h to remove low-molecular-weight fractions of poly(ethylene glycol). The molecular weights of the deuterio poly(ethylene glycol) obtained by size exclusion chromatography are reported in *Table 1*. This deuterio poly(ethylene glycol) was esterified with deuterio docosanoic acid (MSD isotopes), which had been recrystallized twice from Analar toluene, using the same procedure as set out for the hydrogenous PEG ester. One modification was the use of D_2O in the final purification stages rather than distilled water. *Table 1* reports the molecular weights obtained by size exclusion chromatography.

Enthalpy of mixing calorimetry

The enthalpy of mixing of EVA/PEG ester blends as a function of composition was obtained using a purpose-built mixing calorimeter. Major features of this instrument were precise temperature control, $\pm 1 \times 10^{-3}$ K, and sensitivity to enthalpy changes as small as 0.001 J g^{-1} by using Peltier elements as the heat sensors. The design is based on a calorimeter constructed at the National Bureau of Standards for solution calorimetry[19]. A temperature of 341.45 K was used for enthalpy of mixing measurements. For each determination, $\sim$0.5 g of each polymer was accurately weighed into separate compartments of the mixing calorimeter cell. This cell was then placed in the mixing calorimeter where it was allowed to stabilize at the calorimeter temperature for 2 h. During this time the voltage output from the sensing Peltier elements was noted and mixing begun only when a stable 'baseline' value was obtained. Mixing was achieved by inverting the cell and rocking it through 70° about five times a minute. To aid mixing, a small glass bead was placed in one of the cell compartments which acted as a stirrer on inverting and rocking the cell. The voltage output from the Peltier elements was logged at regular time intervals by a computer interfaced to the calorimeter. Data logging continued until the initial baseline voltage was re-established. At this point the calorimeter was calibrated by inserting a small resistor, with a resistance known to a high precision, into the mixture. Known amounts of electrical energy were supplied to the resistor and the ensuing voltage change from the Peltier elements was logged with time. The area under the voltage–time plots varied linearly with electrical energy supplied, hence a calibration constant was obtained to convert the area of the voltage output curves to absolute energies for the mixing of the two polymers. Corrections to the data were applied for any enthalpic effects due to the mechanical agitation of the polymers. Separate experiments on each of the pure polymers showed that this correction was endothermic and amounted to $\sim$0.05 J g^{-1}.

Small-angle neutron scattering

Blends of EVA and DPEG ester were prepared by dissolving the two polymers in chloroform at the desired weights and evaporating off the solvent. Finally, each blend was dried under vacuum at 323 K until constant weight was obtained. The volume fraction of the DPEG ester in the blends was 0.09, 0.19, 0.28, 0.48 and 0.73. Each blend was loaded into a cell composed of two quartz windows separated by a 1 mm PTFE spacer. Loading was achieved by melting the mixture into the cell and enclosing it with the second window. The whole assembly was then placed in a close-fitting brass carrier which could be mounted in a temperature-controlled sample changer. Small-angle neutron scattering data were obtained using the LOQ diffractometer at the UK pulsed neutron source ISIS at the Rutherford–Appleton Laboratory. Temperatures of 353, 368 and 383 K were investigated, this rather limited temperature being due to two causes. First, complete melting of the semicrystalline DPEG ester does not occur until the sample temperature is in excess of 333 K; hence to ensure no influence of this first-order phase transition we limit the lowest temperature to 20 K above the melting point. Second, separate thermogravimetry experiments[20] had shown that thermal degradation of both EVA and the PEG ester became evident at a temperature of $\sim$430 K; consequently, to avoid any complications due to prolonged exposure to high temperatures, the highest temperature used for SANS was 383 K.

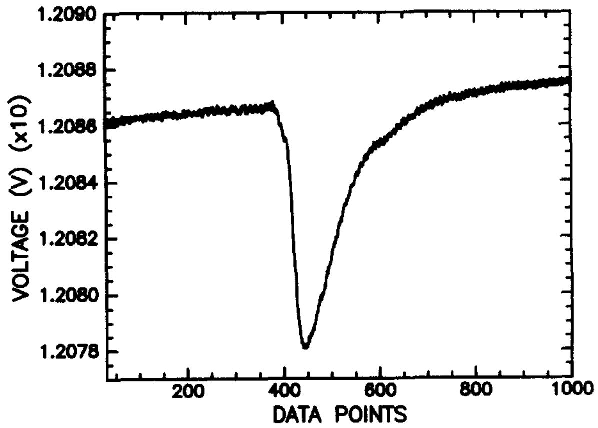


Figure 1 Voltage output curve from mixing calorimeter for an EVA/PEG ester mixture with an EVA volume fraction of 0.51 and at a temperature of 341.45 K

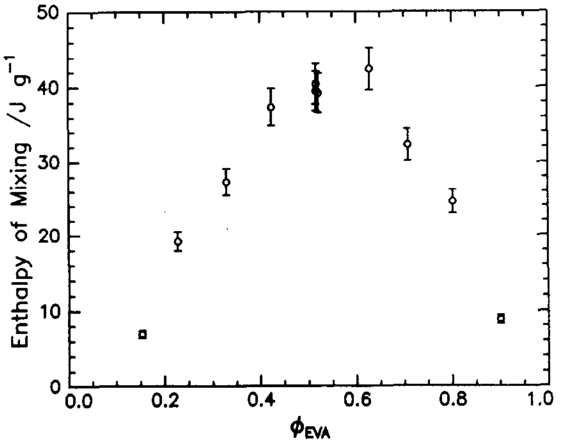


Figure 2 Enthalpy of mixing obtained by mixing calorimetry as a function EVA volume fraction. Temperature of mixing: 341.45 K

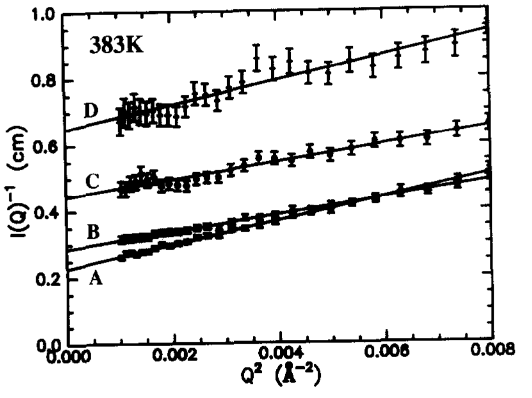


Figure 3 SANS data plotted in the Ornstein–Zernicke form. Volume fraction of EVA in mixtures: 0.27 (A), 0.52 (B), 0.81 (C) and 0.91 (D)

RESULTS

Enthalpy of mixing

Figure 1 shows a typical output voltage as a function of logging event, the endothermic nature of the mixing is evident in output voltages being below the baseline voltage. Enthalpies of mixing calculated from the area of these output curves are plotted as a function of the volume fraction of EVA in the mixture in *Figure 2*. The error bars were obtained by using the spread in values of the enthalpy of mixing obtained for several $\phi_{\rm EVA}$ values. The individual values for the enthalpy of mixing at this EVA volume fraction are shown in *Figure 2*.

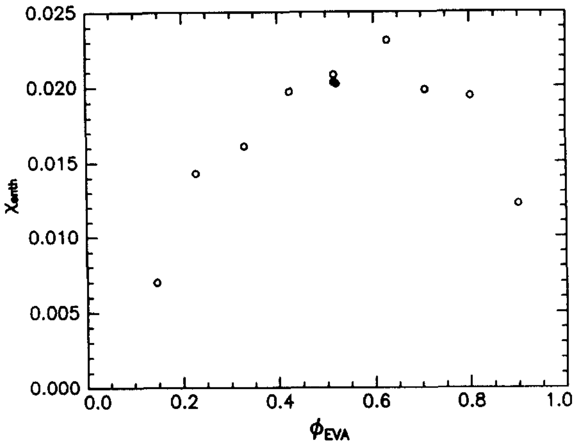


Figure 4 Values of the interaction parameter calculated from enthalpies of mixing ($\chi_{\rm enth}$) as a function of the volume fraction of EVA

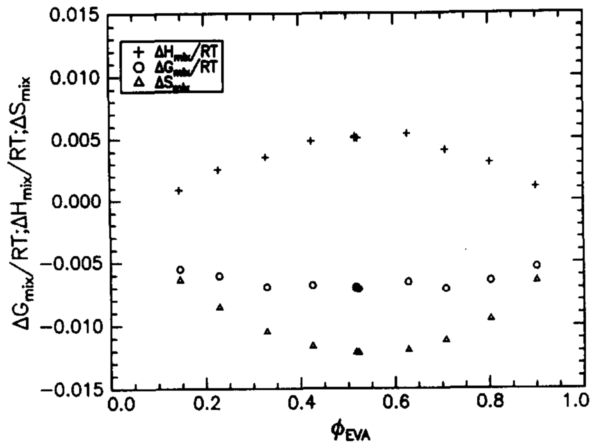


Figure 5 Gibbs free energy of mixing, and the enthalpic and entropic components calculated using equation (1) and the values of $\chi_{\rm enth}$, as a function of the volume fraction of EVA

Small-angle neutron scattering

SANS data for each blend were corrected for thickness and transmission and converted to absolute scattering cross-section scale by multiplying the data by a calibration factor obtained from the scattering of a blend of deuterated polystyrene and hydrogenous polystyrene. For the subtraction of incoherent background scattering, the scattering from pure EVA and pure DPEG ester was obtained at each temperature. These data were then added together in a composition-weighted manner and the result subtracted from the scattering of each blend. These corrected scattering cross-sections were then plotted in the Ornstein–Zernicke form of equation (8) over the Q range used of $0.01 \leq Q/\text{Å}^{-1} \leq 0.1$. *Figure 3* shows such plots and the linear least-squares fits to the data obtained.

DISCUSSION

The endothermic enthalpy of mixing data shown in *Figure 2* suggest that the EVA and PEG ester are immiscible at the temperature of 341.45 K; this result appears to contradict the observation of a large negative value of χ obtained from melting point depression studies[21]. Values of the enthalpic interaction parameter, χ_{enth}, were calculated from these enthalpy of mixing values using equation (2). *Figure 4* shows the variation of χ_{enth} with volume fraction of EVA in the polymer mixture, the positive values indicating unfavourable enthalpic interactions between the two polymers. Combining these values of χ_{enth} with the entropic contributions to the Gibbs free energy of mixing as given by equation (1) shows that it is the entropic part which dominates the Gibbs free energy of mixing. *Figure 5* shows the variation of Gibbs free energy of mixing with volume fraction of EVA and the magnitudes of both enthalpic and entropic contributions. Evidently, the relatively low degrees of polymerization of both polymers make the entropy of mixing term sufficiently negative to overcome the unfavourable enthalpic contribution. However, the values of $\Delta G_{\text{mix}}/RT$ are not strongly negative and a doubling of the molecular weights of the two polymers with retention of the same value of χ_{enth} is sufficient to make them only partially miscible.

Extracting values of χ_{eff} from SANS data is dependent on defining the values of the scattering length density, and thus the definition of the repeat unit in the polymer is important. For the EVA, since this is a random copolymer of vinyl acetate and ethylene in the molar ratio of 1:7, the coherent scattering length was calculated as (1/8)th of that for vinyl acetate plus (7/8)ths of that for ethylene. The necessary molar volume of the segment was calculated in the same way, using the group contribution increments listed by van Krevelen[22]. This process is a little more difficult for the PEG ester which could be viewed as a docosanoic–ethylene oxide–docosanoic triblock copolymer. To calculate an average coherent scattering length, the segments of the docosyl end blocks were defined as ethylene units, and the average molar ratio of ethylene, ethylene oxide and ester linking units calculated. Using this molar ratio the average coherent scattering length was calculated and the scattering length density obtained from group contributions as in the case of EVA. The coherent scattering length obtained for EVA was 0.052×10^{-4} Å and that for the DPEG ester was 4.180×10^{-4} Å. In passing, we also remark here that average segment volumes calculated by this same weighted-contribution method for EVA and PEG ester give almost identical values, hence obviating any need for volume corrections in equations (1) and (6). Using these values and the linear least-squares fits shown in *Figure 3*, the values given in *Table 2* were obtained for χ_{eff} and ξ.

The values of the correlation lengths are small (about one monomer length) and hence these blends are very distant from the spinodal points where ξ has a value of infinity. An estimate of the spinodal temperature of each blend can be obtained from the temperature dependence of χ_{eff} and the values of χ_{Sp} calculated from equation (3). *Figure 6* shows χ_{eff} plotted as a function of $1/T$ for the blend where $\phi_{\text{EVA}} = 0.72$; the

Table 2 Effective interaction parameter and composition fluctuation lengths obtained by SANS from EVA/DPEG ester blends

T (K)	ϕ_{EVA}	$\chi_{\text{eff}} \times 10^{-3}$	ξ (Å)
353	0.91	−23.1	7.6
	0.81	−2.6	7.8
	0.72	2.3	8.2
	0.52	3.2	9.9
	0.27	9.4	12.7
368	0.81	−3.5	8.3
	0.72	−0.2	8.2
	0.52	1.8	10.2
	0.27	7.6	12.5
383	0.81	−7.6	7.50
	0.72	−4.3	7.75
	0.52	−0.3	9.4
	0.27	7.2	12.5

Table 3 Values of spinodal temperature for EVA/PEG ester blends

ϕ_{EVA}	T_{Sp} (K)
0.81	147
0.72	209
0.52	189
0.27	166

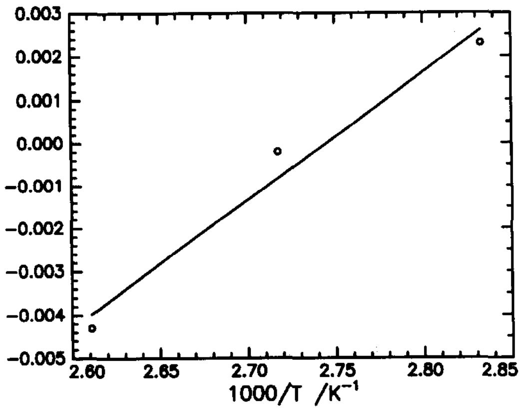


Figure 6 Typical plot of χ_{eff} from SANS as a function of reciprocal temperature of the blend. Volume fraction of EVA: 0.72

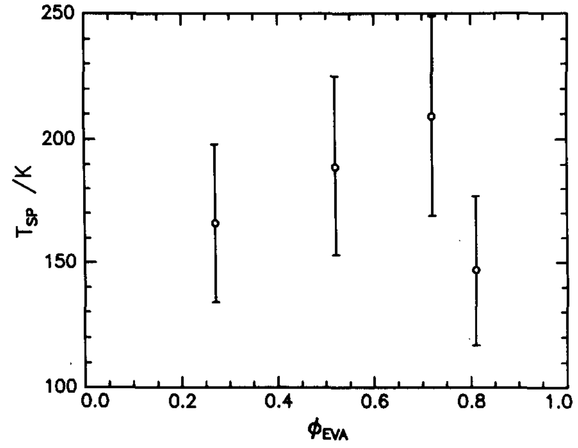


Figure 7 Spinodal temperatures obtained by extrapolations of χ_{eff} as in *Figure 6*, as a function of EVA volume fraction

Table 4 Parameters a and b of the temperature dependence of χ_{eff} (equation (10))

ϕ_{EVA}	$a \times 10^{-2}$	b (K)
0.81	-6.5 ± 2.5	22.1 ± 9
0.72	-8.0 ± 1.3	29.2 ± 5
0.52	-4.1 ± 0.7	15.6 ± 2.5
0.27	-1.9 ± 0.8	10.1 ± 3.1

intersection of the experimental data with the value for χ_{Sp} provides a value for the spinodal temperature. The values obtained by this process are given in *Table 3* and the spinodal temperatures are plotted as a function of EVA volume fraction in *Figure 7*. An upper critical consolute curve is indicated by *Figure 7* which is commensurate with the positive slope of the dependence of χ_{eff} on $1/T$; however, the error bars on the individual points of *Figure 7* are large due to the long extrapolation to the intersection with χ_{Sp} and the limited range of temperatures over which χ_{eff} is available.

Generally, the temperature dependence of χ_{eff} is expressed as an empirical relation

$$\chi_{\mathrm{eff}} = a + b/T \tag{10}$$

The values of a and b obtained for each EVA volume fraction examined are given in *Table 4*. With these temperature dependences available we can now utilize equations (4) and (5) to identify the enthalpic and entropic contributions to χ_{eff} as b/T and a, respectively, and thus we can compare the enthalpic contribution to χ_{eff} (χ_{H}) with the value of χ_{enth} calculated from the enthalpy of mixing data. This comparison is made in *Figure 8*. Due to the limited number of compositions investigated by SANS, the composition dependence of χ_{H} is not so evident as in the χ_{enth} values. Notwithstanding the large error bars on the values of χ_{H}, the value obtained at $\phi_{\mathrm{EVA}} = 0.72$ appears to be somewhat aberrant; however, in the main, the values of χ_{H} obtained from SANS are of the same order of magnitude as values obtained from enthalpy of mixing data although absolute agreement is not obtained.

A noteworthy point about all the data, both from enthalpy of mixing and SANS, is the composition dependence of the interaction parameters. This has been the focus of both theoretical and experimental interest of late[10,11,23–25], but due to the sparsity of our data for the EVA/DPEG ester system we do not attempt here interpretation by the complex equations which result from these theories. Another approach to the composition dependence of χ has been that of Koningsveld[26], in which χ is written as

$$\chi = -\tfrac{1}{2}\left(\frac{\partial^2 g_{12}\phi_1\phi_2}{\partial\phi_2^2}\right) \tag{11}$$

where

$$g_{12} = \alpha + \frac{\beta_{\mathrm{S}} + (\beta_{\mathrm{H}}/T)}{1 - \gamma\phi_2} \tag{12}$$

with α and β_{S} as empirical entropy correction terms, β_{H} an enthalpy term due to the internal energy per contact between segments of type 1 and 2, and

$$\gamma = 1 - \sigma_2/\sigma_1 \tag{13}$$

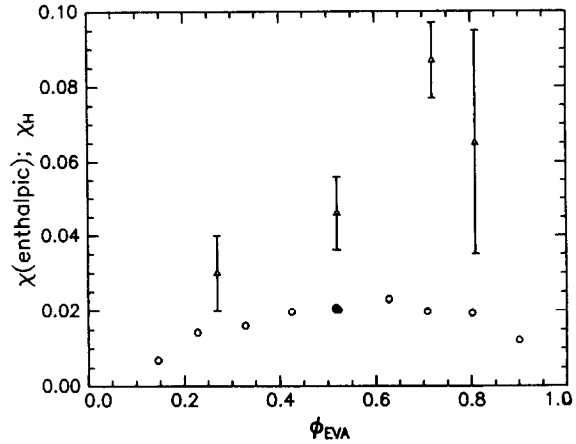


Figure 8 Values of enthalpic interaction parameter calculated from mixing calorimetry (χ_{enth}, ○) and SANS (χ_{H}, △)

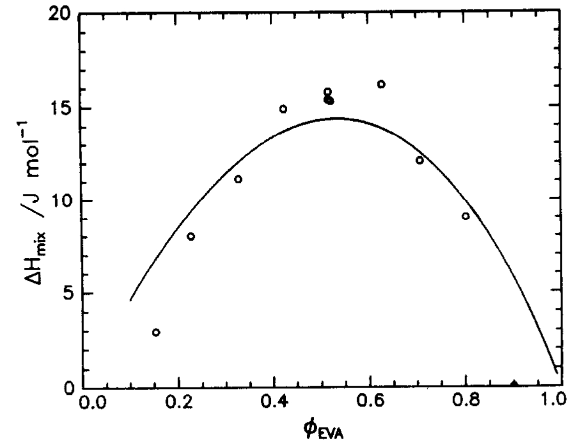


Figure 9 Fit (solid line) of equation (16) to enthalpy of mixing data as a function of EVA volume fraction. Fitting variables: β_{H} and γ

where σ_2/σ_1 is the ratio of the surface areas of the segments of the two polymer molecules. By evaluating the double differential in equation (11) using equation (12), the resultant expression can be identified with the a and b terms in the temperature dependence of χ_{eff}

$$a = \alpha + \frac{\beta_{\mathrm{S}}(1-\gamma)}{(1-\gamma\phi_2)^3} \tag{14}$$

$$b = \frac{\beta_{\mathrm{H}}(1-\gamma)}{(1-\gamma\phi_2)^3} \tag{15}$$

Furthermore, a composition-dependent enthalpy of mixing results from this approach and is given by[27]

$$\Delta H_{\mathrm{mix}} = \frac{R\phi_1\phi_2\beta_{\mathrm{H}}}{(1-\gamma\phi_2)} \tag{16}$$

In principle, equation (15) could be used to obtain values of β_{H} and γ by non-linear least-squares fitting of the equation to values of b. However, we have few values of b and the two fitting parameters β_{H} and γ are coupled in this equation; hence the errors in the separate values will be large. The fitting procedure could be simplified by adopting a value for γ calculated using group contribution values by Bondi[28]. Using this method, the values of σ_1 and σ_2 calculated for the 'average' segment in EVA

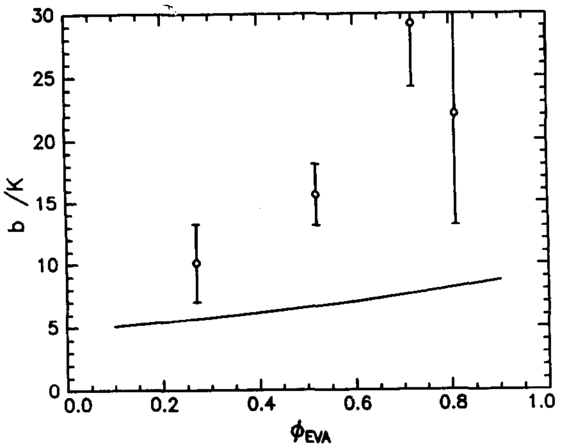


Figure 10 Values of *b* obtained from temperature dependence of χ_{eff} (○) compared with values calculated using values of β_H and γ from the fit to the enthalpy of mixing data (solid line)

and DPEG ester are such that $\gamma \sim 0$ and hence no composition dependence of *a*, *b* or χ_{eff} would be anticipated. This is clearly not the case here, since a reasonably strong composition dependence of all of these parameters is observed by us. In equation (16), β_H and γ are not so strongly coupled as in equation (15) and therefore we have chosen to fit the enthalpy of mixing data to this equation using β_H and γ as the parameters of the least-squares fitting routine. *Figure 9* shows this non-linear least-squares fit, and the values of β_H and γ obtained are $6.0 \pm 1.2\,\mathrm{K}^{-1}$ and 0.24 ± 0.34, respectively. Inserting these values into the right-hand side of equation (15) and comparing the calculated values with the experimental values of *b* (*Figure 10*) exact agreement is not obtained and at first sight this lack of agreement is disturbing.

A rationalization of these data can be obtained by comparing melting points of EVA/DPEG ester mixtures with those for the EVA/PEG ester mixtures. The melting point associated with the docosanyl ends in the hydrogenous PEG ester ranges from 328.31 to 315.52 K as the volume fraction of EVA increases from zero to ~0.72. Over this same range of EVA volume fraction, the melting points of the DPEG ester mixtures range from 315.5 to 307.92 K, i.e. a considerable decrease in melting point is observed on deuterating the PEG ester. This difference in melting point and melting point depression leads to considerable differences in the values of χ calculated from these melting point depression data. Hence, for EVA/DPEG esters, melting point data gave a χ value of -0.39 whereas for the blends containing HPEG ester a value of -0.33 was obtained. This difference is reflected in the discrepancy in the *b* values calculated from SANS and enthalpy of mixing data, and is another example of the isotope labelling effect which was first observed in polyethylene[29] but which has led to the identification of the quantum mechanically driven finite value of the interaction parameter between isotopic homopolymers[30] and has been extensively discussed by Krishnamorti *et al.*[23,24]. Regrettably, we had insufficient DPEG ester available to obtain direct values of the heats of mixing as a function of composition.

Notwithstanding this discrepancy due to isotopic effects, the values of *b* obtained from enthalpy of mixing data are sufficiently close to those obtained from SANS for us to conclude that observations of the temperature dependence of χ_{eff} values can be used to provide reasonable estimates of the enthalpy of mixing in the EVA/PEG ester polymer blends. Although we have a value for χ we have not attempted to evaluate parameters for entropy factors α and β_S due to the large uncertainty that would result from using such a small set of values of *a* in the calculations.

CONCLUSIONS

The enthalpy of mixing of mixtures of an ethylene–vinyl acetate copolymer with a docosanyl diester of poly(ethylene glycol) is endothermic and unfavourable to mixing. Incorporation of this parameter as an enthalpic interaction parameter into the Flory–Huggins expression for the Gibbs free energy of mixing results in negative values for this state function and shows that mixing is dominated by the entropy contribution to the mixing free energy. Even with this large entropy contribution, the free energy of mixing is negative by only a small margin.

Small-angle neutron scattering on similar blends but using a fully deuterated version of the poly(ethylene glycol) diester produces negative values of the effective interaction parameter over most of the temperature and composition range investigated. From the temperature dependence of this effective interaction parameter, spinodal temperatures for this mixture have been defined; these are in the region of 150 K to 220 K but, due to the long extrapolations in determining these temperatures, they are subject to large errors. From the temperature dependence of χ_{eff}, values of the enthalpic and entropic contributions to the interaction parameter have been obtained. In a further step we have attempted to use the composition dependence of χ_{eff} proposed by Koningsveld. Values of the enthalpy of mixing have been used to obtain values of the enthalpic term and a parameter related to the ratio of the surface area of the segments in each of the polymers. A comparison has been made with the enthalpic term, *b*, which arises from the temperature dependence of χ_{eff} obtained by SANS. Although the two values are the same order of magnitude, the agreement between the two values is poor. This has been attributed to differences in the interaction energy between a fully hydrogenous blend and a blend wherein one component has been fully deuterated.

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