Thermodynamics of polymer/diluent systems for thermally induced phase separation: 1. Determination of equation of state parameters

Sung Soo Kim and Douglas R. Lloyd*
Department of Chemical Engineering, Center for Polymer Research,
The University of Texas at Austin, Austin, TX 78712, USA
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The parameters for Flory's equation of state adapted to polymer/oligomer systems were determined to estimate the thermodynamic properties of isotactic polypropylene/diluent systems undergoing thermally induced phase separation. Three kinds of diluents were covered: n-alkanes, n-fatty acids and n,n-bis (2-hydroxyethyl) tallowamine. Reduced volumes and temperatures were determined by measuring the volumetric properties, characteristic pressures were determined by measuring the vapour pressures, and exchange interaction parameters were determined by measuring the heat of mixing for analogous systems of small molecules. The exchange interactional parameters obtained from analogous systems were extrapolated to polymeric systems by using a series of analogous molecules for isotactic polypropylene. The equation of state parameters determined in this study were proved reliable for the thermodynamic analyses covered in other papers in this series.

(Keywords: interaction parameter; phase separation; equation of state)

INTRODUCTION

When thermal energy is removed from a homogeneous polymer/diluent mixture, thermally induced phase separation (TIPS) can occur. The TIPS process has many applications in polymer sciences including the formation of membranes[1-7]. While the TIPS process has been patented for the preparation of microporous polymeric membranes[8-10], little work has been done on the science that underlies the technology[11-13]. The thermodynamic interaction between polymer and diluent is a major factor determining the location and shape of the phase boundaries, such as the equilibrium melting temperatures of semicrystalline polymers for solid–liquid phase separation as well as the spinodal and binodal curves for liquid–liquid phase separation[14]. The phase separation mechanism (solid–liquid *versus* liquid–liquid) significantly influences the final membrane structure.

The objective of this series of papers is to analyse the thermodynamics of the three representative isotactic polypropylene (iPP)/diluent model systems: iPP/n-alkanes, iPP/n-fatty acids and iPP/n,n-bis (2-hydroxyethyl) tallowamine (TA). The formula of TA is $CH_3\text{-}(CH_2)_{16-18}\text{-}N{=}(CH_2OH)_2$. Preliminary evaluation of the classic Flory–Huggins theory, currently used as the thermodynamic basis for the TIPS process[11-13], indicated that this theory does not accurately describe the polymer/diluent system behaviour because the free volume effect is not considered. The polymer/diluent system is expected to have significant free volume effects due to the dissimilarity of equation of state (EOS) properties of the polymer and diluent[15-17]. In this study Flory's EOS theory was adapted to the polymer/oligomer system to represent more accurately the phase behaviour for the model systems listed above.

To make use of the EOS theory, it is necessary to have a number of EOS parameters. Unfortunately, the required parameters for the model systems are not available in the literature. Therefore, experimental generation of this data was necessary. Since the procedures currently used to generate these data are often cumbersome and time consuming, the first paper in this series proposes and tests simplified methodologies for yielding EOS parameters.

THEORY OF EQUATION OF STATE

The Gibbs free energy of mixing is defined for polymer/oligomer systems as:

$$\Delta G/RT = n_1 \ln(\phi_1) + n_2 \ln(\phi_2) + \chi r_1 n_1 \phi_2 \qquad (1)$$

where n_i is the number of moles, ϕ_i is a volume fraction, χ is the Flory–Huggins interaction parameter and subscripts 1 and 2 represent diluent and polymer, respectively[14]. In developing this equation the molar volume of the polymer repeat unit was used as the reference volume, as proposed by Scott[18]; thus, each lattice site is occupied by a unit segment of polymer or diluent. The number of segments of the polymer molecule (r_2) and that of the oligomeric diluent (r_1) are defined as

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* To whom correspondence should be addressed

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$$r_2 = V_2/V_u = DP \qquad (2)$$

$$r_1 = V_1/V_u \qquad (3)$$

where V_1, V_2 and V_u are the molar volume of diluent, polymer and polymer repeat unit, respectively, and DP is the degree of polymerization.

According to the Flory–Huggins theory, the interaction parameter (χ) is purely enthalpic[14]. The combinatorial entropic terms do not accurately represent the entropy change associated with mixing a polymer with a diluent, since they did not consider the free volume effects. EOS theory, which considers the free volume effects as well as the interactional energy change of mixing, was proposed and developed by Prigogine[19], Flory[15,16], Sanchez[20,21], Patterson *et al.*[22,23], Somcynskian and Shimha[24], McMaster[25] and others. These theories differ from one another in the assumptions for defining the partition functions, and it is hard to expect that any theory can describe a system over a wide range of densities of solution[26].

Flory's EOS theory as used in this study is expressed in reduced parameters as

$$(\tilde{P}\tilde{V})/\tilde{T} = \tilde{V}^{1/3}/(\tilde{V}^{1/3} - 1) - 1/(\tilde{V}\tilde{T}) \qquad (4)$$

where $\tilde{P}$ is the reduced pressure ($\tilde{P} = P/P^*$), $\tilde{V}$ is the reduced volume ($\tilde{V} = V/V^*$), $\tilde{T}$ is the reduced temperature ($\tilde{T} = T/T^*$) and P^*, V^* and T^* are the characteristic pressure, volume and temperature, respectively[15–17].

The residual entropy was derived by Flory as

$$\begin{aligned} S^{\mathrm{R}} = {} & -3(n_1V_1^* + n_2V_2^*)\{\phi_1(P_1^*/T_1^*) \\ & \times \ln[(\tilde{V}_1^{1/3} - 1)/(\tilde{V}^{1/3} - 1)] \\ & + \phi_2(P_2^*/T_2^*)\ln[(\tilde{V}_2^{1/3} - 1)/(\tilde{V}^{1/3} - 1)]\} \qquad (5) \end{aligned}$$

where n_1 and n_2 represent the number of moles, ϕ_1 and ϕ_2 are the segment fractions, and $\tilde{V}_1$, $\tilde{V}_2$ and $\tilde{V}$ are the reduced volumes of polymer, diluent and their mixture, respectively[15–17].

For the enthalpy of mixing, Flory obtained

$$\begin{aligned} \Delta H_{\mathrm{mix}} = H^{\mathrm{R}} = {} & (n_1V_1^* + n_2V_2^*)\{\phi_1P_1^*(\tilde{V}_1^{-1} - \tilde{V}^{-1}) \\ & + \phi_2P_2^*(\tilde{V}_2^{-1} - \tilde{V}^{-1}) \\ & + [(\phi_1\theta_2X_{12})/\tilde{V}]\} \qquad (6) \end{aligned}$$

where θ_2 is the surface fraction of polymer and X_{12} is the exchange interactional parameter[15–17]. Residual Gibbs energy (G^{R}) is defined as

$$G^{\mathrm{R}} = H^{\mathrm{R}} - TS^{\mathrm{R}} \qquad (7)$$

The partial molar residual enthalpy and entropy can be obtained by differentiation of equations (5) and (6) in terms of moles of diluent (n_1) or polymer (n_2)[15–17].

$$\begin{aligned} T\bar{S}_1^{\mathrm{R}} = {} & -P_1^*V_1^*\{3\tilde{T}_1\ln[(\tilde{V}_1^{1/3} - 1)/(\tilde{V}^{1/3} - 1)] \\ & - (\alpha T/\tilde{V})(\tilde{T}_1 - \tilde{T})/\tilde{T}\} + V_1^*(\alpha T\theta_2^2X_{12}/\tilde{V}) \qquad (8) \end{aligned}$$

$$\begin{aligned} T\bar{S}_2^{\mathrm{R}} = {} & -P_2^*V_2^*\{3\tilde{T}_2\ln[(\tilde{V}_2^{1/3} - 1)/(\tilde{V}^{1/3} - 1)] \\ & - (\alpha T/\tilde{V})(\tilde{T}_2 - \tilde{T})/\tilde{T}\} + V_2^*(\alpha T\theta_2^2\phi_1^2X_{12}/\phi_2^2\tilde{V}) \qquad (9) \end{aligned}$$

$$\begin{aligned} \bar{H}_1^{\mathrm{R}} = {} & P_1^*V_1^*(\tilde{V}_1^{-1} - \tilde{V}^{-1}) + (\alpha T/\tilde{V})(\tilde{T}_1 - \tilde{T})/\tilde{T}] \\ & + V_1^*(\theta_2^2X_{12}/\tilde{V})(1 + \alpha T) \qquad (10) \end{aligned}$$

$$\begin{aligned} \bar{H}_2^{\mathrm{R}} = {} & P_2^*V_2^*[(\tilde{V}_2^{-1} - \tilde{V}^{-1}) + (\alpha T/\tilde{V})(\tilde{T}_2 - \tilde{T})/\tilde{T}] \\ & + V_2^*(\theta_2^2\phi_1^2X_{12}/\phi_2^2\tilde{V})(1 + \alpha T) \qquad (11) \end{aligned}$$

The residual chemical potential of the diluent or polymer is derived from equation (1) as:

$$\Delta\mu_i^{\mathrm{R}}/RT = \chi_{\mu i}r_i\phi_j^2 \qquad (12)$$

$$= (\bar{H}_i^{\mathrm{R}} - T\bar{S}_i^{\mathrm{R}})/RT \qquad (13)$$

EQUATION OF STATE PARAMETERS

The parameters shown in equations (1)–(13) were experimentally determined or estimated from the literature as described below.

Materials

iPP of weight average molecular weight 243 000 and DP of 1033 was supplied by Himont Co. (Profax 6723, lot no. 79316). Some of the n-alkanes (C_7H_{16}, C_8H_{18}, $C_{10}H_{22}$), n-fatty acids (C_2H_5COOH, C_4H_9COOH, $C_6H_{13}COOH$, $C_7H_{15}COOH$, $C_{14}H_{29}COOH$, $C_{19}H_{39}COOH$) and 2,4-dimethyl pentane (DMP) were purchased from Aldrich Chemical Co.. The other n-alkanes ($C_{12}H_{26}$, $C_{14}H_{30}$, $C_{20}H_{42}$, $C_{32}H_{66}$) were obtained from Alfa Products and TA was obtained from Armak Chemicals.

Reduced volume and temperature

Volumetric data of iPP and the diluents in the temperature range of interest are required for the estimation of thermodynamic interaction. These data were collected from the literature if available[27–33] or experimentally measured. The volume–temperature data were regressed for each component, from which the thermal expansivity (α) was obtained by equation (14):

$$\alpha = 1/V(\partial V/\partial T)_P \qquad (14)$$

Since P^* is much greater than the atmospheric pressure, the zero pressure assumption ($\tilde{P} = 0$) reduced equation (4) to a simple form[15–17].

$$\tilde{T} = (\tilde{V}^{1/3} - 1)/\tilde{V}^{4/3} \qquad (15)$$

from which it follows that

$$\tilde{V}^{1/3} - 1 = \alpha T/[3(1 + \alpha T)] \qquad (16)$$

The reduced volume and the reduced temperature can be determined by equations (15) and (16) with α information at each temperature.

The direct regression of literature data caused serious errors in estimating the reduced parameters. An alternative method to get reliable reduced parameters is proposed in this study. Since the EOS theory, a kind of corresponding state theory, was assumed to be good for any system, direct use of the EOS enables a more reliable estimate of reduced parameters than the rigorous regression of literature data.

V^* and T^* usually change slightly with temperature in Flory's original EOS theory[15–17]. However, in this study V^* and T^* were assumed to be constant within some temperature range around the reference temperature (T_0). Since it was pointed out by Walsh that no EOS theories could accurately describe the PVT properties of liquids[26,34], errors are inevitable in Flory's original theory. The assumption of constant V^* and T^* reduced the number of experiments while producing PVT data in good agreement with the literature data in the temperature range of interest.

Table 1 Characteristic volumes and temperatures of iPP and diluents

Compound	Reference temperature (K)	Characteristic molar volume ($cm^3\ mol^{-1}$)	Characteristic temperature (K)
iPP	453	44.75	8320
$C_{14}H_{30}$	393	221.50	6174
$C_{20}H_{42}$	393	312.00	6835
$C_{32}H_{66}$	393	495.00	7807
$C_{14}H_{29}COOH$	393	232.50	6397
$C_{19}H_{39}COOH$	393	304.00	6572
TA	363	325.49	6674

The volume and α value at T_0 are needed to calculate $\tilde{V}$ by equation (16) and $\tilde{T}$ by equation (15) at T_0, from which V^* and T^* at T_0 can be obtained. Since V^* and T^* are assumed to be constant, $\tilde{T}$ was obtained at any temperature from its definition ($\tilde{T} = T/T^*$) and $\tilde{V}$ was obtained from equation (16). The volume at that temperature can also be obtained from its definition ($\tilde{V} = V/V^*$).

The reference temperature of each n-alkane and n-fatty acid was set at the centre of the temperature range of interest (393 K) to minimize deviations. The volumetric data of TA were experimentally measured from 303 to 368 K and its reference temperature was set at 363 K. Since iPP is semicrystalline, volumetric properties for the amorphous phase are available above its melting temperature[32,33]. Therefore, 453 K was chosen as a reference temperature for iPP. V^* and T^* values determined by this method for iPP and the diluents are listed in *Table 1*.

The densities of the low molecular weight analogues and their mixtures were required to calculate the enthalpic interaction of the analogous systems (X_{12}) from the heat of mixing (ΔH_{mix}) data, and were measured using a density meter (Anton Paar Co. DMA 602 external measuring cell with DMA 60 processing unit). The densities of 2,4-dimethyl pentane (DMP), n-alkanes (carbon number = 7–14), and n-fatty acids (carbon number = 3–8) were meaured at 293, 298 and 303 K to calculate the X_{12} values at 298 K. Since the microcalorimeter used to measure ΔH_{mix} can handle liquid samples only, the operation temperature must be higher than any melting point of the components to be mixed. The melting point of TA (302 K) is the highest among the components, and the operation temperature was set at 308 K. Therefore, the volumetric properties of the low molecular weight analogues, TA and their mixtures were required at 308 K, and their densities were measured at 305, 308 and 311 K to calculate the X_{12} values at 308 K.

The density determination is based on measuring the period of oscillation of a vibrating sample in a U-shaped tube. The following relationship exists between the period (P_0) and density (ρ):

$$\rho = A(P_0^2 - B) \tag{17}$$

where A and B are instrument constants, which are determined by calibration with air and water.

In every case a linear plot was obtained for the specific volume *versus* temperature within the temperature range stated above. The slope of this plot divided by the specific volume at 298 or 308 K was taken as the thermal expansivity (α) at 298 or 308 K. The specific volumes and α values at 298 or 308 K are listed in *Tables 2* and *3* for the pure analogues and their mixtures, respectively. Great care was required in measuring the mixture density, since the volatility of each component is different and the time required for complete mixing may be long. By using equation (16) and the α values, the reduced volumes ($\tilde{V}$) were calculated and are listed in *Tables 2* and *3*.

Characteristic pressures

Flory has shown that equation (4) can be reduced to equation (18) by differentiation with respect to temperature[15–17]:

$$P^* = \gamma T \tilde{V}^2 \tag{18}$$

where $\gamma = (\partial P/\partial T)_V$.

For a limited number of compounds γ values were measured experimentally by direct measurement[35] or by indirect methods, such as measuring isothermal compressibility factors[36] or sound velocities[37]. However, γ values are unavailable for most of the compounds and their experimental accuracies are suspect.

Sanchez used cohesive energy density in the close-packed state (CED*) as P^* in his 'lattice fluid theory'[21].

$$P^* = \text{CED}^* \tag{19}$$

P^* in Sanchez's theory is independent of temperature in contrast to P^* in Flory's theory. Thus, Sanchez proposed another P^* adaptable to Flory's theory[21]:

$$P^* = \tilde{V}^2\text{CED}(T) \tag{20}$$

where CED(T) means cohesive energy density at temperature T.

Hildebrand and Scott[38] and Allen *et al.*[39] proposed a semiempirical relationship between internal pressure and CED:

$$(\partial U/\partial V)_T = T(\partial P/\partial T)_v - P \tag{21}$$

$$= m(U_v/V) \tag{22}$$

where U is the internal energy, U_v is the internal energy change of vaporization and m is an empirical constant. Since low pressure is assumed, equation (22) can be reduced to:

$$T\gamma = m(U_v/V) = m\text{CED}(T) \tag{23}$$

For relatively less polar compounds such as the diluents used in this study, m is known[38,39] to be 1.1. Combining equations (18) and (23) produced an equation similar

Table 2 Volumetric properties of pure analogue molecules

Analogue compound	Temperature (K)	V ($cm^3\ g^{-1}$)	$\alpha \times 10^3$ (1/K)	$\tilde{V}$
DMP	298	1.495	1.306	1.307
DMP	308	1.514	1.326	1.319
C_7H_{16}	298	1.473	1.246	1.296
C_7H_{16}	308	1.491	1.327	1.319
C_8H_{18}	298	1.432	1.164	1.280
C_8H_{18}	308	1.449	1.178	1.291
$C_{10}H_{22}$	298	1.378	1.030	1.254
$C_{10}H_{22}$	308	1.392	1.061	1.267
$C_{12}H_{26}$	298	1.343	0.964	1.240
$C_{12}H_{26}$	308	1.356	0.975	1.249
$C_{14}H_{30}$	298	1.318	0.922	1.231
$C_{14}H_{30}$	308	1.330	0.936	1.241
C_2H_5COOH	298	1.012	1.075	1.263
C_4H_9COOH	298	1.071	0.984	1.244
$C_6H_{13}COOH$	298	1.095	0.910	1.223
$C_7H_{15}COOH$	298	1.104	0.890	1.225
TA	308	1.120	0.830	1.218

Table 3 Volumetric properties of analogue pairs

Analogue pair	Temperature (K)	V (cm^3 g^{-1})	$\alpha \times 10^3$ (1/K)	$\tilde{V}$
C_7H_{16}/DMP	298	1.483	1.273	1.301
C_2H_5COOH/DMP	298	1.256	1.194	1.286
C_2H_5COOH/C_7H_{16}	298	1.242	1.173	1.282
C_2H_5COOH/C_8H_{18}	298	1.222	1.137	1.275
$C_2H_5COOH/C_{10}H_{22}$	298	1.195	1.076	1.263
$C_2H_5COOH/C_{12}H_{26}$	298	1.178	1.041	1.256
$C_2H_5COOH/C_{14}H_{30}$	298	1.165	1.022	1.252
C_4H_9COOH/DMP	298	1.283	1.132	1.274
C_4H_9COOH/C_7H_{16}	298	1.274	1.111	1.270
C_4H_9COOH/C_8H_{18}	298	1.249	1.076	1.263
$C_4H_9COOH/C_{10}H_{22}$	298	1.224	1.017	1.251
$C_4H_9COOH/C_{12}H_{26}$	298	1.208	0.987	1.245
$C_4H_9COOH/C_{14}H_{30}$	298	1.190	0.963	1.240
$C_6H_{13}COOH$/DMP	298	1.292	1.086	1.265
$C_6H_{13}COOH/C_7H_{16}$	298	1.284	1.071	1.262
$C_6H_{13}COOH/C_8H_{18}$	298	1.261	1.036	1.255
$C_6H_{13}COOH/C_{10}H_{22}$	298	1.238	0.973	1.242
$C_6H_{13}COOH/C_{12}H_{26}$	298	1.211	0.944	1.236
$C_6H_{13}COOH/C_{14}H_{30}$	298	1.206	0.920	1.231
$C_7H_{15}COOH$/DMP	298	1.293	1.071	1.262
$C_7H_{15}COOH/C_7H_{16}$	298	1.290	1.111	1.259
$C_7H_{15}COOH/C_8H_{18}$	298	1.268	1.022	1.252
$C_7H_{15}COOH/C_{10}H_{22}$	298	1.238	0.963	1.240
$C_7H_{15}COOH/C_{12}H_{26}$	298	1.220	0.930	1.233
$C_7H_{15}COOH/C_{14}H_{30}$	298	1.208	0.911	1.229
TA/DMP	308	1.304	1.066	1.268
TA/C_7H_{16}	308	1.296	1.079	1.271
TA/C_8H_{18}	308	1.279	1.008	1.256
TA/$C_{10}H_{22}$	308	1.255	0.946	1.243
TA/$C_{12}H_{26}$	308	1.236	0.902	1.236
TA/$C_{14}H_{30}$	308	1.224	0.881	1.229

to equation (20) except for the constant m:

$$P^* = m\tilde{V}^2\mathrm{CED}(T) \qquad (24)$$

In *Table 4*, P^* values from equation (24) show good agreement with the experimental values by Flory[35,40] for several compounds. In this study, equation (24) was used and CED(T) was determined by measuring the heat of vaporization and molar volume of each component.

Table 4 Comparison of characteristic pressures by equation (24) and experimental data

Compound	Experimental P^* [35,40] (J cm^{-3})	P^* by equation (24) (J cm^{-3})
n-C_6H_{14}	423	428
n-C_7H_{16}	430	431
n-$C_{10}H_{22}$	446	440
Cyclohexane	532	517
CCl_4	569	570
Benzene	628	642
Chlorobenzene	600	631

The heat of vaporization of each diluent is required to calculate P^* from equation (24). The Clausius–Clayperon equation relates the heat of vaporization to the vapour pressure as:

$$\begin{aligned} -U_v &= \Delta H_{vap} - RT \\ &= -ZR[\mathrm{d}\ln P/\mathrm{d}(1/T)](1 - V_l/V_v) - RT \end{aligned} \qquad (25)$$

where Z is the compressibility factor and V_l/V_v is the volume ratio of liquid to vapour[41]. The vapour pressures of the diluents in this study are low enough to make Z unity, and V_l/V_v can be neglected. Therefore, equation (25) is simplified to:

$$-U_v = \Delta H_{vap} - RT = -R[\mathrm{d}\ln P/\mathrm{d}(1/T)] - RT \qquad (26)$$

The vapour pressure can be measured by the Knudsen effusion method. The number of molecules colliding with a unit area of the wall, v, is obtained from the kinetic theory of gas

$$v = n(RT/2\pi M)^{1/2} \qquad (27)$$

where n is the number of moles and M is the molecular weight. If the wall has a hole of area A, the mass flux of gas passing through the hole is

$$m/A = Mv/N_0 \qquad (28)$$

where N_0 is Avogadro's number. Combining equations (27) and (28) with the ideal gas law makes the vapour pressure equation[42]:

$$P = m/A(2\pi RT/M)^{1/2} \qquad (29)$$

Mass flux through an orifice (m/A) at various temperatures was measured for the calculation of vapour

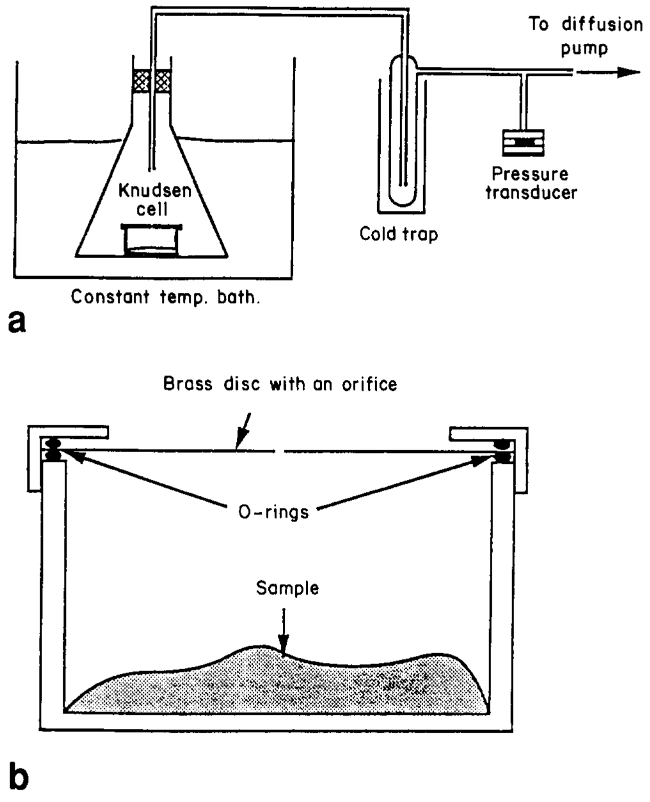

Figure 1 (a) Knudsen effusion apparatus and (b) details of Knudsen cell

pressures and the heats of vaporization. The diluents used in this study have a long aliphatic chain, thus, they have very low vapour pressure. The Knudsen effusion method for measuring sublimation pressure was used to measure the diluent vapour pressure. *Figure 1a* is a diagram of the Knudsen effusion method. The pressure outside the Knudsen cell must be <0.13 Pa to get accurate results. A schematic diagram of a Knudsen cell is shown in *Figure 1b*. The top plate is a thin brass disc (0.05 mm thick) with an orifice in the centre. The diameter of the orifices, which must be smaller than the mean free path of the diluent molecule[42], was chosen from 1.3, 0.8 and 0.4 mm by a trial and error method.

Vapour pressures of n-alkanes, n-fatty acids and TA obtained by this method were plotted in *Figures 2*, *3* and *4* as $\ln P$ *versus* $1/T$. The vapour pressures of $C_{14}H_{30}$ above 333 K were taken from the literature[30], since they were too high to measure by the Knudsen effusion method. The experimental vapour pressures of $C_{20}H_{42}$ were in good agreement with literature data[30]. From the slope of this plot at any temperature, the heat of vaporization at that temperature was obtained and CED was calculated by equation (30):

$$\mathrm{CED} = \Delta U_{\mathrm{vap}}/V = (\Delta H_{\mathrm{vap}} - RT)/V \qquad (30)$$

In *Figures 5*, *6* and *7* CED as a function of temperature was plotted for each diluent. P^* was calculated by equation (24) with $m = 1.1$.

It is hard to measure directly the CED of iPP at various temperatures. In this study the CED of iPP at 298 K was estimated by the group contribution method[43–45], and the empirical temperature dependence equation of CED below was applied to estimate CED at other temperatures using the volumetric information at that temperature[44].

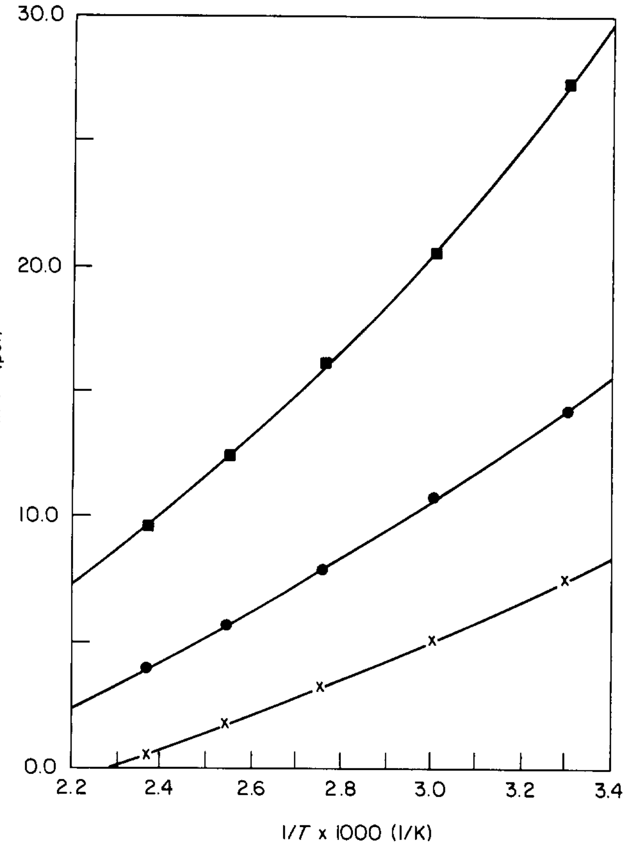

Figure 2 Vapour pressure plot of n-alkanes: (■) $C_{32}H_{66}$; (●) $C_{20}H_{42}$; (×) $C_{14}H_{30}$

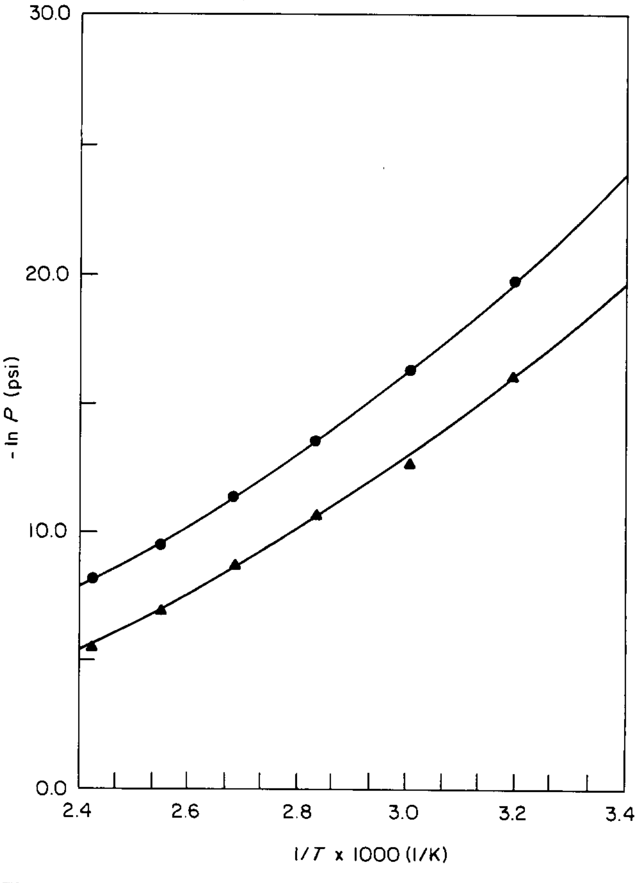

Figure 3 Vapour pressure plot of n-fatty acids: (●) $C_{19}H_{39}COOH$; (▲) $C_{14}H_{29}COOH$

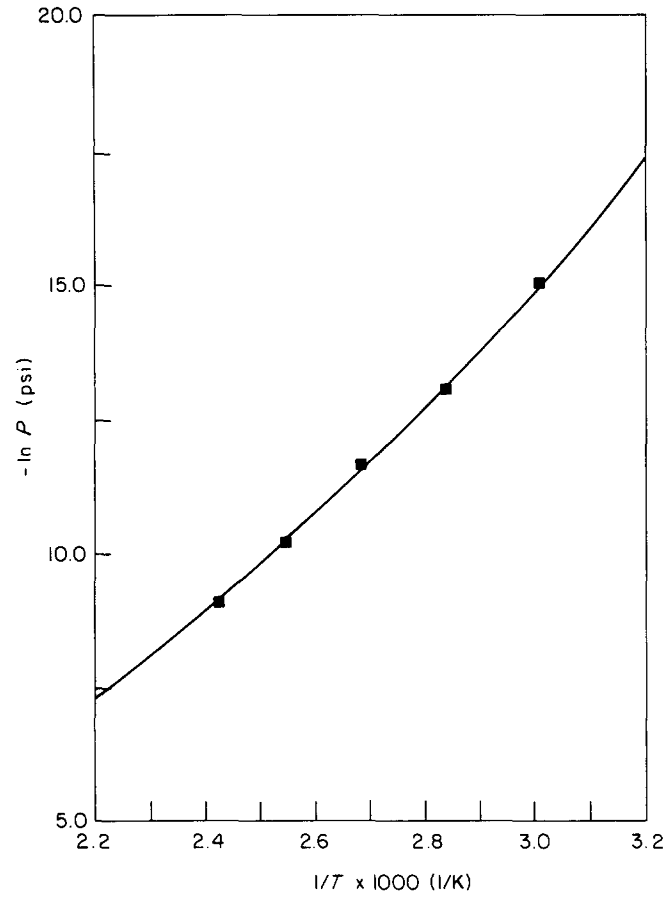

Figure 4 Vapour pressure plot of TA

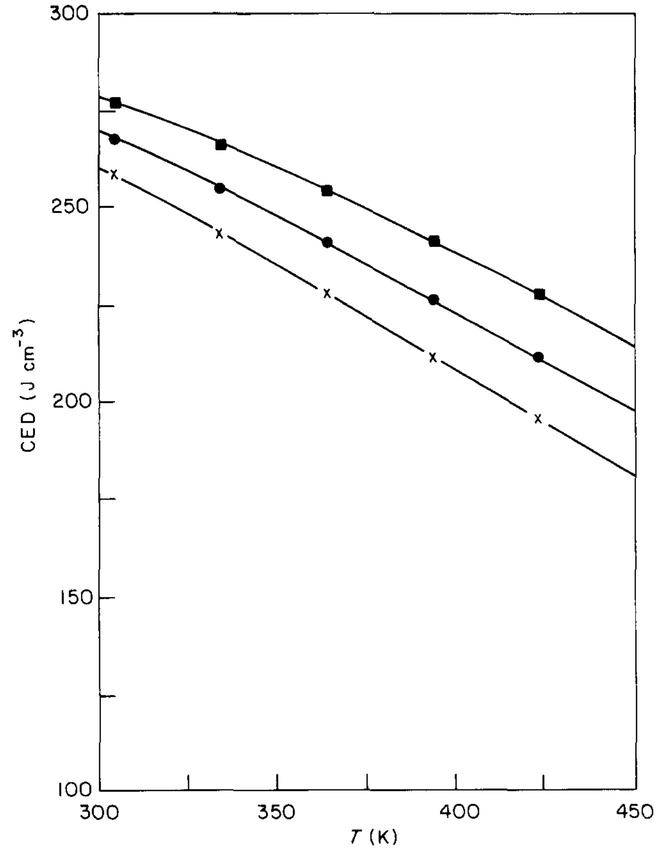

Figure 5 Cohesive energy density of n-alkanes. Symbols as in *Figure 2*

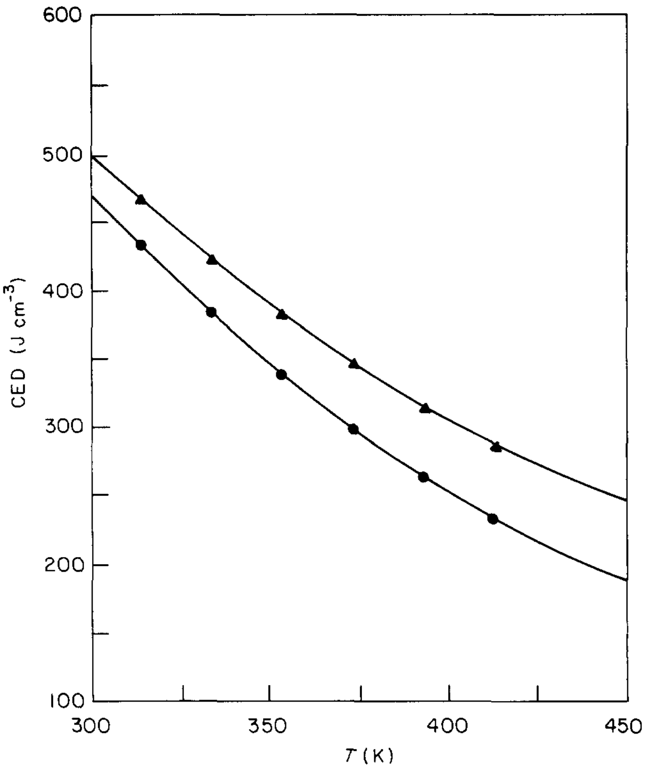

Figure 6 Cohesive energy density of n-fatty acids. Symbols as in *Figure 3*

$$\mathrm{CED}(T) = \mathrm{CED}(298)[V(298)/V(T)]^{2.27} \quad (31)$$

For the low molecular weight analogues and their mixtures, the group contribution method was used for CED estimation at 298 K[43–45].

Analogue system simulation for X_{12}

X_{12} shown in the previous equations is defined by

$$X_{12} = s_1(\eta_{11} + \eta_{22} - 2\eta_{12})/(2v^{*2}) \quad (32)$$

where s_1 is the number of contact sites per diluent segment, η_{ij} is the energy parameter for the ij segment pairs and v^* is the specific core volume of the mixture[15–17]. It is hard to determine X_{12} for the polymer/diluent system, since the parameters in equation (32) are not directly measurable. As shown in equation (6), X_{12} can be calculated from ΔH_{mix} and other EOS parameters. ΔH_{mix} is usually measured at 298 K, but the polymer and diluents are solid at this temperature, hence ΔH_{mix} is hard to measure directly. Since X_{12} is purely enthalpic, X_{12} for low molecular weight analogue systems are usually used for the polymeric systems[25,46,47].

In this study 2,4-dimethylpentane was used as an analogue of iPP, and n-heptane as that of higher molecular weight n-alkanes. Selection of an analogue of n-fatty acids was hard, since there is one carboxyl group located only at the end of the chain. Consequently X_{12} values for 2,4-dimethylpentane with n-fatty acids of carbon number 3–7 were determined individually, from which those for higher molecular weight n-fatty acid diluents were estimated by extrapolation. TA itself was directly used instead of employing its analogue. Equal amounts of mass (0.5–1.0 g each) were mixed at 298 K (or 308 K for TA systems) to measure ΔH_{mix} by using a microcalorimeter (LKB Co. no. 2107).

The EOS parameters needed for the calculation of X_{12} are listed in *Table 5* and ΔH_{mix} and X_{12} values for each pair of analogue molecules are listed in *Table 6*. X_{12} is usually assumed to be constant with temperature, since each η_{ij} parameter changes with temperature in the same manner[48]. Therefore, X_{12} determined from the ΔH_{mix} measurement was used at other temperatures in this study.

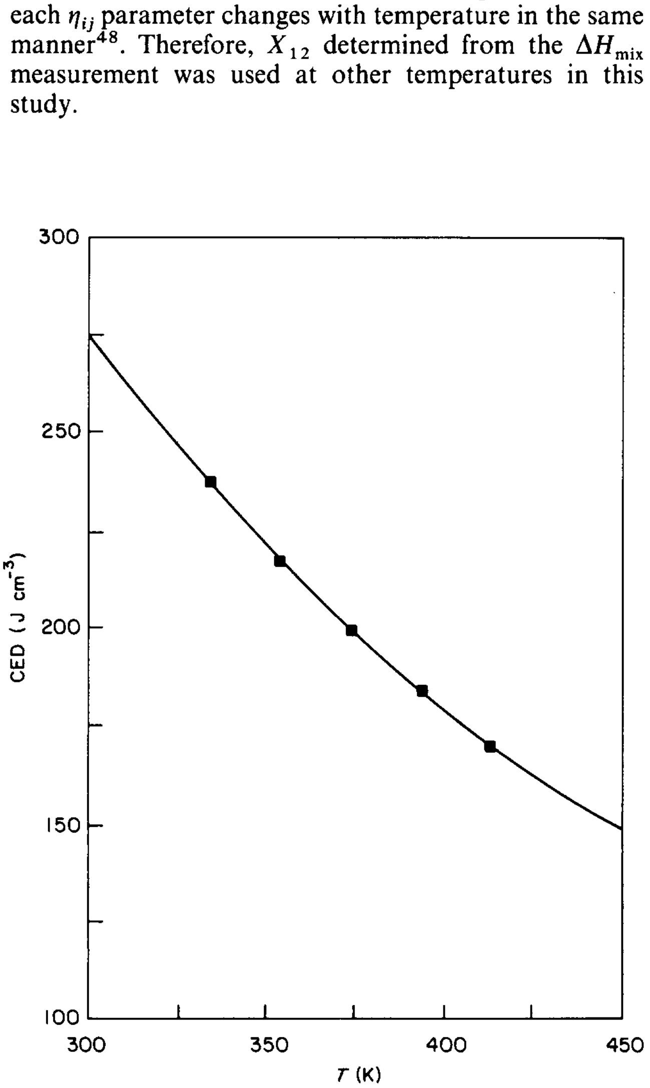

Figure 7 Cohesive energy density of TA

Consideration of the chain end effects on X_{12}

It has been pointed out that X_{12} from analogue systems is not exact for the polymeric system and causes some deviation from the experimental results[25]. The correction for this deviation is not well established and has been done in arbitrary ways just to fit the experimental results without any physical justification[25,46,47]. It has been qualitatively believed that the number of chain ends should affect the interaction between the species. The chain end effect was accounted for in this study by employing a series of low molecular weight analogues.

The X_{12} value for DMP/C_7H_{16} was $0.518\ \mathrm{J\ cm^{-3}}$, which is very small compared with other systems, since both components are non-polar and are similar in structure. So in this case the chain end effect was not significant and $0.518\ \mathrm{J\ cm^{-3}}$ was directly used as the X_{12} value for the iPP/n-alkane systems. From a sample calculation, the difference in χ between $X_{12} = 0.518\ \mathrm{J\ cm^{-3}}$ and $X_{12} = 0\ \mathrm{J\ cm^{-3}}$ (which may be the extreme case, since X_{12} tends to decrease with increasing chain length) was in the order of 10^{-3}.

X_{12} values for DMP/n-fatty acids are much greater than for DMP/C_7H_{16}, and the chain end effects must be considered to obtain X_{12} for iPP/n-fatty acids. Extrapolation of X_{12} to a polymeric unit by employing a series of analogue molecules can help determine X_{12} for the polymeric systems. Unfortunately, it is very hard to provide a series of analogue molecules for iPP. 2,4-Dimethyl pentane is the only commercially available analogue molecule for iPP.

Since X_{12} is purely enthalpic and both DMP and n-alkanes are non-polar, it was postulated that X_{12} for the iPP/n-fatty acid system might be predicted from n-alkane/n-fatty acid systems. This postulation was confirmed by the experimental results shown in *Figure 8*; that is, X_{12} values for DMP/n-fatty acids are nearly the same as those for C_7H_{16}/n-fatty acids, where both DMP and C_7H_{16} have the same number of carbons and hydrogens. This result enables us to examine the chain end effect for iPP/n-fatty acid systems by using a series of n-alkanes.

Since the inverse of the number of carbons per n-alkane

Table 5 EOS parameters for analogue molecules

Analogue molecule	Temperature (K)	P^* (J cm^{-3})	A_w (cm^2 mol^{-1})	V^* (cm^3 mol^{-1})
DMP	298	383.3	10.97	114.3
DMP	308	379.4	10.97	114.8
C_7H_{16}	298	429.2	10.99	113.6
C_7H_{16}	308	431.8	10.99	113.0
C_8H_{18}	298	433.3	12.34	127.5
C_8H_{18}	308	427.0	12.34	128.0
$C_{10}H_{22}$	298	442.5	15.04	156.0
$C_{10}H_{22}$	308	431.7	15.04	156.0
$C_{12}H_{26}$	298	455.0	17.74	184.1
$C_{12}H_{26}$	308	432.2	17.74	184.6
$C_{14}H_{30}$	298	459.3	20.44	211.9
$C_{14}H_{30}$	308	436.1	20.44	212.2
C_2H_5COOH	298	763.0	6.53	59.3
C_4H_9COOH	298	640.4	9.23	87.8
$C_6H_{13}COOH$	298	587.4	11.93	115.8
$C_7H_{15}COOH$	298	569.4	13.28	129.8
TA	308	432.9	32.27	315.6

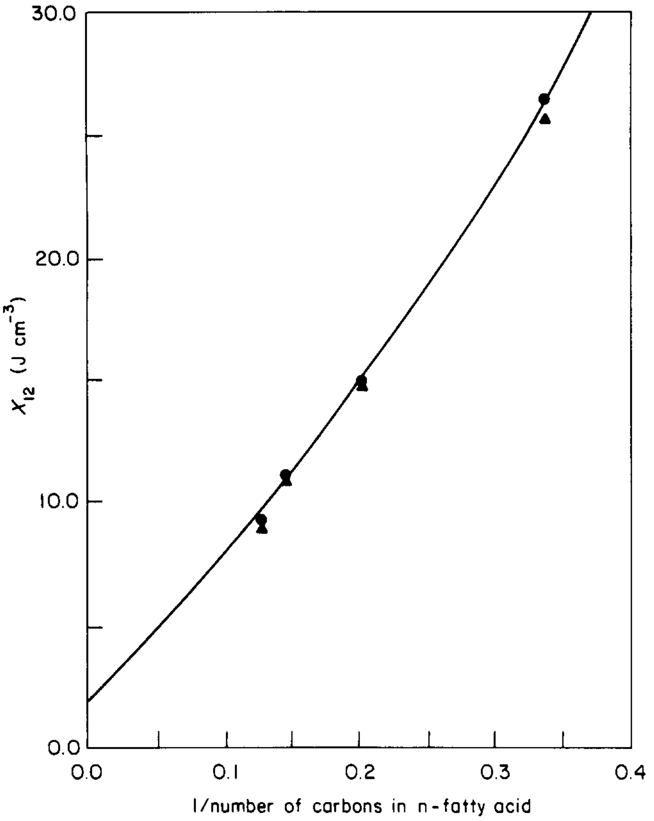

Figure 8 Comparison of X_{12} values for (●) DMP/n-fatty acids and (▲) C_7H_{16}/n-fatty acids

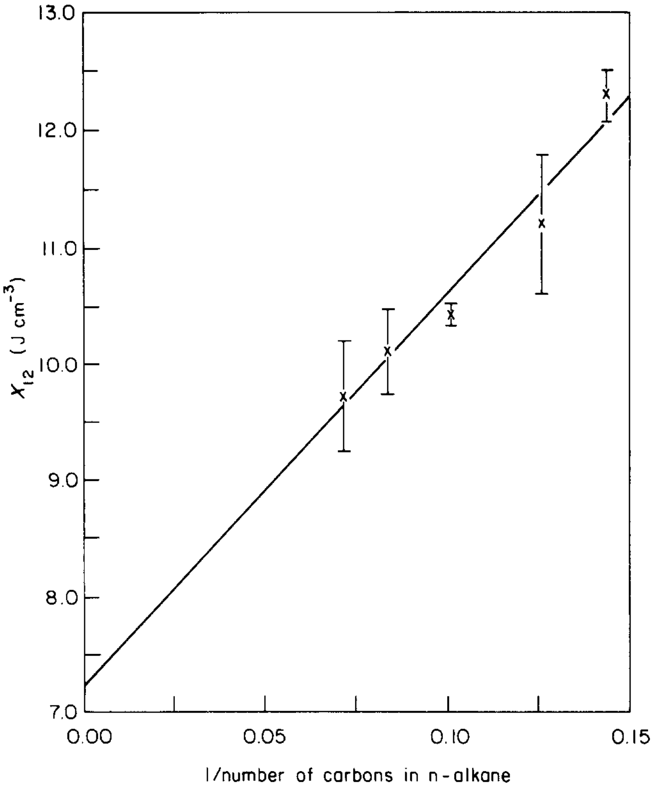

Figure 10 Chain end effect of n-alkane on X_{12} parameter for n-alkane/TA systems

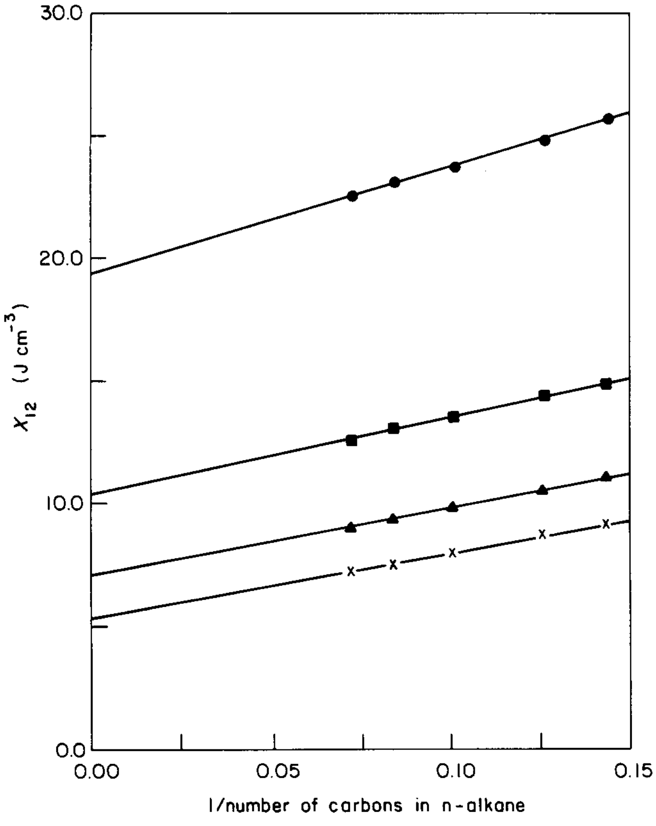

Figure 9 Chain end effect of n-alkane on X_{12} parameter for n-alkane/n-fatty acid systems: (●) n-alkane/C_2H_5COOH; (■) n-alkane/C_4H_9COOH; (▲) n-alkane/$C_6H_{13}COOH$; (×) n-alkane/$C_7H_{15}COOH$

molecule is proportional to the number of chain ends in the same amount of each n-alkane, it was used as a parameter for the number of chain ends. As shown in *Figure 9*, with the decrease in the inverse of the number of carbons in n-alkane (i.e. with increase in chain length), X_{12} linearly decreased for every n-fatty acid. Since the inverse of the number of carbons for a polymer is nearly zero, the intercept in *Figure 9* represents the X_{12} value for each iPP/n-fatty acid system.

As shown in *Table 6*, X_{12} for the TA/DMP system is nearly the same as that of the TA/C_7H_{16} system. Therefore, a series of n-alkanes (C_7H_{16} to $C_{14}H_{30}$) was used as a series of iPP analogue molecules to overcome chain end effects, which are usually generated in analogue system simulation. ΔH_{mix} and X_{12} values at 308 K are listed for every analogue molecule/TA system in *Table 6*.

The inverse of the number of carbon atoms per n-alkane molecule was chosen as a parameter representing the number of chain ends. There is a linear relationship between the X_{12} value and the inverse of the number of carbon atoms in n-alkanes as shown in *Figure 10*. The X_{12} value for the iPP/TA system was obtained from the intercept of the extrapolation plot as 7.2 J cm^{-3}. This X_{12} value was used at temperatures other than 308 K on the assumption that X_{12} is a temperature independent variable[48].

X_{12} *determination for solid n-fatty acid systems*

It is hard to determine X_{12} for solid n-fatty acid systems, since it cannot be experimentally determined by measuring the heat of mixing as was done for the liquid n-fatty acid systems. An extrapolation method to determine X_{12} for solid n-fatty acid systems was developed in this study.

Table 6 Heat of mixing and X_{12} values of analogue pairs

Analogue pair	Temperature (K)	ΔH_{mix} ($J\ g^{-1}$)	Amount mixed (g/g)	X_{12} ($J\ cm^{-3}$)
C_7H_{16}/DMP	298	0.185 ± 0.035	1/1	0.518 ± 0.098
C_2H_5COOH/DMP	298	6.150 ± 0.067	0.5/0.5	26.51 ± 0.289
C_2H_5COOH/C_7H_{16}	298	6.009 ± 0.103	0.5/0.5	25.79 ± 0.442
C_2H_5COOH/C_8H_{18}	298	5.753 ± 0.141	0.5/0.5	24.88 ± 0.610
$C_2H_5COOH/C_{10}H_{22}$	298	5.402 ± 0.091	0.5/0.5	23.71 ± 0.399
$C_2H_5COOH/C_{12}H_{26}$	298	5.201 ± 0.037	0.5/0.5	23.08 ± 0.164
$C_2H_5COOH/C_{14}H_{30}$	298	5.052 ± 0.105	0.5/0.5	22.60 ± 0.470
C_4H_9COOH/DMP	298	3.501 ± 0.140	0.5/0.5	14.93 ± 0.597
C_4H_9COOH/C_7H_{16}	298	3.541 ± 0.135	0.5/0.5	14.85 ± 0.566
C_4H_9COOH/C_8H_{18}	298	3.476 ± 0.070	0.5/0.5	14.40 ± 0.290
$C_4H_9COOH/C_{10}H_{22}$	298	3.275 ± 0.069	0.5/0.5	13.53 ± 0.285
$C_4H_9COOH/C_{12}H_{26}$	298	3.143 ± 0.079	0.5/0.5	13.08 ± 0.329
$C_4H_9COOH/C_{14}H_{30}$	298	2.996 ± 0.081	0.5/0.5	12.58 ± 0.344
$C_6H_{13}COOH$/DMP	298	2.500 ± 0.074	0.5/0.5	11.05 ± 0.327
$C_6H_{13}COOH/C_7H_{16}$	298	2.547 ± 0.005	0.5/0.5	10.96 ± 0.022
$C_6H_{13}COOH/C_8H_{18}$	298	2.498 ± 0.049	0.5/0.5	10.47 ± 0.205
$C_6H_{13}COOH/C_{10}H_{22}$	298	2.401 ± 0.054	0.5/0.5	9.77 ± 0.220
$C_6H_{13}COOH/C_{12}H_{26}$	298	2.304 ± 0.067	0.5/0.5	9.36 ± 0.272
$C_6H_{13}COOH/C_{14}H_{30}$	298	2.210 ± 0.050	0.5/0.5	9.00 ± 0.204
$C_7H_{15}COOH$/DMP	298	2.045 ± 0.018	0.5/0.5	9.32 ± 0.082
$C_7H_{15}COOH/C_7H_{16}$	298	2.039 ± 0.023	0.5/0.5	8.99 ± 0.101
$C_7H_{15}COOH/C_8H_{18}$	298	2.062 ± 0.006	0.5/0.5	8.75 ± 0.025
$C_7H_{15}COOH/C_{10}H_{22}$	298	1.943 ± 0.050	0.5/0.5	7.90 ± 0.203
$C_7H_{15}COOH/C_{12}H_{26}$	298	1.837 ± 0.027	0.5/0.5	7.42 ± 0.109
$C_7H_{15}COOH/C_{14}H_{30}$	298	1.793 ± 0.038	0.5/0.5	7.24 ± 0.153
TA/DMP	308	2.206 ± 0.097	0.5/0.5	12.39 ± 0.544
TA/C_7H_{16}	308	2.152 ± 0.035	0.5/0.5	12.30 ± 0.200
TA/C_8H_{18}	308	2.066 ± 0.110	0.5/0.5	11.21 ± 0.597
TA/$C_{10}H_{22}$	308	1.758 ± 0.013	0.5/0.5	10.43 ± 0.077
TA/$C_{12}H_{26}$	308	1.682 ± 0.062	0.5/0.5	10.11 ± 0.373
TA/$C_{14}H_{30}$	308	1.586 ± 0.078	0.5/0.5	9.73 ± 0.479

Table 7 Group contribution values of surface area[49]

Group	$A_w \times 10^9$ ($cm^2\ mol^{-1}$)
—CH_3	2.12
—CH_2—	1.35
=CH—	0.57
=C=O	1.60
—OH	1.46
=N—	0.20

As shown in *Table 6*, X_{12} apparently decreased with increasing chain length of n-fatty acid; however, X_{12} was actually affected by the density of carboxyl groups in the n-fatty acid, since the interaction between the carboxyl group and n-alkane (or DMP) chain was a dominating factor in determining X_{12}.

With increase in chain length, the density of the carboxyl group decreased. The inverse of the number of carbons per n-fatty acid molecule is proportional to the density of the carboxyl group. Each intercept value in *Figure 9* was taken as X_{12} for iPP with each n-fatty acid. These intercept values were plotted *versus* the inverse of the number of carbons in the n-fatty acid in *Figure 11*. The extrapolation curve in *Figure 11* must meet the origin (i.e. X_{12} is zero where the inverse of the number of carbons in the n-fatty acid is zero). This extrapolated plot was used to estimate X_{12} for each solid n-fatty acid as indicated in *Figure 11*.

Mixing rule

Flory proposed mixing rules that can be used to estimate the volume of the polymer/diluent mixture. The mixing rules for P^* and T^* are defined as follows[15–17]:

$$P^* = P_1^*\phi_1 + P_2^*\phi_2 - \phi_1\theta_2 X_{12} \tag{33}$$

$$T^* = P^*/[(P_1^*\phi_1/T_1^*) + (P_2^*\phi_2/T_2^*)] \tag{34}$$

P^* for the mixture of iPP/diluent and each analogue pair were estimated by the mixing rule as introduced in equation (33) and T^* was obtained from equation (34). $\tilde{T}$ was obtained from its definition and $\tilde{V}$ was estimated by equation (15).

Volume and surface fraction

In Flory's original EOS theory, segment fraction was used rather than volume fraction[15–17]. In this study, Scott's reference volume concept was used and one lattice site was assumed to be occupied by one segment[18]. Therefore, the segment fraction is identical to the volume

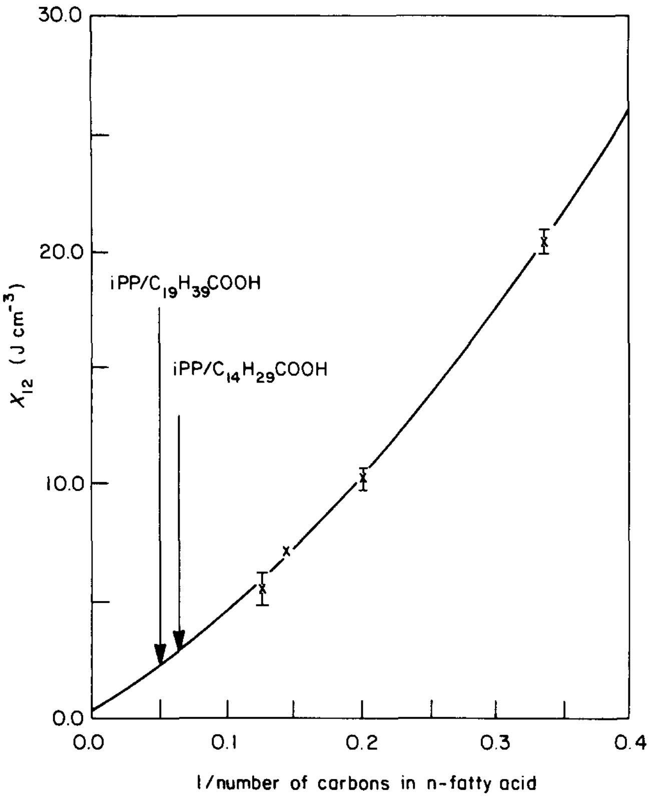

Figure 11 Extrapolation of X_{12} values for iPP/n-fatty acid systems

fraction defined as

$$\phi_i = (r_i n_i)/(r_i n_i + r_j n_j) \qquad (35)$$

where r_i is the number of segments and n_i is the number of moles of component i in the i–j mixture. The surface fraction is approximated from the group contribution method for surface area proposed by Bondi[49]. The group contribution surface area data (A_w) for the groups in this study are listed in *Table 7*.

CONCLUSIONS

Simplified methods to determine the EOS parameters were developed. The assumption of constant characteristic volume and temperature greatly simplified the process of obtaining reduced volumes and temperatures. Characteristic pressures obtained from a semi-empirical equation correlating CED and reduced volume were in good agreement with literature data. The X_{12} parameters extrapolated from a series of low molecular weight analogue systems overcame the chain end effects are not considered in conventional analogue system studies.

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