Inverse gas chromatography study of some triacetin–polymer systems

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Inverse gas chromatographic studies have been carried out on systems consisting of 1,2,3-propanetriyl triacetate (triacetin) as solute and various polar polymers in the molten state: aliphatic α,ω-dihydroxy block and branched poly(ester ethers), and α,ω-dihydroxy polyesters, polyethers and polycarbonates. Thermodynamic sorption and mixing functions and interaction parameters are determined and discussed in relation to the structure of the polymers. Segment interaction parameters calculated from Flory's equation-of-state theory and from lattice-fluid theory are consistent with the experimental data. However, these theories do not exhibit any marked superiority with regard to the previous Flory–Huggins theory, which satisfactorily describes the behaviour of the systems under study.

(Keywords: inverse gas chromatography; 1,2,3-propanetriyl triacetate; α,ω-dihydroxy poly(ester ethers); α,ω-dihydroxy polyesters; α,ω-dihydroxy polyethers; α,ω-dihydroxy polycarbonates)

INTRODUCTION

Inverse gas chromatography (i.g.c.) has proved to be a rapid and consistent method to study polymer–solvent interactions[1–3]. However, most of the systems described in the literature consist of only one polymer, which is not polar in most cases (polystyrene, polyisobutylene, polysiloxane, etc.), and of various low-boiling-point solvents. Furthermore, the study of interactions between polar polymers and polar solvents has been the object of only little attention.

α,ω-Dihydroxy polar polymers can be crosslinked by reaction with di- and triisocyanates to form materials used as binders for solid propellants. These must be able to swell to very high extents in the presence of compounds such as alkyl trinitrates. Formulation of the thermodynamic interactions between such compounds and the initial dihydroxy polymers is therefore of interest.

On evident safety grounds 1,2,3-propanetriyl triacetate (triacetin, TA) is usually taken as a model of 1,2,3-propanetriyl trinitrate (nitroglycerin, NGL) in physicochemical studies, at least in a first approach. The present work is devoted to the i.g.c. study of thermodynamic interactions between triacetin and various polar polymers to determine whether the experimental results obtained by this technique allow the calculations of interaction parameters and reliable comparisons. The chosen polymers are α,ω-dihydroxy poly(di(oxyethylene)oxysuccinyl) (**1**), α,ω-dihydroxy poly(tri(oxyethylene)oxysuccinyl) (**2**), α,ω-dihydroxy poly(oxyethyleneoxysuccinyl)-*block*-poly(oxyethylene) (**3**), α,ω-dihydroxy poly(oxy-3-(2-methoxyethoxy)propyleneoxysuccinyl) (**4**), α,ω-dihydroxy poly(di(oxyethylene)oxyadipyl) (**5**), α,ω-dihydroxy poly(hexamethylenecarbonate) (**6**), α,ω-dihydroxy poly(tetramethylenecarbonate) (**7**), α,ω-dihydroxy poly(oxypropylene) (**8**) and α,ω-dihydroxy poly(oxyethylene) (**9**).

The following article reports the i.g.c. determination of thermodynamic data directly on alkyl trinitrate/polymer systems and their comparison with the results obtained when triacetin is used.

EXPERIMENTAL

Materials

The synthesis and characterization of **1**–**4** have been described in a previous article[4]. Polymers **5**–**9** were obtained from SNPE (France). Their molar masses are given in *Table 1*. Analytical-grade methylene chloride and triacetin (TA) (Prolabo, France) were used without further purification.

In the following, subscripts 1 and 2 are relative to the solute (TA) and the polymer under study (polymer **1** to **9**) respectively.

Column preparation

The polymer was deposited onto Gas Chrom Q (Applied Science, mesh size 80–100) from methylene

Table 1 Specific retention volumes V_g^0 of triacetin in polymers **1**–**9** at different temperatures

Polymer	$\bar{M}_n$ (g mol^{-1}) (end groups)	V_g^0 (m^3 kg^{-1}) 402.1 K	411.8 K	421.6 K	431.1 K
1	890	4.525	2.771	1.766	1.142
2	1250	4.822	2.989	1.863	1.205
3	1810	4.508	2.757	1.690	1.120
4	1820	3.837	2.483	1.620	1.002
5	1910	4.544	2.780	1.757	1.124
6	2410	3.860	2.337	1.522	0.999
7	2210	3.592	2.236	1.435	0.965
8	2010	–	2.371	1.550	1.003
9	1570	5.182	3.148	1.958	1.285

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chloride solution by continuous stirring at room temperature. The coated support was dried in a vacuum oven at 60°C for 24 h, then packed into a stainless-steel column (i.d. 2 mm, length 1 m), and conditioned for 12 h at 180°C with a 10 ml min^{-1} He flow rate. Four columns were prepared for each polymer with different loadings (2%, 4%, 7%, 10%). The exact column loading was determined by thermogravimetry using the required blank correction.

Gas chromatography system

Measurements were carried out on a Girdel 330 dual-column gas chromatograph equipped with a dual-flame ionization detector operated at 210°C. Column temperature was controlled within 0.1°C. Helium was chosen as the carrier gas. Flow rates were varied from 5 to 20 ml min^{-1} using a calibrated Tylan DFC 100 dual-mass-flow controller. Pressures at the inlet and outlet of the columns were measured by a mercury manometer. Triacetin (1% solution in CH_2Cl_2) was introduced by manual injection (injector temperature 210°C). The chart speed of the recorder was calibrated.

Measurement procedure

Measurements were carried out at four temperatures in the range 130–160°C. Temperature was kept below 160°C in order to avoid any polymer decomposition and above 130°C to obtain reasonable retention times. At these temperatures, polymers **1**–**9** are liquids. The highest melting point is that of polycarbonates **6** and **7** ($T_m \approx 60$°C). Four different carrier-gas flow rates (5, 10, 15, 20 ml min^{-1}) were used for each column at each temperature. The values of retention volumes were corrected for the dead volume in the column measured from the retention time of pentane or methane under the same experimental conditions. The corrected values do not depend on the amount of solute (1–10 μg diluted in CH_2Cl_2) and were averaged for each flow rate. Nearly symmetrical peaks were obtained, which allowed the calculation of the net retention time (t_R) from the retention times at peak maxima. The net retention volume $V_N = jFt_R$, where j is the James–Martin carrier-gas compressibility factor[5] and F is the carrier-gas flow rate at 273 K and atmospheric pressure, was extrapolated to zero flow rate by linear regression. It was found to be independent of the gas flow rate. Specific retention volumes (V_g^0) were calculated using[6] $V_g^0 = V_N/m_2$ where m_2 is the mass of the polymer in the column. The reproducibility of V_g^0 for the same column was found to be better than 0.5%. However, for different columns with the same loading of the same polymer, this reproducibility was not better than 2% due to the uncertainty on the determination of m_2. Within this experimental error V_g^0 was independent of m_2, showing that no adsorption took place and that V_g^0 was the desired bulk retention volume. This is also borne out by the independence of retention volumes on the injected mass of solute and by the symmetry of the peaks obtained. The values of V_g^0 discussed below are the average values obtained from the study of four different column loadings.

Specific volumes v and thermal expansion coefficients α were measured using a thermostated Le Chatelier densitometer. The values of triacetin vapour pressure are obtained from literature[7–9] or measured using the chromatographic method described elsewhere[10]. Interpolations in the experimental range were made using the equation proposed by Hass and Newton[11].

DATA REDUCTION

The partial molar free energy of solution, ΔG_1^s, and the partial molar enthalpy of solution, ΔH_1^s, are given by the relations[12,13]:

$$\Delta G_1^s = -RT \ln(M_1 V_g^0/RT_0) \qquad (1)$$

$$\Delta H_1^s = -R\,\partial(\ln V_g^0)/\partial(1/T) \qquad (2)$$

where M_1 is the molar mass of the solute, $R = 8.3144$ J mol^{-1} K^{-1} and $T_0 = 273.15$ K.

The weight fraction activity coefficient of the solute probe at infinite dilution, γ_1^∞, was calculated according to Patterson *et al.*[14]:

$$\gamma_1^\infty = (RT_0/V_g^0 p_1^0 M_1)\exp[-p_1^0(B_{11} - V_1/RT] \qquad (3)$$

where V_1, p_1^0 and B_{11} are the molar volume, vapour pressure and second virial coefficient of the solute. The B_{11} value of triacetin was estimated using the Kreglewski equation[15,16]: $B_{11} = -10\,500$ cm^3 mol^{-1}. The corrective exponential term in equation (3) always lies between 0.99 and 1, and plays only a minor role in calculations.

The partial molar free energy and enthalpy of mixing at infinite dilution of the solute are given by:

$$\Delta G_1^\infty = RT \ln \gamma_1^\infty \qquad (4)$$

$$\Delta \mathrm{H}_1^\infty = R\,\partial(\ln \gamma_1^\infty)/\partial(1/T) \qquad (5)$$

Flory–Huggins interaction parameters were calculated from the equation[14]:

$$\chi_{12}^\infty = \ln \gamma_1^\infty + \ln(v_2/v_1) - 1 + V_1/V_2 \qquad (6)$$

where v_1 and v_2 and V_1 and V_2 are the specific and molar volumes of the solute and the polymer respectively.

According to Flory's equation-of-state theory[17–20] (ES theory), the χ_{ES}^∞ interaction parameter is related to γ_1^∞ through an equation similar to equation (6), where the specific and molar volumes are replaced by characteristic volumes v^* and V^*:

$$\chi_{ES}^\infty = \ln \gamma_1^\infty + \ln(v_2^*/v_1^*) - 1 + V_1^*/V_2^* \qquad (7)$$

The state equation contact energy parameter X_{12} relative to the energy change for the formation of contacts between unlike species is given by:

$$X_{12} = RT\chi_{ES}^\infty \frac{\tilde{v}_2}{v_1^*} - P_1^*\tilde{v}_2\left[3\tilde{T}_1 \ln\left(\frac{\tilde{v}_1^{1/3} - 1}{\tilde{v}_2^{1/3} - 1}\right) + \frac{1}{\tilde{v}_1} - \frac{1}{\tilde{v}_2}\right] \qquad (8)$$

where $\tilde{v}$ and $\tilde{T}$ are reduced parameters and P_1^* is the characteristic pressure of the solute. Reduced parameters verify the following equation of state[17]:

$$\frac{\tilde{P}\tilde{v}}{\tilde{T}} = \frac{\tilde{v}^{1/3}}{\tilde{v}^{1/3} - 1} - \frac{1}{\tilde{v}\tilde{T}} \qquad (9)$$

with

$$\tilde{v}=v/v^* \qquad (10)$$

$$\tilde{T}=T/T^* \qquad (11)$$

$$\tilde{P}=P/P^* \qquad (12)$$

The characteristic values (P^*, v^*, T^*) of a given compound can be computed from equation (9) by a non-linear least-squares fit of experimental (P,v,T) data[21].

In the lattice-fluid theory (LF theory) of Sanchez and Lacombe[22–24], reduced density $\tilde{\rho}$, pressure $\tilde{P}$ and temperature $\tilde{T}$ verify the following equation of state:

$$\tilde{\rho}^2+\tilde{P}+\tilde{T}\left[\ln(1-\tilde{\rho})+\left(1-\frac{1}{r}\right)\tilde{\rho}\right]=0 \qquad (13)$$

where r is the number of lattice sites occupied by the r-mer; reduced parameters are given by the relations:

$$\tilde{\rho}=\rho/\rho^*_{\mathrm{LF}} \qquad (14)$$

$$\tilde{T}=T/T^*_{\mathrm{LF}} \qquad (15)$$

$$\tilde{P}=P/P^*_{\mathrm{LF}} \qquad (16)$$

$$r=\frac{MP^*_{\mathrm{LF}}}{RT^*_{\mathrm{LF}}\rho^*_{\mathrm{LF}}} \qquad (17)$$

where ρ^*_{LF}, T^*_{LF} and P^*_{LF} are the characteristic density, pressure and temperature.

As above, the interaction parameter $\chi^\infty_{\mathrm{LF}}$ is given by:

$$\chi^\infty_{\mathrm{LF}}=\ln\gamma^\infty_1+\ln\left(\frac{\rho^*_{1\mathrm{LF}}}{\rho^*_{2\mathrm{LF}}}\right)-1+\frac{V^*_{1\mathrm{LF}}}{V^*_{2\mathrm{LF}}} \qquad (18)$$

where ρ^*_{LF} and V^*_{LF} are the characteristic densities and molar volumes. The binary mixture is characterized by only one parameter, ΔP^*, equal to the net change of cohesive energy density on mixing in the close-packed state. ΔP^* is related to $\chi^\infty_{\mathrm{LF}}$ in the g.c. conditions (infinite dilution of 1 in 2) by the following relation:

$$\Delta P^*=RT\chi^\infty_{\mathrm{LF}}\frac{\rho^*_{1\mathrm{LF}}}{\tilde{\rho}_2}+\frac{P^*_{1\mathrm{LF}}}{\tilde{\rho}_2}\left[\frac{\tilde{\rho}_1}{\tilde{T}_1}+(\tilde{v}_2-1)\ln(1-\tilde{\rho}_2)\right.$$
$$\left.-(\tilde{v}_1-1)\ln(1-\tilde{\rho}_1)+\frac{1}{r_1}\ln\left(\frac{\tilde{\rho}_2}{\tilde{\rho}_1}\right)\right] \qquad (19)$$

Details on the determination of characteristic quantities are given in another paper[21].

RESULTS AND DISCUSSION

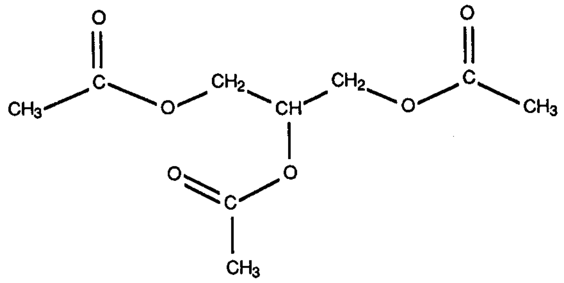
Specific retention volumes and thermodynamic sorption functions

The specific retention volumes V^0_{g} of triacetin in polymers **1**–**9** measured at four temperatures between 400 and 435 K, and extrapolated to zero flow rate, are given in *Table 1*. As found by various authors on other systems[26–30], the variations of $\ln V^0_{\mathrm{g}}$ with $1/T$ could be assumed to be linear within experimental errors. The partial molar enthalpies and entropies of sorption were computed using equations (1) and (2) (*Table 2*).

Table 2 Partial molar enthalpy ΔH^{s}_1 and entropy $T\Delta S^{\mathrm{s}}_1$ of sorption for triacetin at infinite dilution in polymers **1**–**9** at 431.1 K

Polymers	ΔH^{s}_1 (kJ mol^{-1})	$T\Delta S^{\mathrm{s}}_1$ (kJ mol^{-1})
1	−68.2	100.9
2	−69.1	101.6
3	−69.5	102.2
4	−66.3	99.4
5	−69.2	102.0
6	−66.8	99.9
7	−65.4	98.6
8	−65.8	98.9
9	−69.3	101.6

ΔH^{s}_1 depends on the solute heat of vaporization (the same for all systems) and on the solute–polymer interactions. It may be used for the comparison of the behaviour of triacetin in the polymers under study. The most exothermic systems (−68 to −69 kJ mol^{-1}) correspond to polymers containing both ester and ether groups (**1**–**3**, **5**) and for polyoxyethylene **9**. For the polycarbonates **6** and **7**, and for the branched polymers **4** and **8**, the process is less exothermic, ~ −66 kJ mol^{-1}. In the case of **4** and **8**, this may result from sterically unfavourable arrangements between polymers with side chains and triacetin, which is itself a star-like molecule:



Thermodynamic mixing functions

The partial molar free enthalpy of mixing, ΔG^∞_1, was calculated using equation (4) and the partial molar enthalpy and entropy of mixing, ΔH^∞_1 and ΔS^∞_1, by linear regression over the experimental temperature range. The results at 431 K are summarized in *Table 3*. Relatively low values of ΔG^∞_1 are obtained. This probably results from the relatively good miscibility of triacetin with polymers **1**–**9**. Only approximate ΔH^∞_1 and ΔS^∞_1 values could be obtained for polymers **4**, **6** and **8**, owing to the somewhat scattered γ^∞_1 values. Slightly exothermic ΔH^∞_1 values were found for the linear ester- and/or ether-based polymers **2**, **3**, **5** and **9** while endothermic values are found for **1**, branched polymers **4** and **8**, and polycarbonates **6** and **7**. The unfavourable enthalpy situation for (ester ether)-based polymer **1** is compensated by a less negative entropy contribution to ΔG^∞_1. The classification of the polymers with respect to ΔG^∞_1 or to ΔH^∞_1 is the same.

Interaction parameters

According to the thermodynamic theories of polymers, the partial molar free energy of mixing consists of a combinatorial entropic term and a residual non-combinatorial free energy of mixing, χ, characteristic of interactions between solute and polymer. Its value

Table 3 Partial molar free energy ΔG_1^∞, enthalpy ΔH_1^∞ and entropy $T\Delta S_1^\infty$ of mixing for triacetin at infinite dilution in polymers **1**–**9** at 431.1 K

Polymers	ΔG_1^∞ (kJ mol^{-1})	ΔH_1^∞ (kJ mol^{-1})	$-T\Delta S_1^\infty$ (kJ mol^{-1})
1	3.8	0.5	3.3
2	3.6	−0.2	3.8
3	3.8	−0.8	4.6
4	4.2	≈2	≈2
5	3.8	−0.5	4.3
6	4.3	≈2	≈2
7	4.4	3.5	0.9
8	4.2	≈2.5	≈2
9	3.4	−0.6	4.0

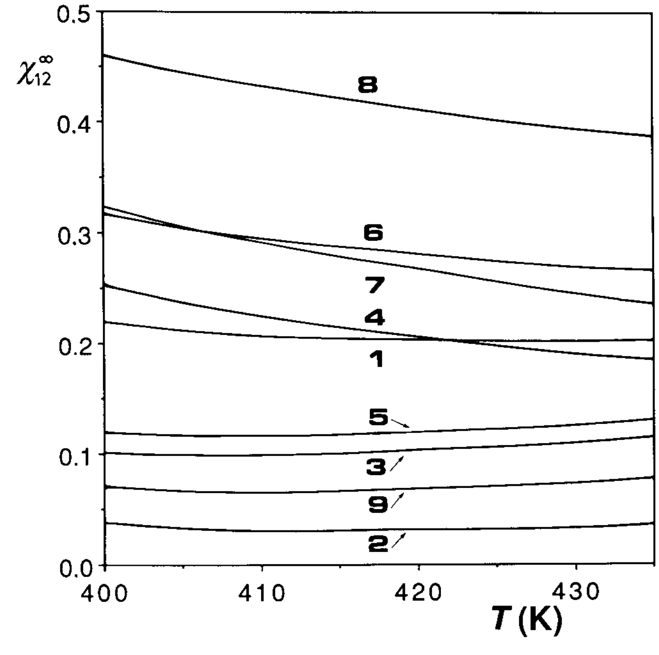


Figure 1 Variations of χ_{12}^∞ with temperature T for triacetin–polymers **1**–**9**

depends on the method of calculation of the combinatorial entropy term. It is denoted χ_{12}^∞ (Flory–Huggins theory), χ_{ES}^∞ (Flory's equation-of-state theory) or χ_{LF}^∞ (lattice-fluid theory) for an infinite dilution of the solute in the polymer.

Since the variations of solute and polymer density, of p_1^0 and of V_g^0 with temperature are known, χ_{12}^∞, χ_{ES}^∞ and χ_{LF}^∞ could be computed for any temperature within the experimental range using equations (3), (6), (7) and (18). Extrapolations to lower temperatures were also carried out. The variations of these parameters with temperature are given in *Figures 1* to *3*.

The values of χ_{12}^∞ are smaller than those of the corresponding χ_{ES}^∞ and χ_{LF}^∞, as expected in view of the equations, since the ratios of specific volumes v_2/v_1 and molar volumes V_2/V_1 are always smaller than that of the corresponding characteristic volumes. Only minor differences could be detected between χ_{ES}^∞ and χ_{LF}^∞ as shown in *Table 4* where the values obtained at 431 K are reported. The polymers can be classified according to their miscibility with triacetin: the lower the χ, the better the miscibility. The same order is found using χ_{12}^∞, χ_{ES}^∞ or χ_{LF}^∞, either in the experimental range or at extrapolated temperatures, with the exception of an inversion between polymers **1** and **4** for 431 K.

The variations of the parameters χ with temperature show a minimum for polymers **1**–**3**, **5** and **9**. This appears more clearly when the values are extrapolated to lower temperatures (*Figure 4*). The minimum indicates the temperature of the highest miscibility of TA with the polymers (*Table 5*). It is not observed for polymers **4** and **6**–**8**, although the trend in slope suggests that it may appear at higher temperatures. These variations are not linear with respect to $1/T$ and cannot fit the commonly used equation:

$$\chi = \alpha + \beta/T \tag{20}$$

Such behaviour has been shown experimentally for some

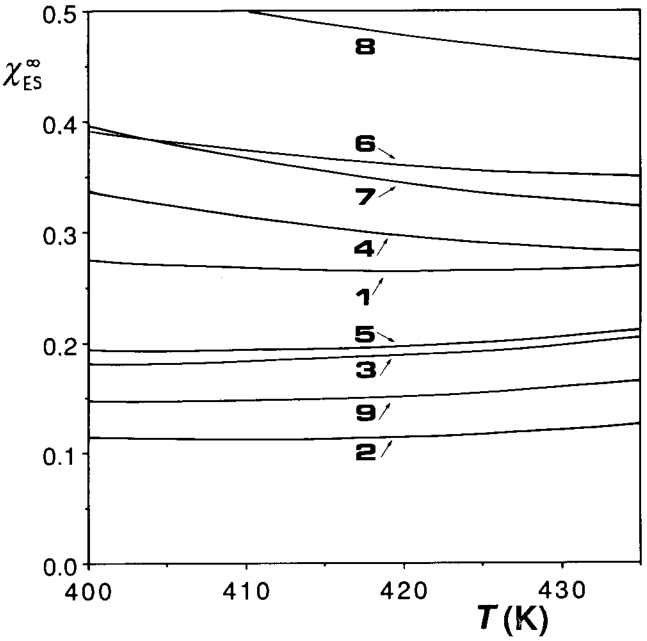


Figure 2 Variations of χ_{ES}^∞ with temperature T for triacetin–polymers **1**–**9**

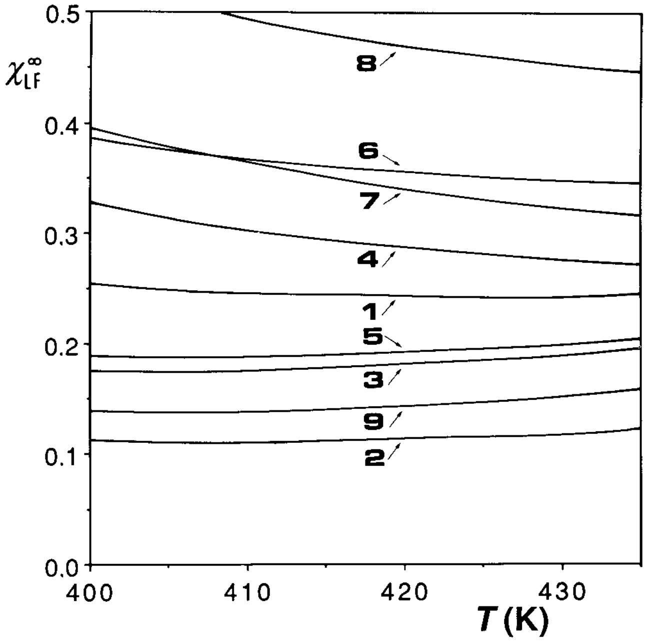


Figure 3 Variations of χ_{LF}^∞ with temperature T for triacetin–polymers **1**–**9**

Table 4 Interaction parameters χ_{12}^{∞}, $\chi_{\mathrm{ES}}^{\infty}$ and $\chi_{\mathrm{LF}}^{\infty}$ for triacetin at infinite dilution in polymers **1–9** at 431.1 and 298.1 K

	431.1 K			298.1 K[a]		
Polymer	χ_{12}^{∞}	$\chi_{\mathrm{ES}}^{\infty}$	$\chi_{\mathrm{LF}}^{\infty}$	χ_{12}^{∞}	$\chi_{\mathrm{ES}}^{\infty}$	$\chi_{\mathrm{LF}}^{\infty}$
1	0.20_0	0.26_4	0.24_4	0.96_7	0.99_9	0.97_9
2	0.03_4	0.12_1	0.11_8	0.71_1	0.75_9	0.75_7
3	0.10_8	0.19_8	0.19_2	0.72_1	0.77_1	0.76_5
4	0.18_7	0.28_0	0.27_3	1.20_8	1.25_9	1.25_2
5	0.12_2	0.20_4	0.19_9	0.76_7	0.81_2	0.80_7
6	0.26_4	0.35_0	0.34_5	1.21_5	1.26_2	1.25_8
7	0.23_9	0.32_1	0.32_1	1.37_1	1.41_3	1.41_4
8	0.38_7	0.45_7	0.45_1	1.47_3	1.51_2	1.50_6
9	0.07_3	0.16_0	0.15_3	0.70_3	0.75_1	0.74_5

[a] Extrapolated values

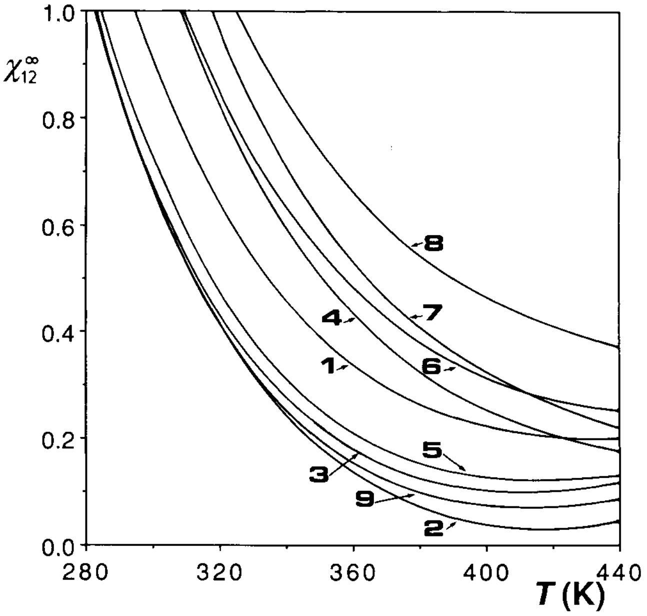


Figure 4 Variations of χ_{12}^{∞} with temperature T for triacetin–polymers **1–9** (extrapolation to lower temperatures)

Table 5 Values of T, χ_{12}^{∞}, $\chi_{\mathrm{ES}}^{\infty}$ and $\chi_{\mathrm{LF}}^{\infty}$ for polymers **1–3**, **5** and **9** at observed minima (*Figures 1–3*)

Polymer	1	2	3	5	9
χ_{12}^{∞}	0.19	0.02	0.09	0.11	0.06
T (K)	430.4	418.9	411.8	415.1	413.1
$\chi_{\mathrm{ES}}^{\infty}$	0.26	0.11	0.17	0.18	0.14
T (K)	423.8	409.0	401.4	404.0	402.6
$\chi_{\mathrm{LF}}^{\infty}$	0.23	0.10	0.17	0.18	0.13
T (K)	427.1	410.8	404.4	407.6	405.9

Table 6 Values of T, χ_{12}^{∞}, $\chi_{\mathrm{ES}}^{\infty}$, $\chi_{\mathrm{LF}}^{\infty}$ and X_{12} at the intersections observed on *Figures 1–3* and *5*

Intersection	1/4	6/7	6/4
χ_{12}^{∞}	0.20	0.02	–
T (K)	421.2	418.9	–
$\chi_{\mathrm{ES}}^{\infty}$	–	0.38	–
T (K)	–	402.1	–
$\chi_{\mathrm{LF}}^{\infty}$	–	0.37	–
T (K)	–	408.0	–
X_{12} (J cm^{-3})	–	1.08	0.52
T (K)	–	422.6	432.8

systems[25–27]. It is explained in the LF theory[22] by a simultaneous decrease of enthalpic contribution $\chi_H = -T\,\partial\chi/\partial T$ and increase of entropic contribution $\chi_S = \partial(T\chi)/\partial T$ with increasing temperature.

The **4**, **7** and **8** curves decrease rapidly with temperature (*Figures 1–4*), resulting for **4** and **7** curves in crossovers with **1** and **6** curves respectively (*Table 6*). For **8**, crossovers would appear only at very high temperatures. Since the slope of the curves is related to χ_H, it follows that the enthalpic contribution to χ is unfavourable to the mixing process of TA with **4**, **7** and **8**. Similar observations were made above from comparisons of the enthalpies of solution, and were connected to sterically unfavourable arrangements between TA and polymers with side groups (**4** and **8**). The behaviour of poly(tetramethylene carbonate) **7** may be discussed in relation to that of poly(hexamethylene carbonate) **6**. The presence of six methylenes between carbonate groups instead of four decreases χ_H and favours the solubility of TA at lower temperatures. This may be assigned to a too short distance between carbonate groups to allow triacetin to fit in properly between them.

The behaviour of the binary mixture of 1 and 2 can be predicted by both equation-of-state theories using only one parameter, the contact interaction parameter X_{12}, defined as the difference of cohesive energy density between interactions of neighbouring pairs of like and unlike species at 0 K (Flory's equation-of-state theory[20]), or ΔP^*, which expresses the net change in cohesive energy density upon mixing at 0 K (LF theory), since all other quantities are known from the pure components. These two quantities have similar definitions and can be computed according to equations (8) and (19). Since the variations with temperature of all the parameters involved in these two equations are known, X_{12} and ΔP^* can be computed for any temperature in the experimental range (*Figures* 5 and 6). The resulting values are of the same order of magnitude, either in the experimental range or after extrapolation to lower temperatures (*Table 4*). For **1–3**, **5** and **9**, the X_{12} values are negative at 431 K. Owing to the polar nature of solute and polymers this could result from specific interactions. Moreover, in spite of their definition as constants, X_{12} and ΔP^* decrease as temperature increases. This may be due to entropic effects which are not taken into account in the theories. Although the variations seem to be linear in the experimental range, in fact they are not, and additional

Table 7 Contact interaction parameter X_{12} and net change in cohesive energy density upon mixing ΔP^* at 431.1 and 298.1 K for triacetin at infinite dilution in polymers **1–9**

	431.1 K		298.1 K[a]	
Polymer	X_{12} (J cm^{-3})	ΔP^* (J cm^{-3})	X_{12} (J cm^{-3})	ΔP^* (J cm^{-3})
1	−0.324	3.83	13.3	14.21
2	−7.27	−7.74	5.16	4.16
3	−6.11	−5.95	5.02	4.33
4	0.70	−0.11	19.8	17.3
5	−3.29	−3.83	7.39	10.5
6	0.67	−0.82	15.7	13.3
7	0.40	−1.98	19.8	15.5
8	7.37	5.10	22.5	19.3
9	−4.68	−6.14	7.20	5.03

[a] Extrapolated values

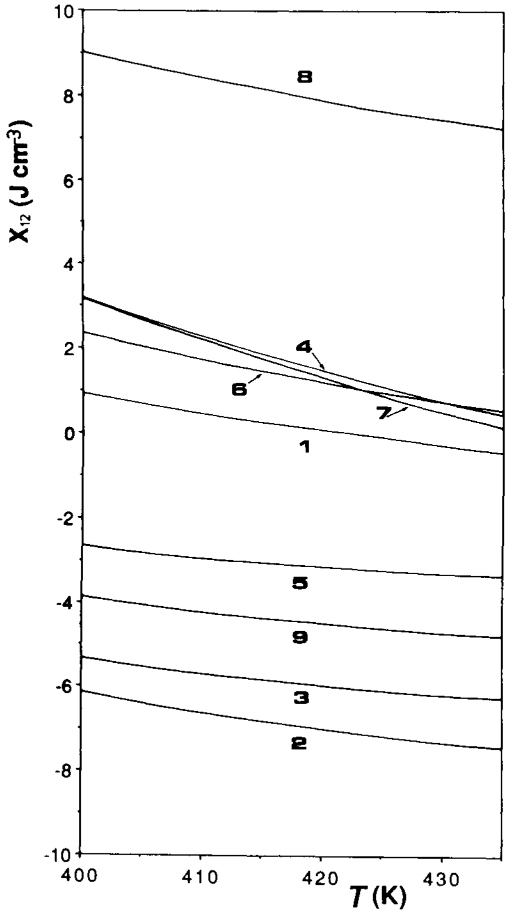


Figure 5 Variations of X_{12} with temperature T for triacetin–polymers 1–9

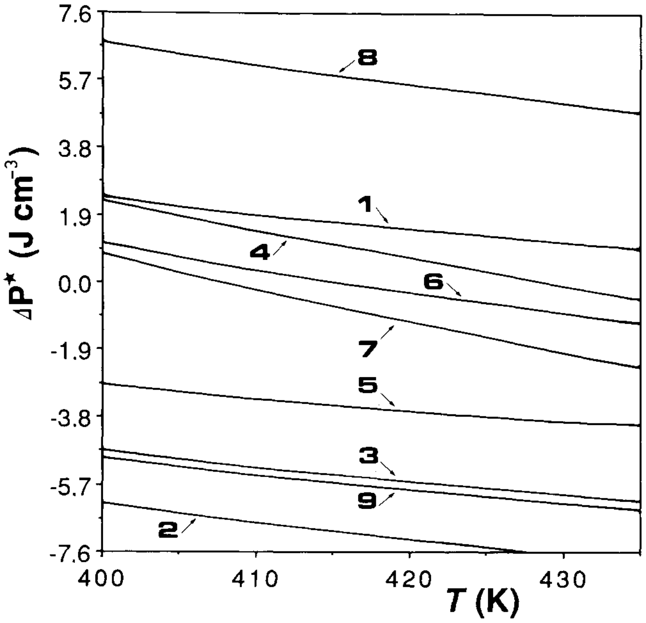


Figure 6 Variations of ΔP^* with temperature T for triacetin–polymers 1–9

entropy parameters, such as Q_{12} in Flory's theory:

$$X_{12}=X_{12,H}-\tilde{v}TQ_{12} \qquad (23)$$

are temperature-dependent.

Similar trends are found for ΔP^*, X_{12}, χ_{LF}^{∞}, χ_{ES}^{∞} or χ_{12}^{∞}. Best miscibilities are found for **3**, **2**, **9** and **5**, and worst for poly(propylene glycol) **8**.

CONCLUSIONS

The present work shows that thermodynamic data relative to systems involving a polar solute, triacetin, and polar polymers such as polyethers, polyesters, poly(ester ethers) and polycarbonates can be obtained by inverse gas chromatography. The data obtained at 130–160°C and those resulting from extrapolation to room temperature show the same trend. The highest miscibilities with triacetin are obtained with the linear poly(ester ethers), while the presence of side groups or of carbonate bonds is unfavourable. The equation-of-state or the lattice-fluid theories do not exhibit any marked superiority on the previously established Flory–Huggins theory as χ_{12}^{∞}, χ_{ES}^{∞} or χ_{LF}^{∞} interaction parameters show similar variations with T and as the contact interaction parameters X_{12} and ΔP^* cannot be considered as constants. This may result from specific interactions and entropy effects which are not taken into account in these theories. Specific interactions have been shown to be Lewis acid–base interactions[31–33]. Since the ether bond is known to be more basic than the ester bond[32], the existence of specific interactions between triacetin and ether-containing polymer is a reasonable assumption.

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