Inverse gas chromatography study of some alkyl trinitrate–polymer systems

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Inverse gas chromatographic studies have been carried out for 1,2,3-propanetriyl trinitrate and 1,2,4-butanetriyl trinitrate in molten α,ω-dihydroxy poly(tetramethylene carbonate) (**7**) and α,ω-dihydroxy polyoxyethylene (**9**). Thermodynamic sorption and mixing functions and the Flory–Huggins interaction parameter were derived for 1,2,3-propanetriyl trinitrate. The results are compared to those obtained using 1,2,3-propanetriyl triacetate as solute in the same polymers. All solutes are more compatible with **9** than with **7**, as shown by the higher values of specific retention volumes and partial molar enthalpy of sorption. The partial molar enthalpies of mixing of 1,2,3-propanetriyl trinitrate with **7** and **9** are markedly higher than those of 1,2,3-propanetriyl triacetate. This unfavourable effect on compatibility is compensated by higher partial molar entropies of mixing in the case of the nitrate, which leads to comparable behaviour for both solutes.

(Keywords: inverse gas chromatography; 1,2,3-propanetriyl triacetate; 1,2,3-propanetriyl trinitrate; 1,2,3-butanetriyl trinitrate; α,ω-dihydroxy polyoxyethylene; α,ω-dihydroxy poly(tetramethylene carbonate))

INTRODUCTION

In the preceding paper[1], thermodynamic studies on various 1,2,3-propanetriyl triacetate (triacetin, TA)/α,ω-dihydroxy polymer systems were carried out using inverse gas chromatography (i.g.c.). It was found that TA is more compatible with linear polyethers or poly(ester ethers) than with polycarbonates or branched poly(ester ethers) or polyethers. Flory–Huggins interaction parameters were found to describe satisfactorily the behaviour of these systems. In order to determine whether TA can be regarded as a good model for alkyl trinitrates, the present work is devoted to the i.g.c. study of thermodynamic interactions between 1,2,3-propanetriyl trinitrate (nitroglycerin, NGL), or 1,2,3-butanetriyl trinitrate (BTN) and α,ω-dihydroxy poly(tetramethylene carbonate) (**7**) or α,ω-dihydroxy poly(oxyethylene) (**9**) and the comparison of the results with those obtained on TA/**7** and TA/**9** systems.

EXPERIMENTAL

Materials

Analytical-grade methylene chloride and triacetin (Prolabo, France) were used without further purification. Solutions of NGL and BTN in CH_2Cl_2 (1 wt %), and α,ω-dihydroxy poly(tetramethylene carbonate) (**7**) and α,ω-dihydroxy poly(oxyethylene) (**9**) were obtained from SNPE (France). These polymers have been described in preceding articles[1,2].

Measurement procedure

Column preparation, gas chromatography system and experimental procedure were the same as those previously described[1]. No degradation of the alkyl trinitrates was observed on an SE30 (5 wt %) test column at 150°C. However, on columns prepared with **7** or **9**, small shoulders began to appear on the solvent peak above 140°C for both NGL and BTN, indicating some degradation during injection (lower than 10% of the injected mass at 160°C). The main peak remained nearly symmetrical, which allowed the calculation of net retention time (t_R) from retention times at peak maxima. The net retention volume V_N was found to be independent of the gas flow rate. Specific retention volumes (V_g^0) were calculated using[3] $V_g^0 = V_N/m_2$, where m_2 is the mass of polymer in the column. For one given column, relation (1) holds:

$$V_g^0(X) = V_g^0(\mathrm{TA})\frac{V_N(X)}{V_N(\mathrm{TA})} \qquad (X = \mathrm{NGL\ or\ BTN}) \qquad (1)$$

Since the V_g^0 of TA for TA/**7** and TA/**9** systems have already been determined[1], the determination of the mass of polymer in the column, which limits the accuracy on V_g^0, is no longer necessary provided that measurements are also carried out with TA on the same column. The experimental measurement procedure[1] may therefore be simplified. The studies were carried out on NGL, BTN and TA using only one column per polymer instead of four[1], and the specific retention volumes were computed using equation (1).

The values of vapour pressure of NGL in the experimental range were extrapolated from data taken from different sources[4–7] using Clausius–Clapeyron regression lines. Densities of NGL in the range 0–60°C[8] were extrapolated to the experimental range assuming a linear variation with temperature. No reliable vapour pressure–temperature data could be found for BTN outside a narrow range near room temperature, thus restricting the discussion for this solute to the values of V_g^0 and of the thermodynamic sorption functions.

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Data reduction is detailed elsewhere[1]. The non-ideality of the gas phase was neglected for NGL and BTN as it was found[1] that this leads to a $V_g{}^0$(TA) correction below 1%. In the following, subscripts 1 and 2 are relative to the solute and the polymer under study respectively.

RESULTS

Specific retention volumes and thermodynamic sorption functions

The specific retention volumes V_g^0 of NGL and BTN in polymers **7** and **9** measured at four temperatures between 400 and 435 K, and extrapolated to zero flow rate, are given in *Table 1* with the values obtained for TA. The variations of ln V_g^0 with $1/T$ could be assumed to be linear within experimental errors for all investigated systems, allowing computation of partial molar enthalpy and entropy of sorption, ΔH_1^s and ΔS_1^s (*Figure 1* and *Table 2*). For both polymers the highest ΔH_1^s values are found for the nitrates, as expected owing to their higher heat of vaporization which constitutes the main part of ΔH_1^s. Whatever the solute, ΔH_1^s values are higher for **9** than for **7**. This means that the three solutes are more compatible with **9** than with **7**. The behaviour of triacetin in these polymers is therefore similar to that of the studied alkyl trinitrates.

Thermodynamic mixing functions

More information can be drawn from the determination of the partial molar free energy of mixing ΔG_1^∞ and the partial molar enthalpy and entropy of mixing, ΔH_1^∞ and ΔS_1^∞. The results obtained at 431 K are summarized in *Table 3*. A somewhat different behaviour can be observed between triacetin and the nitrates. Relatively higher ΔH_1^∞ values are found for NGL (4 and 11 kJ mol^{-1}) than for TA (-0.6 and 3.5 kJ mol^{-1}). This unfavourable effect on the mixing process is compensated by the positive values of $T\Delta S_1^\infty$ for NGL, instead of the negative values found for TA. This results in a more favourable ΔG_1^∞ situation for the trinitrate than for triacetin with regard to their miscibility with polymers **7** and **9**.

Interaction parameters

Negative χ_{12}^∞ values are found for NGL/**7** and NGL/**9** systems in the experimental range. The values are significantly lower than those obtained for TA, indicating a better solubility of NGL in **7** and **9** (*Figure 2*). On the other hand, the values extrapolated at 25°C are close to those found for TA/**7** and TA/**9** systems (*Table 4*). This may be connected with the higher partial molar entropies of mixing obtained for NGL, the decrease of partial molar free energy of mixing with temperature being more pronounced for this compound than for TA. NGL solubilities in **9** are above those in **7** as χ_{12}^∞ is lower for NGL/**9** than for NGL/**7**; this fits the results obtained with TA.

Table 1 Specific retention volumes V_g^0 of triacetin (TA), 1,2,3-propanetriyl trinitrate (NGL) and 1,2,4-butanetriyl trinitrate (BTN) in polyoxyethylene **9** and in poly(tetramethylene carbonate) **7** at different temperatures

	V_g^0 (m^3 kg^{-1})			
Solute/polymer	402.1 K	411.8 K	421.6 K	431.1 K
TA/7	3.593	2.236	1.435	0.965
NGL/7	16.151	9.434	5.790	3.680
BTN/7	39.120	22.547	13.121	8.185
TA/9	5.182	3.148	1.958	1.285
NGL/9	25.973	14.290	8.407	5.201
BTN/9	62.207	33.757	19.225	11.334

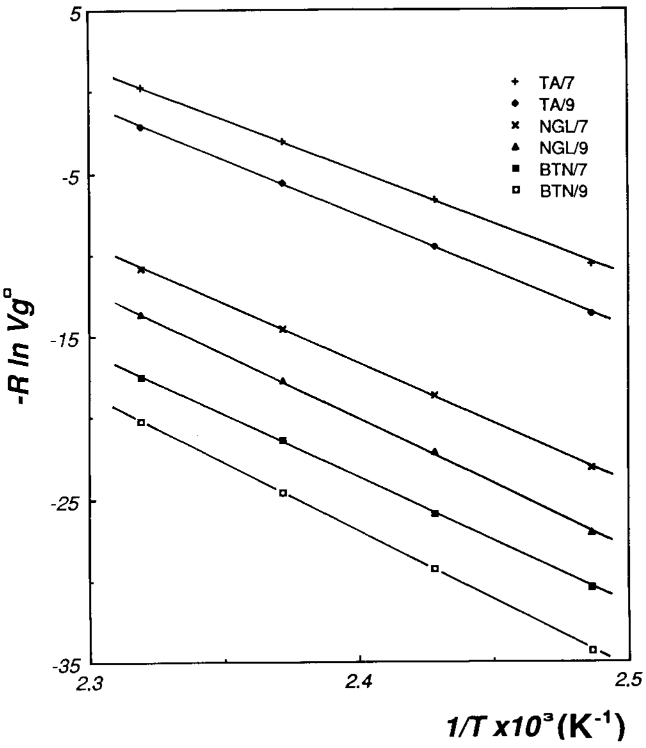

Figure 1 Variations of $-R\ln V_g^0$ with $1/T$ for TA, NGL and BTN in poly(tetramethylene carbonate) (**7**) or polyoxyethylene (**9**)

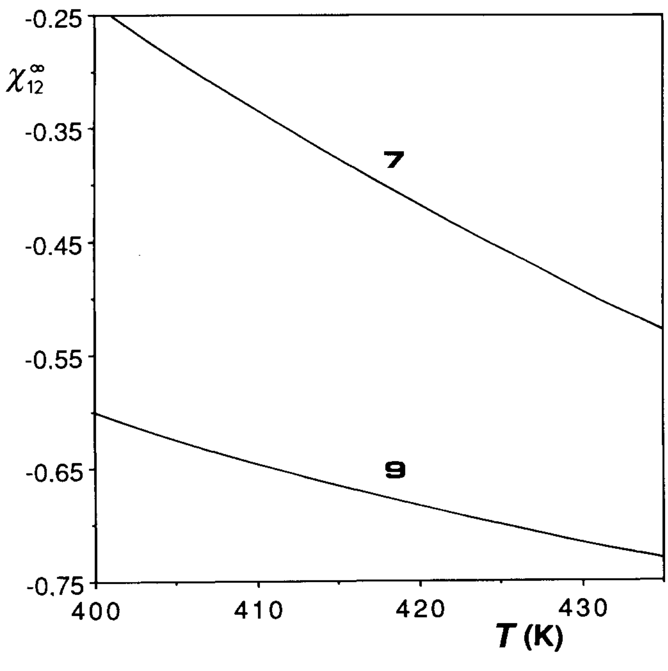

Figure 2 Variations of χ_{12}^∞ with temperature T for NGL/poly(tetramethylene carbonate) (**7**) and NGL/polyoxyethylene (**9**) systems

Table 2 Partial molar enthalpy ΔH_1^s and entropy $T\Delta S_1^s$ of sorption for triacetin (TA), 1,2,3-propanetriyl trinitrate (NGL) and 1,2,4-butanetriyl trinitrate (BTN) at infinite dilution in polyoxyethylene **9** and in poly(tetramethylene carbonate) **7** at 431.1 K

Solute/polymer	ΔH_1^s (kJ mol^{-1})	$T\Delta S_1^s$ (kJ mol^{-1})
TA/7	−65.4	−98.6
NGL/7	−73.1	−101.3
BTN/7	−78.0	−103.5
TA/9	−69.3	−101.6
NGL/9	−79.7	−106.9
BTN/9	−84.4	−108.2

Table 3 Partial molar free energy ΔG_1^∞, enthalpy ΔH_1^∞ and entropy $T\Delta S_1^\infty$ of mixing for triacetin (TA) and 1,2,3-propanetriyl trinitrate (NGL) at infinite dilution in polyoxyethylene **9** and in poly(tetramethylene carbonate) **7** at 431.1 K

Solute/polymer	ΔG_1^∞ (kJ mol^{-1})	ΔH_1^∞ (kJ mol^{-1})	ΔS_1^∞ (kJ mol^{-1})
TA/7	4.38	3.44	−0.94
NGL/7	0.98	10.68	9.70
TA/9	3.36	−0.62	−3.98
NGL/9	−0.26	4.27	4.53

Table 4 Flory–Huggins interaction parameter χ_{12}^∞ for triacetin (TA) and 1,2,3-propanetriyl trinitrate (NGL) at infinite dilution in polyoxyethylene **9** and in poly(tetramethylene carbonate) **7** at 431.1 K and extrapolated to 298.1 K

	χ_{12}^∞	
Solute/polymer	298.1 K	431.1 K
TA/7	1.37	0.23
NGL/7	1.71	−0.50
TA/9	0.70	0.07
NGL/9	0.69	−0.72

DISCUSSION

Reliable thermodynamic data could be obtained by inverse gas chromatography using highly unstable solutes such as alkyl trinitrates, which was not already mentioned in the literature. Such determinations allow rapid and useful classification of different polymers according to their compatibility with respect to a given solute, or the classification of different solutes according to their compatibility with respect to a given polymer, provided that density and vapour pressure–temperature data are available.

The results obtained with NGL and BTN show similar trends to those obtained with TA since they are more compatible with polyoxyethylene (**9**) than with polycarbonate (**7**), as shown by the values of specific retention volumes and enthalpies of sorption. The partial molar energy of mixing and Flory–Huggins interaction parameter χ_{12}^∞ were calculated in the case of NGL only, due to the lack of reliable data on BTN. The use of these two parameters leads to the same conclusions concerning the compatibility of NGL with **7** and **9**. Similar conclusions can be drawn from these values concerning the compatibility of NGL with **7** and **9**. However the behaviour of NGL, even if it seems roughly similar to that of TA, is somewhat different: the values of the partial molar enthalpies of mixing are relatively high but this unfavourable effect on the mixing process is compensated by positive values of the partial molar entropies of mixing. The presence of nitrate instead of acetate groups in NGL makes this compound much more polar ($\mu_{\mathrm{NGL}} = 3.82$ D)[9] than TA ($\mu_{\mathrm{TA}} = 2.50$ D)[9] in the pure liquid state. This corresponds to a higher organization of NGL than TA, which can explain the difference between the ΔS_1^∞ values relative to these compounds. In fact the dipole moment of TA is equal to what can be expected from a conformation where free rotation of functional groups takes place, while the value obtained for NGL suggests that free rotation is hindered and that the conformation is between free rotation and a *trans* form[9]. The higher organization in NGL compared to that in TA is also confirmed by the value of their respective melt viscosities at 55°C: 0.0479 g cm^{-1} s^{-1} for TA[10] and 0.0875 g cm^{-1} s^{-1} for NGL[11]. When the nitrates are absorbed in the polymers this organization is largely destroyed, which leads to an increase of the partial molar entropy of mixing.

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