Thermodynamic studies on Nylon-6/solvent systems by inverse gas chromatography at elevated temperatures

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Activity coefficients Ω^∞, Flory interaction parameters χ^∞ for solutions of Nylon-6/ε-caprolactam (CPL), toluene and ethylbenzene at temperatures ranging from 250 to 290°C have been obtained from inverse gas chromatography retention data. The estimated vapour pressure of the cyclic dimer of CPL at 280–300°C has also been determined. From this data the vapour pressure *versus* composition curves for Nylon-6/CPL and Nylon-6/dimer solutions at various temperatures have been plotted. The experimental data of activity coefficient of CPL in Nylon-6 are shown to be in very good agreement with those calculated by the UNIFAC-free volume model.

(Keywords: Nylon-6; inverse gas chromatography; activity coefficients; Flory–Huggins parameter)

INTRODUCTION

A knowledge of activity coefficients at infinite dilution is useful in order to predict liquid–vapour equilibria by a suitable liquid phase model. The main purpose of our study was to obtain weight fraction activity coefficients (Ω^∞) and Flory interaction parameters (χ^∞) of some solvents (ε-caprolactam (CPL), cyclic dimer of CPL, toluene and ethylbenzene) at infinite dilution in Nylon-6. Measurements have been performed by inverse gas chromatography (IGC), which, in the last decades, has proved to be a good alternative to the static methods for measuring polymer–solvent interactions in very concentrated polymeric solutions.

Very few experimental data of the activity coefficient for Nylon-6 systems are available and these are at temperatures well below those considered in this work; moreover, the polymer used as stationary phase in other work[1] had very different characteristics to the one we used. For these reasons, no significant comparison with reported data can be accomplished.

The study of Nylon-6/solvent systems via IGC is not trivial owing to some characteristics of the components. First of all, the stationary phase (Nylon-6) degrades at high temperatures[2] and the resulting weight loss produces unreliable values of retention volume, activity and interaction coefficients. Furthermore, some of the solvents considered (CPL and its cyclic dimer) are solid at room temperature and have a very low vapour pressure even at the temperatures of interest. Thus, in this study, in order to get reasonable retention times and a sharp chromatographic peak with a good signal-to-noise ratio, experimental parameters like temperature, flow rate, column length and weight of stationary phase have been carefully optimized.

THEORETICAL BACKGROUND

The IGC technique is based on the partition of a volatile solute between the gaseous mobile phase and the polymeric stationary phase. The solute is injected at the column inlet and is transported by a carrier gas to a detector. The gas volume required for elution of the injected probe depends on the partition coefficient K:

$$K = \frac{\text{solute conc. in stationary phase}}{\text{solute conc. in mobile phase}} \tag{1}$$

K is a thermodynamic quantity, a function of temperature and of the chemical potential variation caused by the passage from the mobile phase to the stationary phase. A knowledge of K allows evaluation of thermodynamic parameters such as activity coefficient, solubility and Flory–Huggins interaction parameter, at infinite dilution in the polymer.

Generally, the results are expressed as a function of the retention volume rather than the partition coefficient and are conventionally referred to a column temperature of 0°C[3]:

$$V_g^0 = J_3^2 \frac{273.2}{T} \frac{V_n}{w} = \frac{273.2K}{T} \tag{2}$$

where J_3 = James–Martin compressibility factor; V_g^0 = specific retention volume at 0°C (cm^3 g^{-1}); V_n = net retention volume at temperature T (cm^3); w = weight of stationary phase in column (g); K = partition coefficient.

At infinite dilution the relation between retention volume and weight fraction activity coefficient is given by[4]:

$$\ln \Omega^\infty = \ln \frac{273.2R}{V_g^0 p_1^0 M_1} - \frac{p_1^0(B_{11} - V_1)}{RT} \tag{3}$$

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where p_1^0 = vapour pressure of the solute; M_1 = molecular weight of the solute; B_{11} = second virial coefficient of the solute; V_1 = molar volume of the solute.

Calculation of the χ^∞ parameter from chromatographic data is also possible[5]:

$$\ln \Omega^\infty = \ln \frac{v_1}{v_2} + 1 - \frac{V_1}{M_n v_2} + \chi^\infty \qquad (4)$$

where v_1 and v_2 are solute and polymer specific volumes, respectively, and M_n is the number average molecular weight of the polymer. From χ^∞ parameters obtained by equation (4), according to the Flory–Huggins[6] theory and assuming that χ does not depend on concentration, it is possible to obtain the vapour pressure of a polymeric solution as follows:

$$\ln \frac{p}{p_0} = \ln \Phi_i + \Phi_j + \chi \Phi_j^2 \qquad (5)$$

where p and p^0 are solvent vapour pressure over the polymer–liquid system and over the pure liquid, respectively, and Φ_i, Φ_j are the liquid and polymer volume fractions. Although it is known that the χ parameter may depend on concentration, the error arising from considering it constant and equal to χ^∞ can be regarded as negligible, if the polymer concentration is very high.

EXPERIMENTAL

Materials

Nylon-6 (NIVIONPLAST™) was supplied by Enichem. Its number average molecular weight and its melting point were 18 000 and 220°C, respectively.

CPL was supplied by Enichem industrial plant for Nylon-6 (Porto Marghera, Italy). The oligomers mixture was obtained by Nylon-6 water extraction. In order to obtain a standard sample of dimer, fractional sublimation according to Heikens[7] was carried out. The chosen dimer fraction had a purity of 96.7%, as measured by h.p.l.c.[8].

Toluene, ethylbenzene (Carlo Erba RP) and 2,2,2-trifluoroethanol (Janssen) were used without further purification.

Column preparation

For the particular system under investigation (see Introduction), a preliminary study to set up experimental conditions was performed by testing three packed columns of lengths 150, 100 and 50 cm. From these tests no serious problems arose for CPL, ethylbenzene and toluene elution, while the analysis of dimer was possible only with the shortest column and with rather high flow rates. After optimizing the operating conditions, two new columns of lengths 150 cm (column A) and 50 cm (column B) were prepared, and all the data were obtained with these columns in the shortest time, to avoid decomposition of Nylon-6.

The stationary phase was coated onto Chromosorb W-DMCS 80–100 mesh (Carlo Erba) after dissolution in 2,2,2-trifluoroethanol by gentle mixing and slow evaporation. The coated support was dried in a vacuum oven at 40°C for 72 h, and then packed in a stainless steel column (4 mm i.d., 6 mm o.d.). The amount of column loading was determined by t.g.a. using the blank correction; the resultant coverage ratio was 14.72%. The same t.g.a. was performed after the chromatographic tests in order to check the stationary phase stability. The column characteristics are summarized in *Table 1*.

Table 1 Summary of column characteristics

Column	Length (cm)	Packing weight (g)	Nylon weight (g)
A	150	8.90	1.3101
B	50	2.849	0.4194

Equipment

The measurements were performed on a Carlo Erba HRGC 5300 Mega series gas chromatograph, equipped with a flame ionization detector (f.i.d.). Retention times were detected with the program Baseline 810 (Millipore).

CPL and dimer were dissolved in ethanol and injected with a 1 μl Hamilton syringe. Aromatic solvents were injected as vapour, the sampling head space of the liquid being kept at room temperature. Helium was used as gas carrier and the flow rates were measured by means of a common soap-bubble flowmeter at the detector outlet. Flow rates ranged between 18 and 30 $\text{cm}^3\ \text{min}^{-1}$ for column A and between 66 and 90 $\text{cm}^3\ \text{min}^{-1}$ for column B. Pressure and temperature in the laboratory were recorded for each test. Pressure drop in the column was measured with a mercury manometer.

RESULTS AND DISCUSSION

ε-Caprolactam and aromatics

Tables 2–4 show specific retention volumes (V_g^0), activity coefficients (Ω^∞) and χ^∞ parameters calculated for CPL, toluene and ethylbenzene, respectively, at temperatures ranging from 250 to 290°C. All these measurements were performed on column A.

According to the theory[3], the log of V_g^0 *versus* the inverse of temperature gives a linear plot for temperatures well above the melting point of the polymer (*Figure 1*). The curves of the aromatics have a lower correlation coefficient, probably due to a larger error in measurement of V_g^0 for very volatile probes. No data concerning these solvents at these temperatures are reported, but we remark that Ω^∞ and χ^∞ parameters appear to be reliable. χ^∞ values higher than 0.5 measured for aromatics are characteristic of a non-solvent for a polymer, while very low values, like those of CPL, indicate strong interactions between polymer and solvent. *Figure 2* shows the plot of χ^∞ *versus* the inverse of the temperature.

The vapour pressure *versus* composition curves were calculated for the Nylon-6/CPL system at various temperatures, according to equation (5) and assuming the χ parameter to be independent of composition (*Figure 3*).

Finally, the experimental values of the activity coefficient of Nylon-6/CPL system were compared with those calculated by the UNIFAC-free volume model[9]. The model is based on the group contribution approach and appears to be highly convenient in treating polar systems like those involving Nylon-6. As the interaction parameters[10] for the groups concerned are available, the only data required for the calculation are the densities at various temperatures. A very good agreement between the experimental and the calculated activity coefficient has been observed (*Table 2*).

Table 2 Specific retention volume (V_g^0), experimental and calculated weight fraction activity coefficients at infinite dilution (Ω^∞), and Flory–Huggins interaction parameters (χ^∞) of CPL in Nylon-6 at various temperatures

Temperature (°C)	V_g^0 (ml g^{-1})	Ω^∞	Ω^∞ (calculated)	χ^∞
250	127.1	2.68	2.68	−0.152
260	98.6	2.76	2.68	−0.131
270	77.5	2.84	2.67	−0.110
280	61.3	2.94	2.67	−0.085
290	48.9	3.03	2.67	−0.058

Table 3 Specific retention volumes (V_g^0), weight fraction activity coefficients at infinite dilution (Ω^∞) and Flory–Huggins interaction parameters (χ^∞) of toluene in Nylon-6 at various temperatures

Temperature (°C)	V_g^0 (ml g^{-1})	Ω^∞	χ^∞
250	2.0	9.09	0.72
260	1.7	9.77	0.76
270	1.5	9.65	0.72
280	1.3	9.84	0.70
290	1.2	9.75	0.64

Table 4 Specific retention volumes (V_g^0), weight fraction coefficients at infinite dilution (Ω^∞) and Flory–Huggins interaction parameters (χ^∞) of ethylbenzene in Nylon-6 at various temperatures

Temperature (°C)	V_g^0 (ml g^{-1})	Ω^∞	χ^∞
250	2.4	10.45	0.91
260	1.9	11.29	0.96
270	1.7	10.92	0.90
280	1.6	10.54	0.84
290	1.4	10.89	0.84

Table 5 Specific retention volumes (V_g^0), weight fraction activity coefficients at infinite dilution (Ω^∞) calculated by UNIFAC-free volume model of the dimer CPL in Nylon-6 and vapour pressure of the pure dimer at various temperatures

Temperature (°C)	V_g^0 (ml g^{-1})	Ω^∞ (calculated)	p^0 (mmHg) (calculated)
280	4571	2.65	6.2
290	3307	2.65	8.6
300	2282	2.64	12.5

CPL dimer

The measurements on the dimer were performed on column B at 280, 290 and 300°C. The very low vapour pressure of dimer (already observed during the sublimation), together with the good interactions of this component with Nylon-6, made its elution in longer columns impossible, and high gas flow rates were needed. Three tests with different flow rates were performed at each temperature in order to exclude the influence of the flow rate on specific retention volume. Values of V_g^0 are shown in *Table 5* and the trend of log V_g^0 *versus* $1/T$ is shown in *Figure 1*.

Using equation (3) activity coefficients can be obtained from V_g^0 data. For the dimer the second term of this equation can be neglected owing to the high temperature and the very low vapour pressure. This makes the problem easier because, in order to calculate B_{11} (second virial coefficient), it is necessary to know a

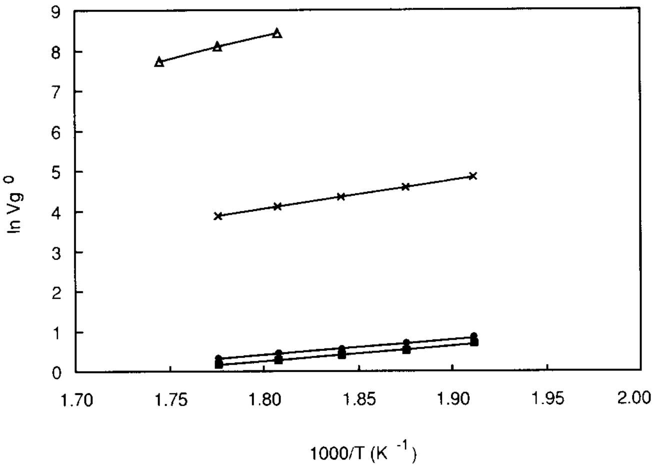

Figure 1 Temperature dependence of the specific retention volume V_g^0 for Nylon-6 binary systems: ■, toluene; ●, ethylbenzene; ×, CPL; △, cyclic dimer

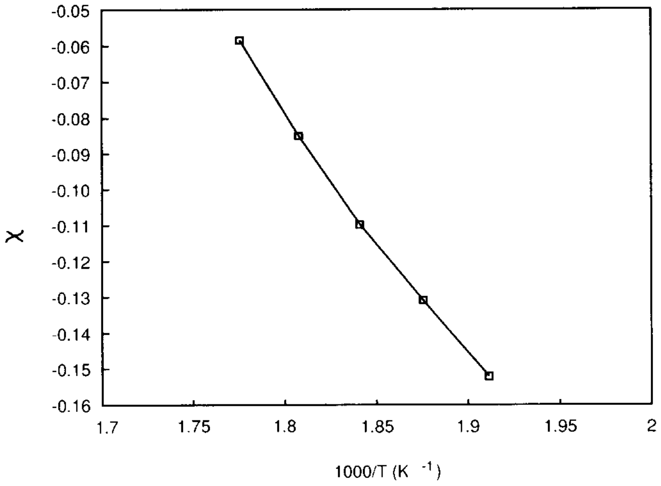

Figure 2 Plot of Flory interaction parameter at infinite dilution *versus* the inverse of temperature for Nylon-6/CPL system

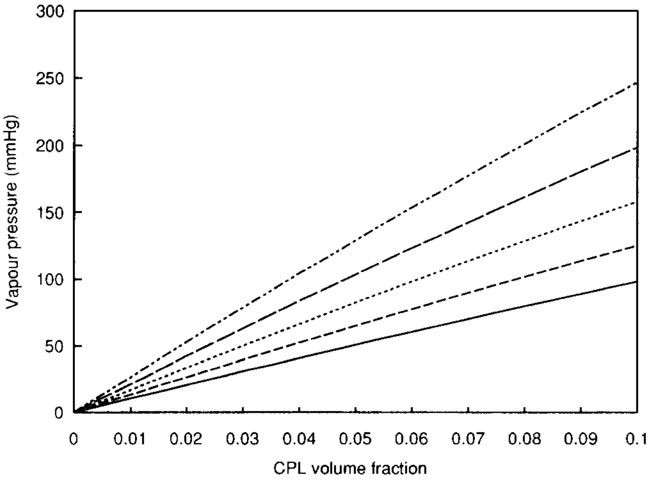

Figure 3 Volatilities of CPL in Nylon-6 for small volume fractions of CPL at various temperatures: ——, 250°C; – – – –, 260°C; ······, 270°C; — —, 280°C; –·–·–·, 290°C

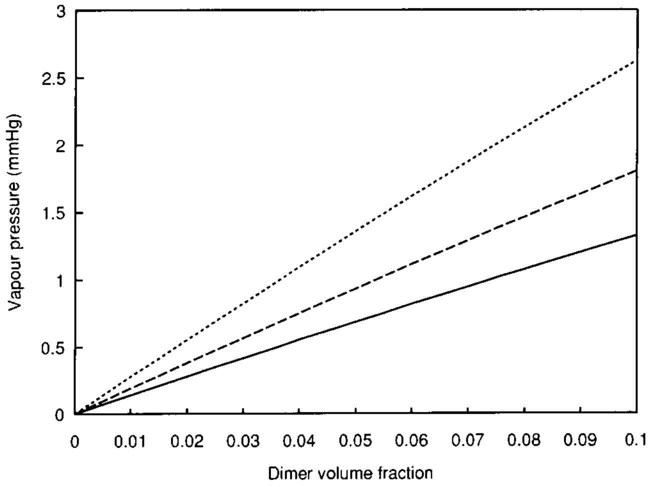

Figure 4 Volatilities of cyclic dimer of CPL in Nylon-6 for small volume fractions of dimer at various temperatures: ——, 270°C; – – – –, 280°C; ······, 290°C

series of constants (critical temperature, pressure, and compressibility factor, mean radius of gyration, dipole moment, association parameter) which are not yet available. Nevertheless, it was not possible to calculate the activity coefficient because the vapour pressure–temperature relationship of the dimer is not known.

An alternative approach, leading to a vapour pressure prediction for the dimer, was therefore attempted. A UNIFAC-free volume simulation, analogous to that for Nylon-6/CPL, was performed in order to calculate the activity coefficients for the dimer in Nylon-6 at infinite dilution, at temperatures ranging from 280 to 300°C. The dimer density was assumed to be identical to that of CPL, taking into account that different values of density did not significantly affect the final results. The calculated activity coefficients are reported in *Table 5*.

Introducing the Ω^{∞} values of dimer and the measured V_g^0 data into the simplified equation (3), the vapour pressure of Nylon-6/dimer solutions as a function of composition has been calculated, assuming once more that the χ parameter is not a function of the dimer volume fraction (*Figure 4*).

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