Journal of Chromatography, 607 (1992) 145–149
Elsevier Science Publishers B.V., Amsterdam

CHROM. 24 369

Short Communication

Measurement of infinite dilution diffusion coefficients of ε-caprolactam in nylon 6 at elevated temperatures by inverse gas chromatography

Luisa Bonifaci and Gian Paolo Ravanetti

Enichem Polimeri, Mantua Research Centre, Via G. Taliercio 14, 46100 Mantua (Italy)

(First received March 16th, 1992; revised manuscript received May 25th, 1992)

ABSTRACT

The diffusion coefficients of ε-caprolactam in nylon 6 were measured by inverse gas chromatography on a capillary column at temperatures between 250 and 280°C. The values obtained ranged between $2 \cdot 10^{-8}$ and $4 \cdot 10^{-8}$, in good agreement with the reported values obtained by a static technique. The activity coefficients at infinite dilution of ε-caprolactam in nylon 6 were also determined and compared with values obtained previously using packed columns. The two data sets differed by less than 7%.

INTRODUCTION

The knowledge of diffusion and activity coefficients of small molecules in melt polymers is useful in order to analyse fundamental processing steps, such as devolatilization, bulk polymerization and plasticization of polymers.

Inverse gas chromatography (GC) has been recognized [1,2] as a useful tool for the determination of the infinite dilution activity coefficient (Ω^∞) of a solvent in a polymer. This technique is simpler, more economical and less time consuming than the static method, and requires only small amounts of polymer and solvent.

Inverse GC has also been proposed [3–6] for studying the diffusion of a solute within a polymer. Owing to the slow diffusion of the sample in the stationary phase, the chromatographic peak turns out broadened and distorted. Under suitable experimental conditions, the shape of the elution curve can be related to the diffusion coefficient of the probe at infinite dilution in the polymer (D_p).

Most of these studies have been performed using packed columns. However, there is considerable uncertainty about the accuracy of diffusion data obtained by inverse GC, owing to the difficulty in describing correctly the stationary phase geometry in the column [7]. According to Pawlisch *et al.* [8], this difficulty can be overcome by using capillary columns with a uniform distribution of polymeric stationary phase on the wall of the tube. This technique allows the simultaneous determination of the diffusion and activity coefficients.

In a previous work [9] we studied the thermodynamic properties of nylon 6–solvent systems by inverse GC on packed column and we determined

---

Correspondence to: Dr. L. Bonifaci, Enichem Polimeri, Mantua Research Centre, Via G. Taliercio 14, 46100 Mantua, Italy.

the infinite dilution activity coefficient of ε-caprolactam (CPL) and the specific retention volume of its cyclic dimer in nylon 6 at temperatures ranging from 250 to 290°C.

The main purpose of this work was to determine the diffusion coefficients of ε-caprolactam at infinite dilution in nylon 6 at elevated temperatures using inverse GC on a capillary column, according to Pawlisch *et al.*'s method [8]. Moreover, we aimed to compare the chromatographic data and the activity coefficients obtained using capillary columns with those obtained with packed columns.

Very few experimental data of the activity and diffusion coefficients for nylon 6 systems are available. Newman and Prausnitz [10] measured Ω^∞ for some solvents but at temperatures well below those considered here and using a stationary phase with very different characteristics. Nagasubramanian and Reimschuessel [11] measured the diffusion of CPL in melted nylon 6 using a non-chromatographic method.

EXPERIMENTAL

Equipment

The analyses were performed using a Carlo Erba HRGC Mega series gas chromatograph, equipped with a flame ionization detector and a split-splitless injector. The splitting ratio was 100:3.

Helium was used as the carrier gas and the flow-rates were measured by a soap-bubble flow meter at the column outlet. They ranged from 0.3 to 1 ml/min for CPL and from 1.1 to 2 ml/min for the cyclic dimer. The influence of the flow-rate was examined, performing tests at three different flow-rates at each temperature.

The samples were dissolved in ethanol and injected using a 1-μl Hamilton syringe. Three consecutive injections were made for each set of measurements.

For data acquisition, the Baseline program (Millipore) was used for monitoring the detector output. The raw data were corrected for the baseline offset and then the mean retention time (μ_1), the second central moment (μ_2^*) and the area of the elution peak were calculated by numerical integration.

The whole system was tested by performing experiments on several capillary columns coated with polystyrene in order to obtain data corresponding to those obtained by Pawlisch *et al.* [8].

Materials

Nylon 6 (Nivionplast) and CPL were supplied by Enichem (Porto Marghera, Italy). The number-average molecular weight and the melting point of the polymer were 18 000 and 220°C, respectively.

An oligomers mixture was obtained by extraction of nylon 6 with water. In order to obtain a standard sample of dimer, fractional sublimation according to Heikens [12] was carried out. The chosen dimer fraction had a purity of 96.7%, as measured by high-performance liquid chromatography [13].

Glass capillary tubing was supplied by Carlo Erba (Milan Italy) with I.D. = 0.32 and O.D. = 1 mm.

Column preparation

The column was prepared using an 8-m long glass capillary tube. The nylon 6 film was applied on the wall by a static coating technique that allows deposition of films with uniform and known thickness [14].

The polymer solution in 2,2,2-trifluoethanol (Janssen) was forced into the tube using a nitrogen back-pressure and the filled column was then sealed at one end with a silicone-rubber–glass plug. This was a critical step of the experimental procedure as it is crucial that no air bubbles are trapped in the column, especially at the sealed end.

The tube was then placed in a water-bath and connected to vacuum via the open end until the complete evaporation of the solvent was obtained (about 48 h). The column was conditioned in the chromatographic oven, raising the temperature at 0.5°C/min until a satisfactory baseline was obtained.

The final coating film on the wall was uniform and even. Its thickness (2.037 μm at 250°C) was evaluated from the concentration of the coating solution [14]:

$$\tau = \frac{Rc}{2\rho_p} \tag{1}$$

where τ = film thickness (μm), R = column inner radius (mm), c = coating solution concentration (g/l) and ρ_p = polymer density (g/ml)

Data analysis

Inverse gas chromatography on capillary columns was proposed by Pawlisch *et al.* [8] in order to obtain simultaneously infinite dilution activity and diffusion coefficients of a sample in a polymer. A solvent injected into a capillary column arrives at the detector after a time (or with a retention volume) that depends on the interaction between the solvent and the polymer, and therefore on the activity coefficient Ω^∞. If experimental parameters are properly selected, the shape and the broadening of the elution peak depend on the diffusion coefficient of the probe in the stationary phase.

The model used by Pawlisch *et al.*, in order to relate chromatographic data with thermodynamic and transport properties, was described in detail elsewhere in the original paper [8]; here we examine only its fundamental equations for the determination of Ω^∞ from the first statistical moment, μ_1 (mean retention time), and D_p from the second statistical moment, μ_2^*, of the elution curve.

The mean retention time, μ_1, is related to the partition coefficient, K, by the equation

$$\mu_1 = \frac{\sum t_i A_i}{\sum A_i} = \frac{1 + 2\tau K}{R} \cdot t_c \qquad (2)$$

where A_i = slice area of the peak at the time t_i, t_c = residence time of the gas carrier = L/V, where L is the column length and V the mean carrier gas velocity, and K = partition coefficient. The knowledge of the partition coefficient allows the evaluation of thermodynamic parameters, such as Henry constant, Flory–Huggins interaction parameter and activity coefficient at infinite dilution in a polymer.

It is common practice to express the chromatographic results as a function of specific retention volume (V_g^0) rather than partition coefficient:

$$V_g^0 = \frac{273.2K}{T\rho_p} \qquad (3)$$

where T is the column temperature.

The relationship which correlates the specific retention volume with the activity coefficient is

$$\ln \Omega^\infty = \ln\left(\frac{273.2R_g}{p_1^0 V_g^0 M_1}\right) - \frac{p_1^0(B_{11} - V_1)}{R_g T} \qquad (4)$$

where R_g is the universal gas constant, M_1 the molecular weight, p_1^0 the vapour pressure, B_{11} the second virial coefficient and V_1 the molar volume, all referring to the sample.

The shape and broadening, and therefore the second central moment of the elution curve (variance of the concentration distribution), can be related to the diffusion coefficient of the probe in the polymeric phase:

$$\mu_2^* = \frac{\sum(t_i - \mu_1)^2 A_i}{\sum A_i} = \left[\frac{4\tau^3 K}{3Rt_c D_p} + \frac{2D_g t_c}{L^2}\cdot\left(1 + 2\tau\cdot\frac{K}{R}\right)^2\right] t_c^2 \qquad (5)$$

where L = column length and D_g = diffusion coefficient of the sample in the gas phase.

For polymeric stationary phases, the diffusion coefficient in the stationary phase (D_p) can be 8–10 orders of magnitude smaller than D_g. In this case the term containing D_g in eqn. 5 is negligible and it is possible to calculate D_p by a single elution curve [15]. Otherwise, D_p can be obtained from the slope of the straight line obtained plotting μ_2^*/t_c^3 *versus* $1/t_c^2$, carrying out several tests at different flow-rates.

RESULTS AND DISCUSSION

The peculiarities of the nylon 6–CPL system have been underlined in our previous study, carried out using packed columns. Nylon 6 degrades [16] at elevated temperatures, and the resulting weight loss produces unreliable values of the retention volume. Therefore, tests at elevated temperatures should be performed as quickly as possible, and at the end of experiments the weight of the stationary phase in the column should be checked.

In the particular case of a capillary column it should be taken into account that the coated film can deteriorate at high temperatures. On the other hand, the chromatographic tests have to be performed at least 30°C above the melting temperature, in order to avoid the presence of a crystalline fraction in the stationary phase.

In this study, optimum experimental conditions (in particular the flow-rate for dimer elution) were rapidly found with the aid of partition coefficient values previously measured by means of packed columns. In fact, if partition coefficient is known the elution time can be predicted at a particular flow-rate.

Table I shows the values of the diffusion coefficient obtained at temperatures from 250 to 280°C (average values calculated from measurements at three different flow-rates).

According to the theory [17], the diffusion coefficient increases with increase in temperature, but the

TABLE I

DIFFUSION COEFFICIENT OF ε-CAPROLACTAM IN NYLON 6 AT VARIOUS TEMPERATURES

Temperature (°C)	D_p (cm²/s)	Standard deviation (cm²/s)
250	$2.5 \cdot 10^{-8}$	$6.9 \cdot 10^{-9}$
260	$1.7 \cdot 10^{-8}$	$4.2 \cdot 10^{-9}$
270	$3.3 \cdot 10^{-8}$	$1.5 \cdot 10^{-8}$
280	$3.8 \cdot 10^{-8}$	$9.1 \cdot 10^{-9}$

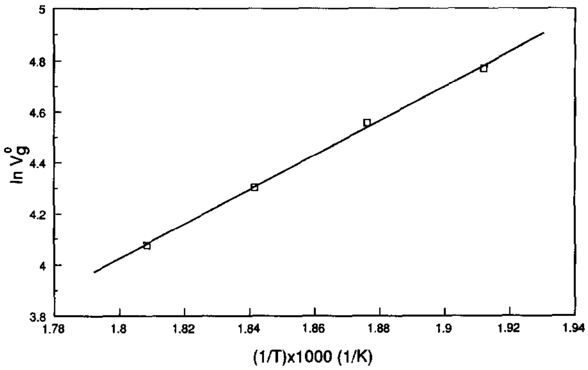

Fig. 1. Retention plot for ε-caprolactam in nylon 6.

rate of increase is smooth, because the temperatures of measurement are well above the T_g of the polymer (40°C [18]). The data obtained appear to be reliable within the experimental errors (30%).

To our knowledge, only one study concerning the diffusion of CPL in nylon 6 has been published [11]. There, D_p was measured at 265°C without using a chromatographic method, and the reported average value was $8 \cdot 10^{-8}$ cm²/sec, with limiting values of $1 \cdot 10^{-8}$ and $15 \cdot 10^{-8}$ cm²/sec, therefore in good agreement with out data.

Table II shows the specific retention data; as expected, V_g^0 varies with temperature. The data were plotted on a retention diagram (*i.e.*, ln V_g^0 *versus* 1 T). It is known that such plots are linear, except in the proximity of a phase transition of the polymer, where a discontinuity can exist owing to a change in the retention mechanism. In this study, a linear plot was obtained (Fig. 1), indicating that the retention volume was determined by bulk retention over the whole range of experimental temperatures.

A comparison between the values of V_g^0 and Ω^∞ obtained on packed and capillary columns is also shown in Table II. Except for those obtained at 250°C, the values differ by less than 5%. By common opinion an acceptable error in the IGC technique is between 2 and 5% [19], so the two sets of data can be considered to be consistent. The agreement suggest also that the stationary phase of the capillary column has not undergone a significant weight loss.

Finally, by using the data obtained at temperatures ranging from 260 to 280°C (Table II), the thermodynamic parameters of the system were calculated [20], as summarized in Table III, which also gives the thermodynamic data for CPL.

TABLE II

SPECIFIC RETENTION VOLUMES AND WEIGHT FRACTION ACTIVITY COEFFICIENTS AT INFINITE DILUTION OF ε-CAPROLACTAM AND DIMER IN NYLON 6 AT VARIOUS TEMPERATURES MEASURED ON PACKED AND CAPILLARY COLUMNS

Temperature (°C)	ε-Caprolactam					
	V_g^0 (ml/g)		Ω^∞		Dimer: V_g^0 (ml/g)	
	Packed column	Capillary column	Packed column	Capillary column	Packed column	Capillary column
250	127.1	117.84	2.68	2.89		
260	98.6	95.21	2.76	2.86		
270	77.5	73.86	2.84	2.98		
280	61.3	58.91	2.94	3.06	4571	4555

TABLE III

PARTIAL MOLAR HEATS OF MIXING AND HEATS OF SOLUTION OF CPL IN NYLON 6 AND HEATS OF VAPORIZATION AND SOLUBILITY PARAMETER AT 270°C OF CPL

Parameter	Packed column	Capillary column
$\Delta \bar{H}_1^\infty = R \cdot \frac{\partial \ln \Omega^\infty}{\partial(1/T)}$ (kcal/mol)	-2.00 ± 0.2	-1.76 ± 0.07
$\Delta H_s = -R \cdot \frac{\partial \ln V_g^0}{\partial(1/T)}$ (kcal/mol)	-13.36 ± 0.35	-13.96 ± 0.03
$\Delta H_v = \Delta \bar{H}_1^\infty - \Delta H_s$ (kcal/mol)	11.36 ± 0.55	12.2 ± 0.1
$\delta_{270} = \left(\frac{\Delta H_v - RT}{V_1}\right)^{\frac{1}{2}}$ $(\mathrm{cal/cm^2})^{\frac{1}{2}}$	8.7 ± 0.2	9.02 ± 0.04

REFERENCES

1 J. R. Laub and L. R. Pecsok, *Physicochemical Applications of Gas Chromatography*, Wiley, New York, 1978.
2 J. M. Braun and J. E. Guillet, *Adv. Polym. Sci.*, 21 (1976) 107.
3 D. G. Gray and J. E. Guillet, *Macromolecules*, 6 (1973) 223.
4 J. M. Braun, S. Poos and J. E. Guillet, *Polym. Lett.*, 14 (1976) 257.
5 M. Oner and S. Dincer, *Polymer*, 28 (1987) 279.
6 J. Miltz, *Polymer*, 27 (1986) 105.
7 S. T. Hu, C. D. Han and L. I. Stiel, *J. Appl. Polym. Sci.*, 33 (1987) 551.
8 A. C. Pawlisch, A. Macris and L. R. Lawrence, *Macromolecules*, 20 (1987) 1564.
9 L. Bonifaci, G. Cavalca, D. Frezzotti, E. Malaguti and G. P. Ravanetti, *Polymer*, in press.
10 J. D. Newman and J. M. Prausnitz, *J. Paint Technol.*, 45 (1973) 33.
11 K. Nagasubramanian and H. K. Reimschuessel, *J. Appl. Polym. Sci.*, 17 (1973) 1663.
12 D. Heikens, *Recl. Trav. Chim. Pays-Bas*, 75 (1956) 1199.
13 L. Bonifaci, G. Cavalca, D. Frezzotti, E. Malaguti and G. P. Ravanetti, *J. Chromatogr.*, 585 (1991) 333.
14 W. Jennings, *Gas Chromatography with Glass Capillary Columns*, Academic Press, New York, 2nd ed., 1980.
15 C. A. Pawlisch, *Ph.D. Dissertation*, University of Massachusetts, Amherst, MA, 1985.
16 A. A. Hanna, *Thermochim. Acta*, 76 (1984) 97.
17 J. L. Duda, J. S. Vrentas and H. T. Liu, *AIChE J.*, 28 (1982) 279.
18 P. Engler and S. H. Carr, *Polym. Eng. Sci.*, 18 (1978) 450.
19 I. Kikic, P. Alessi and M. Fermeglia, *Fluid Phase Equilib.*, 14 (1983) 363.
20 G. Di Paola-Baranyi and J. E. Guillet, *Macromolecules*, 11 (1978) 228.