Solubility of 6-Caprolactam in Supercritical Carbon Dioxide

Antero Laitinen* and Matti Jäntti

VTT Chemical Process Technology, Supercritical Technology, P.O. Box 1401, FIN-02044 VTT, Finland

Solubility of 6-caprolactam in supercritical carbon dioxide was measured at temperatures from 307 K to 324 K and pressures from 100 bar to 230 bar. The mole fraction solubilities ranged from 0.02 to 0.07. A static variable volume view cell apparatus was used for the measurements. The solubility data were modeled using the Peng−Robinson equation of state with two adjustable mixture parameters.

Introduction

Caprolactam (2-oxohexamethylenimine) is one of the most widely used chemical intermediates. Almost all of the annual world production 3.0×10^6 tons (Fisher and Crescentini, 1992) is consumed as the monomer for Nylon-6 fibers and plastics. Due to legislation and growing environmental awareness, the demand for recycling polymer products is increasing. Continuous recovery of caprolactam from blended waste stream containing Nylon-6 by using near-critical or supercritical solvent is described in the literature (Anon, 1993). The separated polyamide can be depolymerized by steam and phosphoric acid to caprolactam and some byproducts in continuous or batch reactors. Finally, caprolactam can be purified by distillation or extraction. According to Venema and van de Ven (1993) caprolactam and oligomers can be effectively extracted from Nylon-6 by use of supercritical fluid extraction with carbon dioxide containing methanol as an entrainer.

Development of new purification and recycle processes is hindered by the lack of basic engineering data. The solubility of caprolactam in pure supercritical carbon dioxide was measured to make possible feasibility studies and accurate design of equipment.

Experimental Section

Apparatus. A static view cell apparatus was used for measuring the solubility. The main component of this system is a variable volume view cell, which allows the visual determination of the phases present at equilibrium. The maximum operating temperature of the system is approximately 373 K and the maximum operating pressure is 400 bar. The piston inside the cell is driven by a high-pressure syringe pump (Isco 260D). The maximum internal volume of the cell with the piston inside is 30.4 ± 0.5 mL. The cell is placed in an air bath, and the temperature is maintained constant within ±0.5 K by a controller (Rex-F900, RKC Instrument Inc.). The temperature in the cell is measured by a calibrated J-type thermocouple, and the pressure is measured by a pressure sensor (Philips P21) and registered by a digital indicator (Philips Digital 380). The maximum estimated error for temperature measurements is ±0.5 K and for pressure measurements ±0.5 bar. The data are collected by Notebook Pro 8.01 data acquisition and process control software (Labtech). The cell content is mixed with a magnetic stirrer. A borescope (Olympus F080-024-000-55), light source (Olympus KLS-201), camera (Hitachi VK-C220E), and monitor are used to make the visualization easier. Most of the experiments are tape-recorded for later examination.

Experimental Procedure. The solubility of naphthalene at 308 K was measured to test the apparatus. Results were compared with the results published by other authors (Bartle *et al*., 1991). The measured solubilities of naphthalene agreed within approximately 7% with those of previous measurements.

The desired amount of 6-caprolactam was weighted to an accuracy of 10^{-3} g and charged to the cleaned cell. The cell was then purged several times with carbon dioxide gas to remove any entrapped air. After thermal equilibrium in the air bath was reached, the cell was slowly pressurized by pumping (Isco 260D) in carbon dioxide. The density of carbon dioxide in the cell was calculated from the cell temperature and pressure by the modified Benedict−Webb−Rubin equation of state (Angus et al., 1976). The amount of carbon dioxide loaded in the cell was then obtained by multiplying the density by the known volume of the cell. Since 6-caprolactam dissolved carbon dioxide during loading, it was necessary to independently measure the amount of the loaded carbon dioxide. This was done by the pump control unit, which shows how much the volume of the pump cylinder changes during the pressure vessel loading while the piston is adjusted to maintain constant pressure.

The pressure in the closed cell was slowly increased by moving the piston until complete miscibility was reached. After this, the pressure was slowly decreased until a second phase appeared. This solubilization and precipitation procedure was typically repeated two or three times. The average deviation of measured phase transition pressures from one phase to two phases was approximately ±5%. The solubility of 6-caprolactam was calculated from the masses of the lactam and carbon dioxide.

Materials. 6-Caprolactam was obtained from Fluka Chemie AG (purity >98%), and carbon dioxide (purity 99.7%) from AGA.

Theoretical Section

For solid−supercritical solvent equilibria, the fugacity of the solid component in the supercritical fluid phase can be calculated from

$$f_2^{\mathrm{F}}(T,p,y_2) = y_2\phi_2^{\mathrm{F}}p \tag{1}$$

The solid was modeled as a pure solid phase, even though it was noted that caprolactam was also dissolving carbon dioxide. The extent of dissolution cannot be measured with the experimental system. The assumption of solid phase

---

* To whom correspondence should be addressed. Fax: +358 0 456 7026. E-mail: Antero.Laitinen@vtt.fi.

S0021-9568(96)00031-3 CCC: $12.00

being pure solid phase is probably not strictly valid, but for simplicity this assumption was made. The fugacity of the solid component is

$$f_2^{S}(T,p) = \phi_2^{\mathrm{Sat}}(T)p_2^{\mathrm{Sat}}(T)\exp\left(\int_{p_2^{\mathrm{Sat}}}^{p}\left(\frac{v_2^{S}}{RT}\right)\mathrm{d}p\right) \qquad (2)$$

The fugacity coefficient ϕ_2^{Sat} can be set equal to 1 due to the relatively small value of the saturation pressure of the solid, and the molar volume of the solid can be considered to be constant over the pressure range. After these simplifications eqs 1 and 2 are set equal and the solubility of the solid in the supercritical fluid phase is obtained

$$y_2 = \frac{p_2^{\mathrm{Sat}}(T)\exp\left(\dfrac{v_2^{S}(p - p_2^{\mathrm{Sat}})}{RT}\right)}{\phi_2^{F}p} \qquad (3)$$

where y_2 is the mole fraction of the solid component in the fluid phase, p_2^{Sat} (T) is the saturation pressure of the pure solid at the system temperature, v_2^{S} is the molar volume of the pure solid, p is the system pressure, R is the gas constant, T is the system temperature, and ϕ_2^{F} is the fugacity coefficient of the solid in the fluid phase. The Peng–Robinson equation of state was used to calculate the fugacity coefficient ϕ_2^{F} (McHugh and Krukonis, 1994). The following combining and mixing rules were applied to describe the mixing of the components

$$a_{\mathrm{mix}} = \sum_{i=1}^{2}\sum_{j=1}^{2} y_i y_j a_{ij} \qquad b_{\mathrm{mix}} = \sum_{i=1}^{2}\sum_{j=1}^{2} y_i y_j b_{ij} \qquad (4)$$

$$a_{ij} = (1 - k_{ij})(a_{ii}a_{jj})^{0.5} \qquad b_{ij} = (1 - \eta_{ij})\frac{(b_{ii} + b_{jj})}{2} \qquad (5)$$

k_{ij} is a mixture parameter describing the intermolecular interaction between the unlike molecules, and η_{ij} stands for the effect of the different size and structure of unlike components. These parameters were fitted to the experimental data by minimizing the following function with the Simplex search method (Press et al., 1992)

$$S = \sum_{n=1}^{\mathrm{NEP}}\left(\frac{y_2^{\mathrm{cal}} - y_2^{\mathrm{ep}}}{y_2^{\mathrm{ep}}}\right)^2 \qquad (6)$$

where superscript cal refers to the value predicted by the model and ep refers to the experimentally obtained point. NEP is the number of experiments. The absolute average relative deviation is given by the following equation

$$A = \frac{1}{\mathrm{NEP}}\sum_{n=1}^{\mathrm{NEP}}\frac{|y_2^{\mathrm{cal}} - y_2^{\mathrm{ep}}|}{y_2^{\mathrm{ep}}} \qquad (7)$$

Physical Properties. Physical properties of 6-caprolactam were obtained online from the Design Institute for Physical Property Data (DIPPR) database (1990) and are seen in Table 1. The critical pressure and temperature were estimated by the method of Lydersen (1955).

Results and Discussion

Experimental data points at temperatures 307 K, 314 K, and 324 K and in the pressure range from 100 bar to 230 bar are reported in Table 2. The reproducibility of the data was calculated to be within ±5.7%. This was obtained by determining the absolute average relative deviation (AARD) of the two measurement series. The equilibrium mole fraction y of 6-caprolactam in supercritical carbon dioxide as a function of pressure is seen in Figure 1. The solid lines are calculated by the Peng–Robinson model.

Table 1. Physical Properties of Carbon Dioxide and 6-Caprolactam

component	M/g mol^{-1}	p_c/bar	T_c/K	ω	v^{s}/cm^3 mol^{-1}	$10^5 p^{s}$/bar
carbon dioxide	44.01	73.8	304.2	0.239		
6-caprolactam	113.16	47.7	806	0.474	162	0.69[a] 1.40[b] 4.53[c]

[a] 307.2 K. [b] 314.2 K. [c] 324.2 K.

Table 2. Mole Fraction Solubility of 6-Caprolactam in Supercritical Carbon Dioxide

T = 307 K			T = 314 K			T = 324 K		
p/bar	ρ_{CO_2}/kg m^{-3}	$10^3 y$	p/bar	ρ_{CO_2}/kg m^{-3}	$10^3 y$	p/bar	ρ_{CO_2}/kg m^{-3}	$10^3 y$
101	730.1	20.1	138	752.2	22.1	141	666.5	21.5
108	750.2	22.5	149	772.2	29.2	154	701.9	22.1
114	764.3	25.2	156	783.2	32.7	172	738.2	29.2
124	784.2	28.3	169	801.2	40.2	172	738.2	32.7
134	800.7	35.8	179	813.5	50.4	200	779.3	42.2
142	812.1	40.2	180	814.7	48.0	201	780.5	48.0
145	816.1	42.2	191	826.4	58.2	203	783.0	40.2
149	821.2	39.9	196	831.4	54.6	217	799.0	50.4
151	823.7	45.4	208	842.7	73.3	227	809.3	54.6
152	824.9	43.5						
154	827.3	48.8						
154	827.3	58.2						
168	842.6	58.3						
173	847.6	73.3						

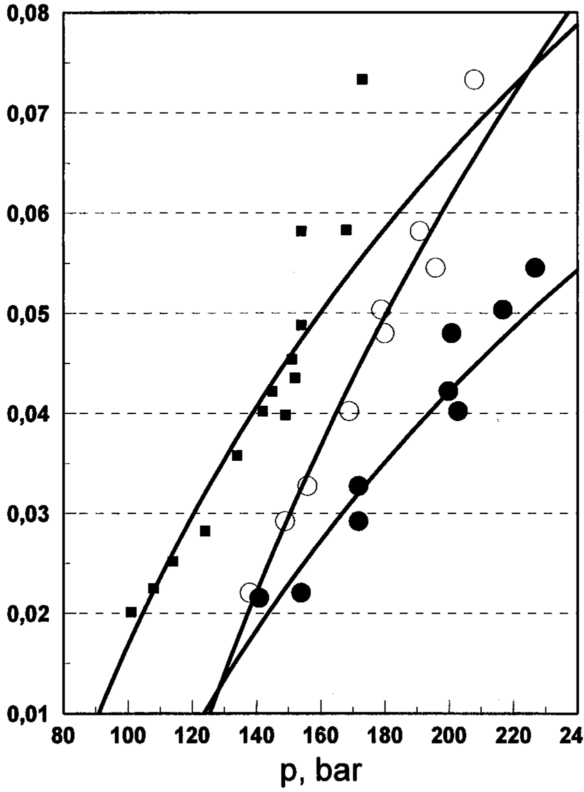

Figure 1. Mole fraction solubility of 6-caprolactam in supercritical carbon dioxide as a function of pressure: (■) 307 K; (○) 314 K; (●) 324 K; (—) calculated with PR-EOS.

6-Caprolactam is found to exhibit a relatively high solubility in supercritical carbon dioxide, i.e. up to around 17%. This was expected, since according to Fisher and Crescentini (1992), 6-caprolactam is very soluble in most common organic solvents. The shape of the isotherms is relatively similar at all three temperatures, and the

Table 3. Values of PR-EOS Fitting Parameters and Average Absolute Relative Deviation (AARD) of Calculated and Experimental Data

T/K	k	η	AARD/%
307	−0.044	−0.089	9.96
314	−0.041	−0.096	2.91
324	−0.083	−0.209	5.95

solubility curves increase deeply with pressure. The system temperature usually has a significant effect on the solid solubility in supercritical fluids, because it influences the solid vapor pressure, solvent density, and solute−solvent interactions. In these experiments the temperature range was relatively narrow, and there were no significant temperature effects. The solubility is mostly affected by the solvent density, as seen from Table 2. No crossover pressure, i.e. the pressure where two isotherms cross each other, was found at the experimental conditions, although according to the model, isotherms at 314 K and 324 K seem to cross at 130 bar.

The Peng−Robinson model with two adjustable parameters fits to the experimental data relatively well at lower pressures. At higher pressures there seems to be a severe deviation especially at 307 K. The values of the fitting parameters and the average absolute relative deviations (AARD) at 307 K, 314 K, and 324 K are seen in Table 3. According to the model, the 324 K isotherm seems to have a different behavior compared to the other isotherms.

Literature Cited

Angus, S.; Armstrong, B.; de Reuck, K. M. *Carbon Dioxide*, The IUPAC International Thermodynamic Tables of the Fluid State-3; Pergamon Press: Oxford, U.K., 1976.

Anon. Continuous Recovery of Caprolactam from Feed Containing Nylon 6 Using near Supercritical or Supercritical Fluid Polymer Separation. *Res. Discl.* **1993**, *353*, 602.

Bartle, K. D.; Clifford, A. A.; Jafar, S. A.; Shilstone, G. F. Solubilities of Solids and Liquids of Low Volatility in Supercritical Carbon Dioxide. *J. Phys. Chem. Ref. Data* **1991**, *20*, 713−756.

Fisher, W. B.; Crescentini, L. Caprolactam, in *Kirk-Othmer Encyclopedia Of Chemical Technology*, 4th ed.; Wiley: New York, 1992.

Lydersen, A. L. Estimation of Critical Properties of Organic Compounds. *Univ. Wis. Coll. Eng. Exp. Stn.* Madison, Wis. **1955**, Rep. 3.

McHugh, M. A.; Krukonis, V. J. *Supercritical Fluid Extraction, Principles and Practice*, 2nd ed.; Butterworth-Heinemann: Boston, 1994.

Press, W. H; Teukolsky, S. A; Vetterling, W. T.; Flannery, B. P. *Numerical Recipes in C*, 2nd ed.; Cambridge University Press: New York, 1992.

Venema, A.; van de Ven, H. J. F. M. Supercritical Fluid Extraction of Nylon 6: An Investigation into the Factors Affecting the Efficiency of Extraction of Caprolactam and its Oligomers. *J. High Res. Chromatogr.* **1993**, *16*, 522−524.

The DIPPR Database for chemistry and materials science; Design Institute for Physical Property Data, produced by AIChE, New York, 1990.

Received for review January 29, 1996. Revised manuscript received June 19, 1996. Accepted August 13, 1996.⊗

JE9600313

⊗ Abstract published in *Advance ACS Abstracts,* September 15, 1996.