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# Phase behaviour of the system 4′-pentyloxy-4-cyanobiphenyl + $CO_2$

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ABSTRACT

Isoplethic phase diagrams were measured for the system 4′-pentyloxy-4-cyanobiphenyl + $CO_2$ for $CO_2$ mole fractions up to 0.72, in temperature range 280–360 K and at pressures up to 12 MPa using a synthetic method with visual observation. It is found that pure 4′-pentyloxy-4-cyanobiphenyl shows two different solid phases, a nematic liquid phase (N) and an isotropic liquid phase ($I_2$). For the binary system, liquid–liquid demixing ($I_1 + I_2$) was found. The following phase equilibria were measured: $I_2$ + gas ↔ $I_2$, N + gas ↔ N, solid + N ↔ N, solid + $I_2$ ↔ $I_2$, N ↔ N + $I_2$ and N + $I_2$ ↔ $I_2$. Further, points of the three-phase curves (solid + N + gas), (N + $I_2$ + gas), (solid + N + $I_2$), (solid + $I_1$ + $I_2$) and ($I_1$ + $I_2$ + gas) were determined experimentally. Based on these measurements a *P,T*-projection of the system was constructed. At 341 K, the molar Henry coefficient of the isotropic phase was determined to be 13.7 MPa.

## 1. Introduction

Liquid crystals were proposed recently as solvents with a solubility switch for capturing $CO_2$ [1,2]. One of the characteristics of liquid crystals is the presence of a structured liquid phase, either nematic or smectic, which is found at temperatures between the solid and the isotropic liquid phase. The proposed $CO_2$ capture process as presented in [1,2] is based on a solubility difference between this structured phase and the isotropic liquid phase: less $CO_2$ will dissolve in the structured liquid phase than in the isotropic phase [2]. As in this process only cooling a few degrees at constant pressure is required to switch from the isotropic phase to the structured phase, this process has the potential to use less energy than the currently used $CO_2$ capture processes [3]. The nematic phase, being a structured liquid phase with orientational ordering and a relatively low viscosity compared to the smectic phase, can be used in particular for this process.

To be able to design such a capture process, the *P,T,x*-phase diagram of a liquid crystal with $CO_2$ should be known. In our preceding paper, phase diagrams of five different binary mixtures of liquid crystal + $CO_2$ for mass fraction $w_{CO2} = 0.05$ have been reported using a static visual method for the determination of the phase equilibria [1]. In this publication, an indication was found that for 4′-pentyloxy-4-cyanobiphenyl (5OCB), the liquid crystal examined in this study, two different solid phases were present. Other liquid crystals measured, octyloxy cyanobiphenyl, ethyl-propyl bicyclohexyl and propyl butyl bicyclohexyl, gave a lower solubility of $CO_2$, whereas pentyl cyanobiphenyl gave a higher solubility [4]. Other articles in literature describe only the solubility of $CO_2$ in the liquid and nematic phase determined at low pressure up to 1.5 MPa with a gravimetric method [4–6].

In this article, the results of a detailed experimental investigation on the phase behaviour of the system pentyloxy cyanobiphenyl (5OCB) (1) + $CO_2$ (2) are presented at varying $CO_2$ concentrations, whereas in the former publication only the isopleth at a concentration of $w_2 = 0.05$ was studied. Based on the experimentally determined *P,T*-diagrams (isopleths at constant $CO_2$ concentration) a proposal is made for a *P,T*-projection of the binary system. The isopleths were studied up to a CO2 mol fraction of 0.72, at a temperature range of 280–360 K, and at pressures up to 12 MPa. For the isotropic phase, the molar Henry coefficient was calculated at 341 K to be 13.7 MPa based on the *f,x*-diagram up to $x_2 = 0.327$. This manuscript is organized as follows. In Section 2, the experimental method will be described, in Section 3 the measured isopleths and in Section 4 the discussion of these isopleths with a proposal for a *P,T*-projection.

## 2. Experimental methods

### 2.1. Materials

4′-(Pentyloxy)-4-biphenylcarbonitrile, 99 mass% (5OCB) was obtained from Alfa Aesar and used as received. Carbon dioxide was obtained from Linde Gas, with a purity of 4.5. See table 1 for an overview of the chemicals used in this study.

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**TABLE 1**
Overview of chemicals used in this study.

| Chemical name | Source | Purity | Purification |
|---|---|---|---|
| $CO_2$ CAS: 85540-96-1 | Linde gas | Volume fraction 0.99995 | Used as received |
| 4′-Pentyloxy-4-cyanobiphenyl (5OCB) CAS: 52364-71-3 | Alfa Aesar | Mass fraction (GC) 0.999 | Used as received |

**TABLE 2**
Experimental data for pure 5OCB at temperature $T$ and pressure $P$. $S_1$ denotes the solid phase, N the nematic phase and $I_2$ the isotropic liquid. The uncertainties of temperature and pressure are denoted by $u(T)$ and $u(P)$, respectively.

| $T$/K | $P$/MPa | Phase boundary |
|---|---|---|
| 326.84 | 0.399 | $S_1 \leftrightarrow N$[a] |
| 327.21 | 1.399 | $S_1 \leftrightarrow N$[a] |
| 328.20 | 4.401 | $S_1 \leftrightarrow N$[a] |
| 327.72 | 3.001 | $S_1 \leftrightarrow N$[a] |
| 327.52 | 2.400 | $S_1 \leftrightarrow N$[a] |
| 327.86 | 3.400 | $S_1 \leftrightarrow N$[a] |
| 328.54 | 5.401 | $S_1 \leftrightarrow N$[a] |
| 328.84 | 6.402 | $S_1 \leftrightarrow N$[a] |
| 329.23 | 7.403 | $S_1 \leftrightarrow N$[a] |
| 329.55 | 8.403 | $S_1 \leftrightarrow N$[a] |
| 329.86 | 9.405 | $S_1 \leftrightarrow N$[a] |
| 330.08 | 10.005 | $S_1 \leftrightarrow N$[a] |
| 341.58 | 0.399 | $N \leftrightarrow I_2$[b] |
| 341.96 | 1.399 | $N \leftrightarrow I_2$[b] |
| 342.38 | 2.400 | $N \leftrightarrow I_2$[b] |
| 342.75 | 3.401 | $N \leftrightarrow I_2$[b] |
| 343.13 | 4.401 | $N \leftrightarrow I_2$[b] |
| 342.91 | 3.901 | $N \leftrightarrow I_2$[b] |
| 343.32 | 4.902 | $N \leftrightarrow I_2$[b] |
| 343.51 | 5.402 | $N \leftrightarrow I_2$[b] |
| 343.90 | 6.403 | $N \leftrightarrow I_2$[b] |
| 344.30 | 7.404 | $N \leftrightarrow I_2$[b] |
| 344.70 | 8.404 | $N \leftrightarrow I_2$[b] |
| 345.10 | 9.405 | $N \leftrightarrow I_2$[b] |
| 345.33 | 10.005 | $N \leftrightarrow I_2$[b] |

[a] $u(T) = 0.05$ K, $u(P) = 0.005$ MPa.
[b] $u(T) = 0.01$ K, $u(P) = 0.005$ MPa.

### 2.2. Phase equilibria measurements

Phase diagrams were visually measured according to the synthetic method using a Cailletet apparatus, described in detail by De Loos *et al.* [7] For the preparation of a mixture, 50–125 mg 5OCB was inserted in a Pyrex glass tube, the so-called Cailletet tube. The accuracy of the balance used to weigh the sample of 5OCB was 0.1 mg. Prior to the addition of $CO_2$, the sample was degassed by repeatedly melting and freezing the sample with liquid nitrogen under vacuum. A gas-volumetrically determined amount of $CO_2$ was added after completion of the degassing. Mercury was used to pressurize the sample. The pressure was measured with a De Wit dead weight gauge with an accuracy of 0.005 MPa, the temperature was controlled with a Lauda RC 20 thermostatic bath within 0.02 K and the temperature was measured with an ASL Pt100 resistance thermometer with an estimated error of 0.01 K. Phase equilibria involving the disappearance of a solid phase were measured by changing the temperature while keeping the pressure constant, with an accuracy of 0.05 K unless stated otherwise. The phase boundaries between the two-phase regions nematic + isotropic and the homogeneous one-phase regions nematic or isotropic were measured at constant pressure with an accuracy of 0.01 K. The other phase equilibria were measured by varying the pressure while the temperature was kept constant, with an accuracy of 0.005 MPa, unless stated otherwise.

## 3. Results

*P,T*-phase diagrams of pure 5OCB and of 5OCB + $CO_2$ mixtures $[(1 - x_{CO_2})$ 5OCB + $x_{CO_2}$ $CO_2]$ for mole fractions $x_{CO_2} = 0.057$, 0.159, 0.241, 0.329, 0.400, 0.497 and 0.720 have been measured. The experimental results are presented in tables 2–9 and figures 1–8. In the binary system, next to two solid modifications of 5OCB ($S_1$ and $S_2$) also two isotropic liquid phases ($I_1$ and $I_2$) were found.

The pressure dependence of the solid ($S_1$) to nematic (N) and of the nematic (N) to isotropic ($I_2$) phase transition of pure 5OCB is shown in figure 1 and table 2. According to DSC measurements in literature, 5OCB has a nematic to isotropic liquid transition at 340.6 K and two different solid to nematic phase transitions at 320.5 and 325.5 K [8–10] at atmospheric pressure. The extrapolated data of the phase transitions to a pressure of 0.1 MPa, gave a solid to nematic phase transition at 326.8 K and a nematic to isotropic phase transition at 341.5 K, which corresponds well with the results in literature [8–10], the maximum deviation is 1.3 K. In literature, also a transition of another solid modification ($S_2$) to nematic is reported [8]. However, this transition was not found in this study for pure 5OCB.

The phase diagram of 5OCB + $CO_2$ at $x_{CO_2} = 0.057$, shown in figure 2, shows behaviour which is to be expected for a binary mixture of a liquid crystal with $CO_2$ [1]. For this composition, the bubble points of the nematic phase ($N + G \leftrightarrow N$) and of the isotropic liquid phase ($I_2 + G \leftrightarrow I_2$) were measured. The two-phase region $N + I_2$ is very narrow, the width is only 0.13 K. This two-phase region separates the homogeneous one-phase region N found at lower temperature from the one-phase region $I_2$ at higher temperature. At low pressure this two-phase region is separated from the two-phase region N + G by the $NI_2G$ three-phase curve (see insert

**TABLE 3**
Experimental data for the system 5OCB (1) + $CO_2$ (2) for mole fraction $x_2 = 0.057$. $I_2$ denotes the isotropic phase, G the gas phase, $S_1$ the solid phase, N the nematic phase. The uncertainties of temperature and pressure are denoted by $u(T)$ and $u(P)$, respectively.[a]

| $T$/K | $P$/MPa | Phase boundary |
|---|---|---|
| 344.11 | 0.829 | $(I_2 + G) \leftrightarrow I_2$[b] |
| 348.92 | 0.864 | $(I_2 + G) \leftrightarrow I_2$[b] |
| 354.05 | 0.898 | $(I_2 + G) \leftrightarrow I_2$[b] |
| 358.31 | 0.923 | $(I_2 + G) \leftrightarrow I_2$[b] |
| 364.01 | 0.963 | $(I_2 + G) \leftrightarrow I_2$[b] |
| 338.85 | 0.798 | $(I_2 + G) \leftrightarrow I_2$[b] |
| 336.12 | 0.783 | $(I_2 + G) \leftrightarrow I_2$[b] |
| 335.22 | 0.800 | $(N + G) \leftrightarrow N$[b] |
| 330.24 | 0.790 | $(N + G) \leftrightarrow N$[b] |
| 325.30 | 0.764 | $(N + G) \leftrightarrow N$[b] |
| 320.27 | 0.729 | $(N + G) \leftrightarrow N$[b] |
| 324.06 | 2.905 | $(S_1 + N) \leftrightarrow N$[c] |
| 324.66 | 4.906 | $(S_1 + N) \leftrightarrow N$[c] |
| 325.46 | 6.909 | $(S_1 + N) \leftrightarrow N$[c] |
| 326.16 | 8.911 | $(S_1 + N) \leftrightarrow N$[c] |
| 335.86 | 0.904 | $N \leftrightarrow (N + I_2)$[d] |
| 336.63 | 2.905 | $N \leftrightarrow (N + I_2)$[d] |
| 337.39 | 4.906 | $N \leftrightarrow (N + I_2)$[d] |
| 338.17 | 6.908 | $N \leftrightarrow (N + I_2)$[d] |
| 338.94 | 8.909 | $N \leftrightarrow (N + I_2)$[d] |
| 339.72 | 10.910 | $N \leftrightarrow (N + I_2)$[d] |
| 335.98 | 0.903 | $(N + I_2) \leftrightarrow I_2$[b] |
| 336.75 | 2.904 | $(N + I_2) \leftrightarrow I_2$[b] |
| 337.52 | 4.906 | $(N + I_2) \leftrightarrow I_2$[b] |
| 338.29 | 6.908 | $(N + I_2) \leftrightarrow I_2$[b] |
| 339.06 | 8.909 | $(N + I_2) \leftrightarrow I_2$[b] |
| 339.82 | 10.910 | $(N + I_2) \leftrightarrow I_2$[b] |

[a] $u(P) = 0.005$ MPa.
[b] $u(T) = 0.01$ K.
[c] $u(T) = 0.05$ K.
[d] $u(T) = 0.02$ K.