Binary and Ternary Mixtures of Liquid Crystals with CO_2

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Liquid crystals, elongated molecules with a structured liquid phase, may be used as new solvents for CO_2 capture. However, no molecule has been found yet with optimal properties. Therefore, mixtures of two liquid crystals and CO_2 are investigated. Also, the phase behavior of some binary subsystems of the investigated ternary systems is studied for comparison. In the mixtures investigated, 4,4′-pentyloxycyanobiphenyl + 4,4′-heptyloxycyanobiphenyl + CO_2 and 4,4′-propylcyclohexylbenzonitrile + 4,4′-heptylcyclohexylbenzonitrile + CO_2, the nematic phases form a nematic homogeneous solution and the solid phases form an eutectic system, leading to a material with improved properties for CO_2 capture. Moreover, the ternary mixture of 4,4′-propylcyclohexylbenzonitrile + 4,4′-heptylcyclohexylbenzonitrile + CO_2 showed an increased solubility of CO_2 compared with the binary subsystems. © 2015 American Institute of Chemical Engineers *AIChE J*, 61: 2977–2984, 2015
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Introduction

Liquid crystals can be described as rigid rods, composed of two or more ring structures, with one or more end groups attached to it, which can be flexible.[1] Because of the shape of the molecules, they can form a so-called nematic phase (N). This is a liquid crystalline phase in which the rod-like molecules have orientational ordering, but no positional ordering. This nematic phase has a similar viscosity as the isotropic phase.[2]

Liquid crystals can be used as novel solvents for CO_2 capture process as proposed by Gross and Jansens.[3] This method uses the idea that creating the orientational ordered nematic phase, which can be obtained by cooling down the liquid crystal in the isotropic phase (I), leads to a lower free volume of the solvent.[1] If one absorbs CO_2 in the isotropic liquid, it will be desorbed as a gas (G) when the nematic phase is formed, because the solubility of CO_2 will be lower in the nematic phase due to this free volume effect. Due to lack of thermodynamic data of systems of LCs and CO_2, it is currently unknown whether or not this process is economically feasible.

Two parameters are of utmost importance for this process: the CO_2 solubility and the CO_2 solubility difference (Δx) between the nematic and the isotropic phases. A higher solubility leads to a lower working pressure, or a reduction of the amount of solvent needed for the CO_2 capture process. In our previous work,[4–6] we outlined the influence of different molecular groups of liquid crystals on the solubility of CO_2. The liquid crystals with the highest CO_2 solubility are 4,4′-pentylcyanobiphenyl or 4,4′-pentyloxy cyanobiphenyl (5OCB),[4,6] molecules which can be described as weakly polar molecules. The apolar and polar molecules investigated have a lower CO_2 solubility.[4,6] The CO_2 solubility difference between the nematic and isotropic phase depends on the free volume change and the enthalpy change of the N ↔ I phase transition.[1,4] A larger enthalpy change leads to a larger solubility difference, according to the Van 't Hoff equation. The CO_2 solubility difference can be determined when the complete phase diagram is measured. This is performed previously for the system 5OCB + CO_2.[5] The solubility difference has a large influence on the amount of solvent needed for the CO2 capture process.

None of the liquid crystals tested so far has suitable properties for CO_2 capture. Of most liquid crystals, the temperature range of the existence of the nematic phase is too small, or the temperature of the N ↔ I phase change is too low, leading to an infeasible process. To create a liquid crystal solvent with optimal properties, a mixture of two or more liquid crystals can be considered. A classification of all possible phase diagrams of a mixture of two liquid crystals is provided by Pestov et al.[7] It shows that if two nematic liquid crystals are mixed, the nematic phase is in most cases a homogeneous solution and the same holds for the isotropic phase. Furthermore, the phase behavior of a mixture of two liquid crystals shows a nematic solid behavior analogous to a eutectic system. However, if the difference in polarity of the liquid crystals used in the mixture is too large, an induced smectic phase may form. By carefully choosing the liquid crystals, one can create a solvent with a significant lower solid to nematic phase transition temperature and therefore a larger Δx.

To investigate the influence of replacing the pure liquid crystal with a mixture of two liquid crystals, two ternary mixtures were chosen. An overview of the liquid crystals used is shown in Table 1. The ternary mixture 4,4′-heptyloxycyanobiphenyl (7OCB) + 4,4′-pentyloxycyanobiphenyl (5OCB) + CO_2

Additional Supporting Information may be found in the online version of this article.

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Table 1. Overview of Chemicals Used in This Study

Chemical Name	Abbreviation	Source	Purity	Purification
4,4′-Propylcyclohexyl benzonitrile	PCH3	Merck	≥98% mass	Used as received
4,4′-Heptylcyclohexyl benzonitrile	PCH7	Merck	≥98% mass	Used as received
4,4′-Pentyloxy cyanobiphenyl	5OCB	Alfa Aesar	99% mass	Used as received
4,4′-Heptyloxy cyanobiphenyl	7OCB	Alfa Aesar	99.9% mass	Used as received
Carbondioxide	CO_2	Linde gas	Volume fraction 0.99995	Used as received

is measured at constant 7OCB/5OCB composition of $x_{5OCB}/x_{7OCB} = 1.77 \pm 0.02$ with a different mole fraction of CO_2, namely $x_{CO2} = 0.062$, 0.138, 0.248, 0.337. Also, the phase behavior of the ternary system of 4,4′-propylcyclohexylbenzonitrile (PCH3) + 4,4-heptylcyclohexylbenzonitrile (PCH7) + CO_2 with the ratio of PCH3 and PCH7 fixed at $x_{PCH7}/x_{PCH3} = 3.00$, at CO_2 concentrations $x_{CO2} = 0.138$, 0.244 and 0.332, was studied. The main conclusion of this work is that the mixture of PCH3 + PCH7 is most promising for CO_2 capture, as this mixture has highest CO_2 solubility and largest Δx.

Materials and Methods

An overview of the materials used in this study is given in Table 1. The liquid crystals used were 4,4′-pentyloxycyanobiphenyl and 4,4′-heptyloxycyanobiphenyl, 99 wt % purity, obtained from Sigma-Aldrich, and 4,4′-propylcyclohexylbenzonitrile and 4,4-heptylcyclohexylbenzonitrile, 98 wt % purity, provided by Merck KGaA. CO_2, purity 4.5, was obtained from Linde Gas.

The measurements were performed using a Cailletet setup, which is of the synthetic, visual type. A detailed description can be found in the article of de Loos et al.[8] A sample is prepared by putting a specified sample of 0.1 g liquid crystalline material in a measurement tube. It is degassed under vacuum using liquid nitrogen to prevent sample evaporation. A known amount of gaseous CO_2 is added to the sample using a calibrated volume. The amount of CO_2 used is determined by measuring the temperature and pressure of the calibrated volume. The number of moles of CO_2 is calculated using the second order virial equation. The maximum inaccuracy of the amount of CO_2 added is $u(x) = 0.001$ mol/mol, for a value of $x_{CO2} = 0.062$ mol/mol. The measurement tube is sealed with liquid mercury. The tube is then placed in a Cailletet setup, in which the temperature and pressure can be changed with an accuracy of 0.02 K and 0.005 MPa, respectively. Phase equilibria measured with an accuracy of 0.005 MPa and 0.02 K were the two-phase equilibria I + G ↔ I, N + G ↔ N, N + I ↔ N, N + I ↔ I, and the three-phase equilibria N + I + G, N + I + G ↔ N + I, N + I + G ↔ I + G, N + I + G ↔ N + G. Phase equilibria involving the solid (S) phase were the two-phase equilibria S + I ↔ I, S + N ↔ N and the three-phase equilibria S + N + G and S + I + G, all measured with an accuracy of 0.005 MPa and 0.05 K.

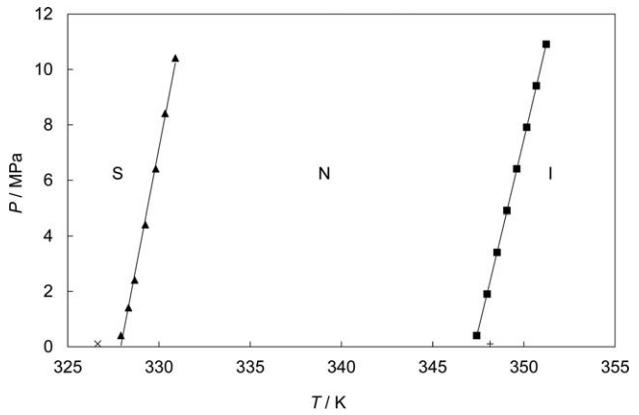

Figure 1. P,T-diagram of pure 4,4-heptyloxy cyanobiphenyl.

S denotes the solid phase, N the nematic phase and I the isotropic phase. ▲ S ↔ N; ■ N ↔ I; S ↔ N phase transition at P = 0.1 MPa[2]; + N ↔ I phase transition at P=0.1 MPa[2]. The lines are linear fits of the data points.

Results

To investigate the phase behavior of the ternary mixtures of two liquid crystals with CO_2, first of all the unary and binary phase diagrams of the substances used should be known. Therefore, the unary and binary phase diagrams will be discussed prior to the description of the ternary phase diagrams. The results for the ternary system 5OCB + 7OCB + CO_2 will be presented followed by the system of PCH3 + PCH7 + CO_2. The tabulated measurement data are available as Supporting Information.

The P,T-diagram of pure 7OCB, shown in Figure 1, was measured in the Cailletet-setup for comparison with literature data. The S ↔ N and N ↔ I phase transitions were measured. The S ↔ N phase transition at atmospheric pressure was found at a temperature 2 K higher than the literature value, the N ↔ I phase transition was 1 K lower.[2] These uncertainties are comparable with other values in literature.[9]

The results of the mixture of 7OCB with CO_2, $x_{CO2} = 0.260$, are shown in Figure 2. Phase transitions

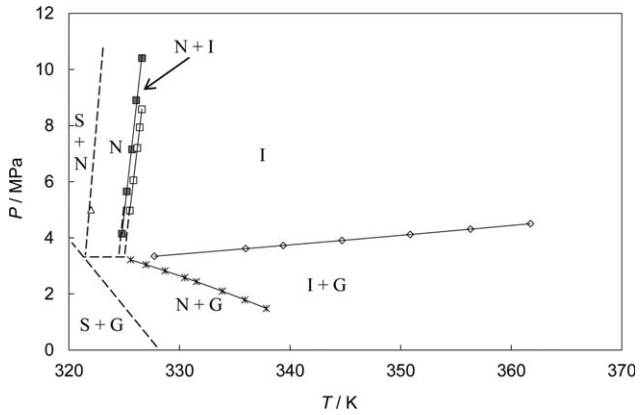

Figure 2. P,T-diagram of the binary mixture 4,4-heptyloxy cyanobiphenyl + CO_2 at $x_{CO2} = 0.260$.

S denotes the solid phase, N the nematic phase, I the isotropic phase and G the gas phase. △ S + N ↔ N; ■ N + I ↔ N; □ N + I ↔I; ✳ N + I + G; ◇ I + G ↔ I. The dashed lines are added as a guide to the eye, the solid lines are polynomial fits through the data points.

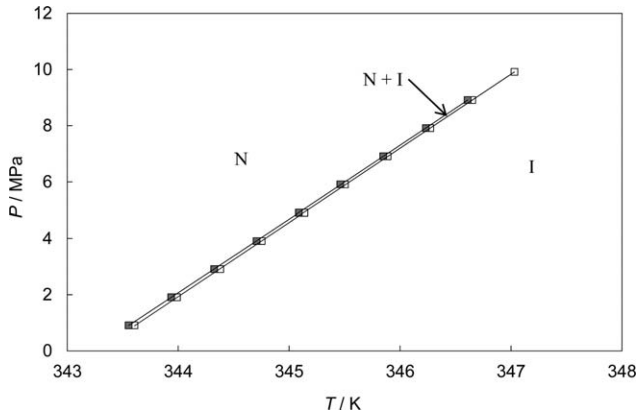

Figure 3. P,T-diagram of the binary mixture 4,4-heptyloxy cyanobiphenyl + 4,4-pentyloxy cyanobiphenyl, x_{5OCB}/x_{7OCB}= 1.79.

N denotes the nematic phase, I the isotropic phase. ■ N ↔ N + I; □ N + I ↔ I. The solid lines are linear fits through the data points.

measured for this mixture were the two-phase equilibria I ↔ I + G, N ↔ N + G, N ↔ N + I, I ↔ N + I, and the three-phase equilibria N + I + G which is located between the two-phase regions N + G and I + G. The extrapolation of this line should end in the triple point N + I + G of the pure LC. The coordinates of the triple point of 7OCB are 347 K at 0.1 MPa, estimated from the pure component phase transition. The S + N ↔ N phase equilibrium of the mixture of 7OCB with CO_2, $x_{CO2} = 0.260$, was estimated to be at $T = 322$ K at $P = 5.0$ MPa.

The experimental results of the binary mixture of 5OCB + 7OCB at $x_{5OCB}/x_{7OCB} = 1.79$ is shown in Figure 3. The equilibria measured were the N ↔ N + I and I ↔ N + I two-phase equilibria. The S ↔ S + N ↔ N phase transition was difficult to detect visually. A slow increase of the temperature at a constant pressure of $P = 0.91$ MPa showed that the phase transition temperature was between $T = 300.6$ and 300.8 K. The temperature range (ΔT) of the two-phase area N + I is very small, $\Delta T = 0.05$ K.

When CO_2 is added to the binary mixture of 5OCB + 7OCB, the temperature range of the N + I two-phase area becomes larger. The temperature range for $x_{CO2} = 0.062$ is $\Delta T = 0.15$ K. Equilibria measured were N + G ↔ N, I + G ↔ I, N + I ↔ I, N ↔ I + N, and the three-phase equilibria N + I + G ↔ I + G. The system is shown in Figure 4, the insert shows an enlargement of the N + I ↔ I two-phase area. The system can be described as a pseudo-binary system, composed of CO_2 and a mixture of 7OCB + 5OCB with a fixed composition, namely $x_{5OCB}/x_{7OCB} = 1.77$. In this case the extrapolation of the three-phase equilibria of the ternary mixture to $P = 0.1$ MPa should yield approximately the same point as is obtained by extrapolating the N + I ↔ I phase transition of the binary mixture of the two liquid crystals to $P = 0.1$ MPa.

In Figures 5–7, the influence of adding a larger amount of CO_2 to the binary mixture of 5OCB and 7OCB is clearly visible. In Figure 5, $x_{CO2} = 0.131$, in Figure 6, $x_{CO2} = 0.248$ and in Figure 7 $x_{CO2} = 0.337$. The N + I two-phase area becomes wider and shifts to lower temperature. The three-phase area N + I + G is made visible in Figure 6; its width is approximately 0.005 MPa, which is close to the experimental error. Though this is a very small difference, the N + I + G ↔ N + G phase transition was measured at a lower pressure than the N + I + G ↔ I + G three-phase equilibrium, independent of the measurement method. Other phase transitions measured for these mixtures were I + G ↔ I and N + G ↔ N.

The other system investigated was the system PCH3 + PCH7 + CO_2. The pure component phase equilibria of the liquid crystals at $P = 0.1$ MPa are published in

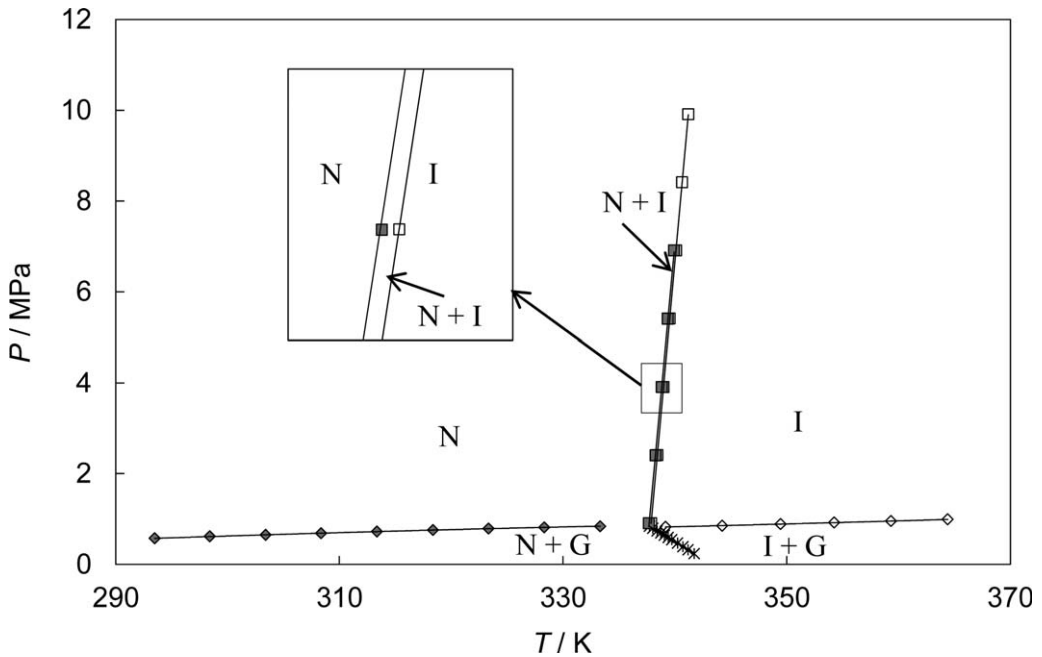

Figure 4. P,T-diagram of the ternary mixture 4,4-heptyloxy cyanobiphenyl + 4,4-pentyloxy cyanobiphenyl + CO_2, $x_{5OCB}/x_{7OCB} = 1.77$, $x_{CO2} = 0.062$.

N denotes the nematic phase, I the isotropic phase and G the gas phase. ■ N + I ↔ N; □ N + I ↔I; ✳ I + G ↔ N + I + G; ◆ N + G ↔N; ◇ I + G ↔ I. The solid lines are fits through the data points.

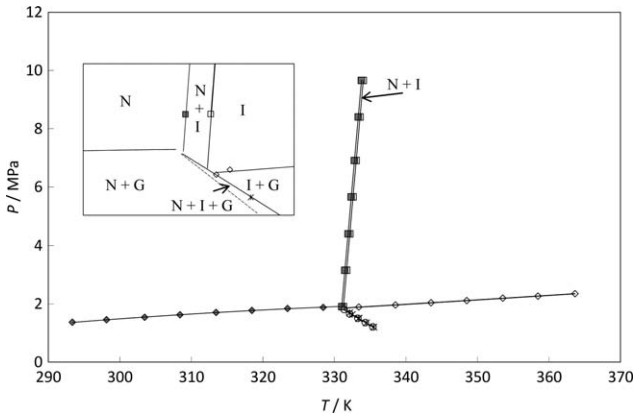

Figure 5. *P,T*-diagram of the ternary mixture 4,4-heptyloxy cyanobiphenyl + 4,4-pentyloxy cyanobiphenyl + CO_2, x_{5OCB}/x_{7OCB} =1.77, x_{CO2} = 0.131.

N denotes the nematic phase, I the isotropic phase and G the gas phase. ■ N + I ↔ N; □ N + I ↔I; ✳ I + G ↔ N + I + G; ◆ N + G ↔N; ◇ I + G ↔ I. The dashed line is added as a guide to the eye, the solid lines are fits through the data points.

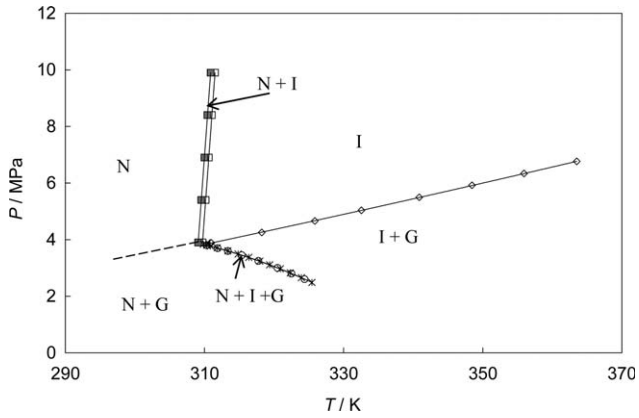

Figure 7. P,T-diagram of the ternary mixture 4,4-heptyloxy cyanobiphenyl + 4,4-pentyloxy cyanobiphenyl + CO_2, x_{5OCB}/x_{7OCB} = 1.77, x_{CO2} = 0.337.

N denotes the nematic phase, I the isotropic phase and G the gas phase. ■ N + I ↔ N; □ N + I ↔I; ✳ I + G ↔ N + I + G; ○ N + G ↔ N + I + G; ◆ N + G ↔N; ◇ I + G ↔ I. The dashed line is added as a guide to the eye, the solid lines are fits through the data points.

literature.[2] For comparison, the pure component phase equilibria have been measured and are shown in Figures 8 and 9 together with the literature data. Pure PCH3 has a S ↔ N and a N ↔ I phase transition at T = 316.5 and 319.5 K, respectively.[2] Pure PCH7 has a phase transition from S ↔ N and from N ↔ I at T = 306 and 332 K, respectively.[2] PCH3 has a smaller temperature range of the nematic phase than PCH7.

The binary phase diagram of PCH7 + CO_2 at x_{CO2} = 0.213 is shown in Figure 10. Phase equilibria measured were the S + N ↔ N, N ↔ I + N, I ↔ N and I, N + G ↔ N, I + G ↔ I, and the three-phase equilibria S + N + G and N + I + G. For this liquid crystal the three-phase curve S + N + G does not end in the pure components' triple point. This is an indication that another solid phase has crystallized. Unless the phase diagram is fully known, we cannot judge if this solid phase is stable at this conditions. Compared to the binary systems 5OCB + CO_2[5] and 7OCB + CO_2 (this work), this liquid crystal has a broader N + I two-phase area.

The binary phase diagram of PCH3 + CO_2 at x_{CO2} = 0.050, which is quite close to the quadruple point composition, is shown in Figure 11. At pressures lower than the I + G ↔ I phase equilibria the two three-phase curves S + I + G and N + I + G intersect with each other. The third three-phase equilibrium, S + N + I, is partly measured and should intersect with these two lines as well, but as the concentration of CO_2 is slightly higher than the CO_2 concentration at the quadruple point, this curve is intersected by the two-phase equilibrium S + I ↔ I. The N + I ↔ I and the N ↔ N + I two-phase equilibria as well as the N + I + G are partly stable, at the right side of the S + N + I three-phase curve, and at the left side they can only be measured if the solid phase is not crystallizing. The N + G ↔ N equilibria are also metastable. The S + N ↔ N phase equilibrium should intersect with the intersection of the N + I ↔ N and the three-phase curve S + N + I, but this was not measured.

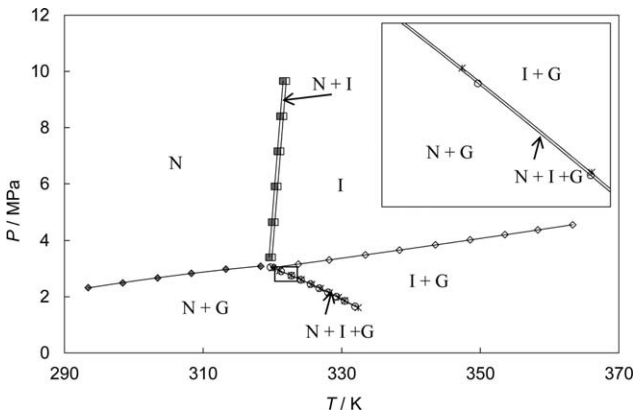

Figure 6. P,T-diagram of the ternary mixture 4,4-heptyloxy cyanobiphenyl + 4,4-pentyloxy cyanobiphenyl + CO_2, x_{5OCB}/x_{7OCB} = 1.76, x_{CO2} = 0.248.

N denotes the nematic phase, I the isotropic phase and G the gas phase. ■ N + I ↔ N; □ N + I ↔I; ✳ I + G ↔ N + I + G; ○ N + G ↔ N + I + G; ◆ N + G ↔N; ◇ I + G ↔ I. The solid lines are fits through the data points.

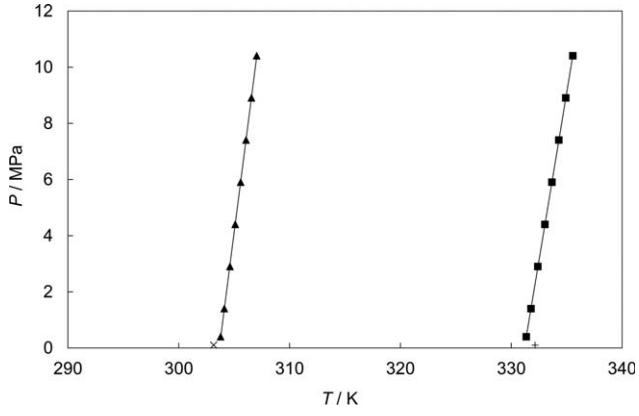

Figure 8. P,T-diagram of pure 4-heptyl-4′-cyclohexylbenzonitrile. S denotes the solid phase, N the nematic phase and I the isotropic phase.

▲ S ↔ N; ■ N ↔ I; S ↔ N phase transition at P=0.1 MPa^2; + N ↔ I phase transition at P=0.1 MPa^2 . The lines are linear fits of the data points.

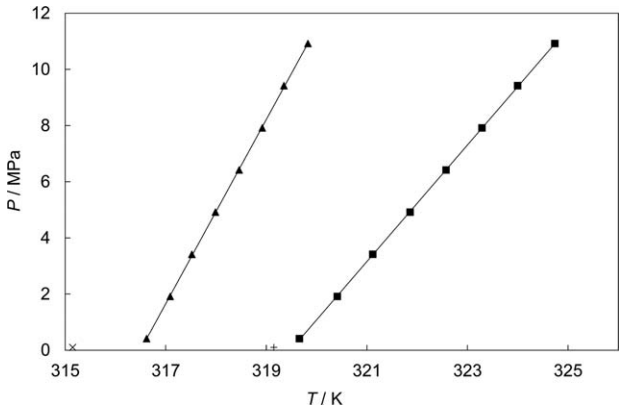

Figure 9. P,T-diagram of pure 4-propyl-4′-cyclohexylbenzonitrile. S denotes the solid phase, N the nematic phase and I the isotropic phase.

▲ S ↔ N; ■ N ↔ I; S ↔ N phase transition at P=0.1 MPa^2; + N ↔ I phase transition at P=0.1 MPa^2 . The lines are linear fits of the data points.

The binary P,T-phase diagram of PCH3 + CO_2 at $x_{CO2} = 0.214$ is shown in Figure 12. Only equilibria involving the solid phase, the isotropic phase and the G phase are stable, because the concentration is higher than the quadruple point concentration. The equilibria measured for this substance are I + G ↔ I, S + I ↔ I and S + I + G.

To create a mixture with a larger nematic temperature range, ternary mixtures of PCH3, PCH7, and CO_2 are considered at a composition $x_{PCH7}/x_{PCH3} = 3.00$ with a varying amount of CO_2. In Figure 13, the binary phase diagram of PCH3 and PCH7 is shown at the aforementioned composition. Phase equilibria for this system are S + N ↔ N and N + I ↔ N and N + I ↔ I. The N + I two phase area is quite small, $\Delta T = 0.04$ K. An insert in Figure 13 shows the two-phase area N + I. The mixture is liquid at room temperature, for the S + N ↔ N phase transition is at 282 K.

The pseudobinary system PCH3 + PCH7 + CO_2 at $x_{PCH7}/x_{PCH3} = 3.00$ shows similar behavior as the pseudobinary

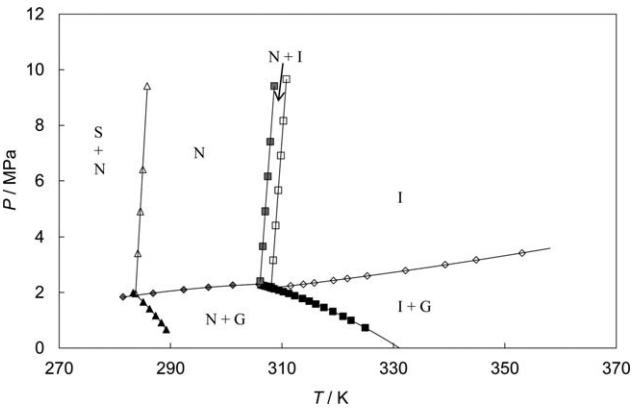

Figure 10. P,T-diagram of the binary mixture 4-heptyl-4′-cyclohexylbenzonitrile + CO_2 at x_{CO2} = 0.213. S denotes the solid phase, N the nematic phase, I the isotropic phase and G the gas phase.

△ S + N ↔ N; ▲ S + N + G; ■ N + I ↔ N; □ N + I ↔I; ✳ N + I + G; ◇ I + G ↔ I. The solid lines are first and second order polynomial fits through the data points.

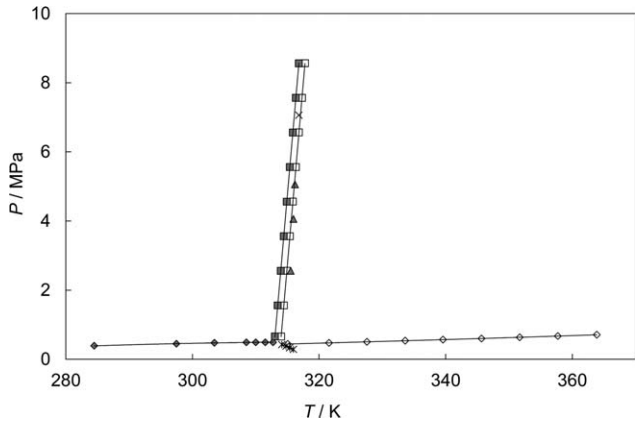

Figure 11. P,T-diagram of the binary mixture 4-propyl-4′-cyclohexylbenzonitrile + CO_2 at x_{CO2} = 0.050. S denotes the solid phase, N the nematic phase, I the isotropic phase and G the gas phase.

▲ S + I ↔ I; ■ N + I ↔ N; □ N + I + I; × S + N ↔ I; ◆ N + I ↔ G; ◇ I + G ↔ I;. The solid lines are first or second order polynomial fits through the data points.

system 5OCB + 7OCB + CO_2. Phase equilibria measured for this system were the two-phase equilibria I + G ↔ I, N + G ↔ N, N ↔ N + I, and N + I ↔ I. Three-phase equilibria measured are N + I + G ↔ N + I and N + I + G ↔ I + G and N + I + G ↔ N + G. Figures 14–16 show the results of $x_{CO2} = 0.138$, 0.244, and 0.332, respectively.

Discussion

To determine the best solvent for CO_2 capture, both the overall solubility and the solubility difference between the I and N phases, Δx, should be examined. To compare the solubility of CO_2 for the six different LC solvents, P,x-diagrams at a constant temperature of 330 K are created and shown in Figure 17. The solubility of CO_2 is larger in PCH3, PCH7, and the mixture of PCH3 + PCH7 than in the other materials. If we examine the different materials further, it shows

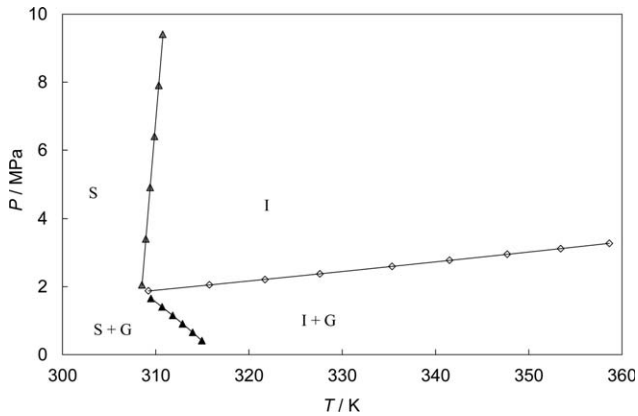

Figure 12. P,T-diagram of the binary mixture 4-propyl-4′-cyclohexylbenzonitrile + CO_2 at x_{CO2} = 0.214. S denotes the solid phase, N the nematic phase, I the isotropic phase and G the gas phase.

◆ S + I ↔ I; ◇ I + G ↔ I; ▲ S + I + G;. The solid lines are first or second order polynomial fits through the data points.

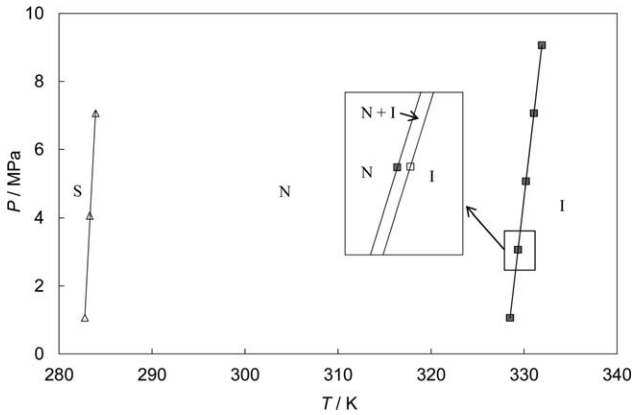

Figure 13. *P,T*-diagram of the binary mixture 4-propyl-4′-cyclohexylbenzonitrile + 4-heptyl-4′-cyclohexylbenzonitrile, $x_{PCH7}/x_{PCH3} = 3.00$.

S denotes the solid phase, N the nematic phase and I the isotropic phase. △ S + N ↔ N; ■ N ↔ N + I; □ N + I ↔ I. The lines are linear fits of the data points.

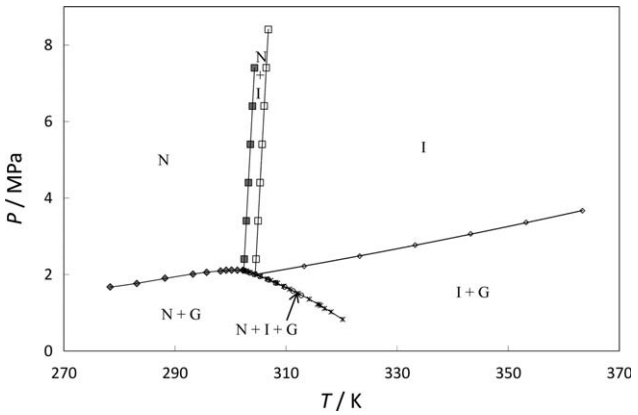

Figure 15. *P,T*-diagram of the ternary mixture 4-propyl-4′-cyclohexylbenzonitrile + 4-heptyl-4′-cyclohexylbenzonitrile + CO_2, $x_{PCH7}/x_{PCH3} = 2.99$, $x_{CO2} = 0.244$.

N denotes the nematic phase, I the isotropic phase and G the gas phase. ■ N + I ↔ N; □ N + I ↔I; ✳ I + G ↔ N + I + G; ○ N + G ↔ N + I + G; ◆ N + G ↔N; ◇ I + G ↔ I. The solid lines are fits through the data points.

that the mixtures of 5OCB + CO_2, 7OCB + CO_2 and 5OCB + 7OCB + CO_2 have an almost comparable CO_2 solubility, whereas for PCH3 + CO_2, PCH7 + CO_2, and PCH3 + PCH7 + CO_2 it seems that mixing the two liquid crystals leads to a lower I + G ↔ I equilibrium pressure, and thus to a higher CO_2 solubility. This may be explained by the difference in size between PCH3 and PCH7, which is larger than that of 5OCB and 7OCB. Based on this size difference, the mixture of 5OCB and 7OCB is more ideal than of PCH3 and PCH7.

The proposed CO_2 capture process is a process at constant pressure.[3] *T,x*-diagrams at constant pressure show the total amount of CO_2 which can be removed during one absorption-desorption cycle. In next paragraphs the *T,x*-diagram of the binary mixtures of one liquid crystal with CO_2 are compared with the *T,x*-diagram of its ternary mixture. The pressure of the *T,x*-diagrams was chosen such that the N + I + G equilibrium was above 300 K. The reason for this is that such a process does not need cryogenic cooling. Therefore, the pressure of *T,x*-diagram of the ternary mixture 5OCB + 7OCB + CO_2 is $P = 4.00$ MPa, and for the ternary mixture PCH3 + PCH7 + CO_2, $P = 2.00$ MPa.

The data used for creating the *T,x*-diagram of 5OCB + CO_2 were taken from our previous publication.[5] In Figure 18, the *T,x*-diagram is shown. Absent in this figure is the N + I + G equilibrium, because the three-phase equilibrium S_2 + N + I is more stable than the N + I + G equilibrium. As explained in the introduction, the presence of the N + I + G equilibrium is essential for the CO_2 capture process. Therefore, at this pressure 5OCB is not suitable for CO_2 capture.

If we examine the *T,x*-diagram of the ternary mixture of 5OCB + 7OCB + CO_2, shown in Figure 19, at the same pressure as the binary mixture of 5OCB + CO_2, it is clear that this ternary mixture at the aforementioned conditions is

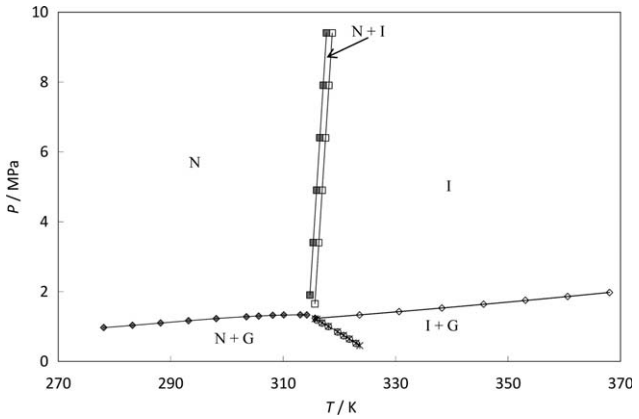

Figure 14. *P,T*-diagram of the ternary mixture 4-propyl-4′-cyclohexylbenzonitrile + 4-heptyl-4′-cyclohexylbenzonitrile + CO_2, $x_{PCH7}/x_{PCH3} = 2.93$, $x_{CO2} = 0.138$.

N denotes the nematic phase, I the isotropic phase and G the gas phase. ■ N + I ↔ N; □ N + I ↔I; ✳ I + G ↔ N + I + G; ○ N + G ↔ N + I + G; ◆ N + G ↔N; ◇ I + G ↔ I. The solid lines are fits through the data points.

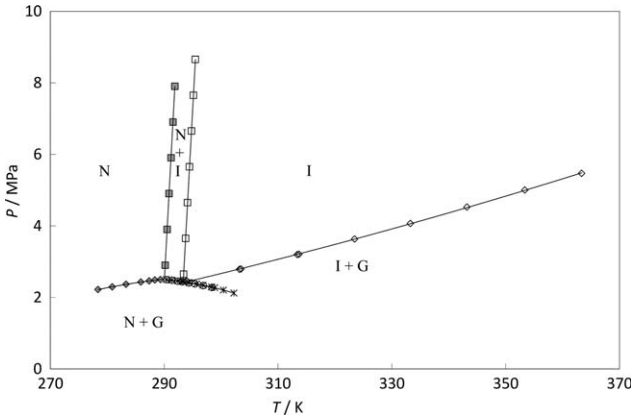

Figure 16. *P,T*-diagram of the ternary mixture 4-propyl-4′-cyclohexylbenzonitrile + 4-heptyl-4′-cyclohexylbenzonitrile + CO_2, $x_{PCH7}/x_{PCH3} = 3.02$, $x_{CO2} = 0.332$.

N denotes the nematic phase, I the isotropic phase and G the gas phase. ■ N + I ↔ N; □ N + I ↔I; ✳ I + G ↔ N + I + G; ○ N + G ↔ N + I + G; ◆ N + G ↔N; ◇ I + G ↔ I. The solid lines are fits through the data points.

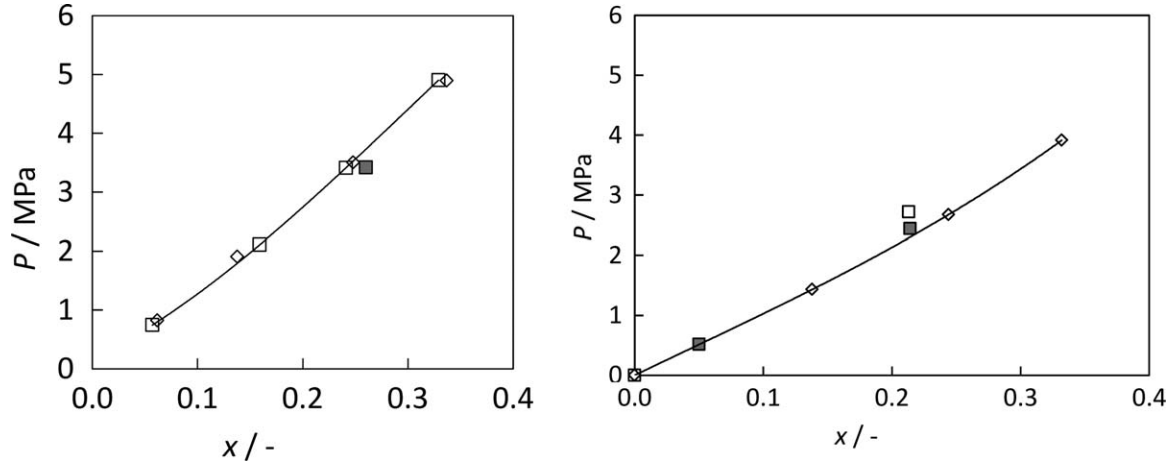

Figure 17. ***Left: P,x*-diagram of the I + G ↔ I equilibria of 5OCB, 7OCB and CO_2. ■ 7OCB + CO_2; □ 5OCB + CO_2; ◇ 5OCB + 7OCB + CO2.** ***Right: P,x*-diagram of the I + G ↔ I equilibria of PCH3, PCH7 and CO_2. ■ PCH7 + CO_2; □ PCH3 + CO_2; ◇ PCH3 + PCH7 + CO2.**

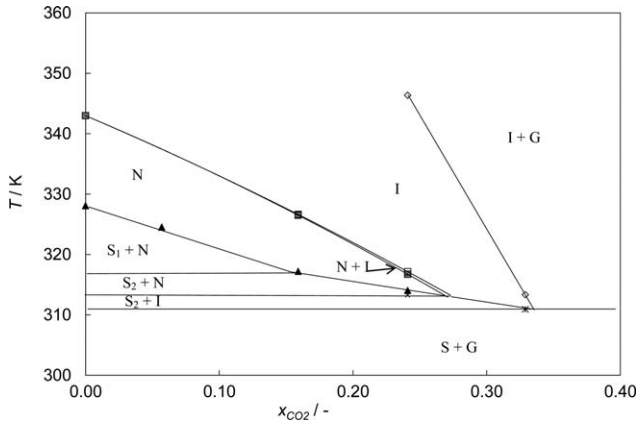

Figure 18. ***T,x*-diagram of the binary mixture 4,4-pentyloxy cyanobiphenyl + CO_2 at $P = 4.00$ MPa, S_1 and S_2 denote the solid phases, N denotes the nematic phase, I the isotropic phase and G the gas phase.**

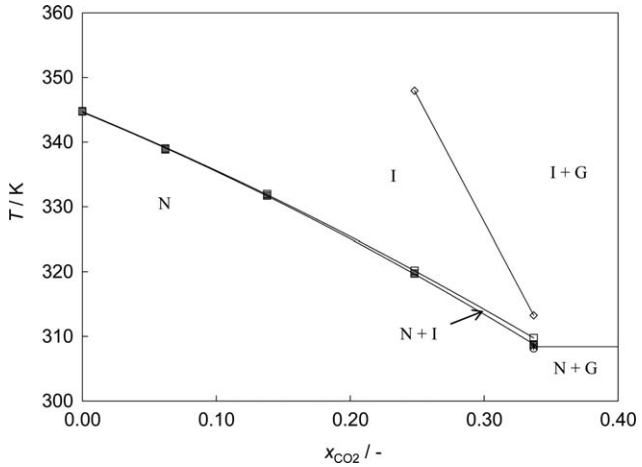

Figure 19. ***T,x*-diagram of the ternary mixture 4,4-heptyloxy cyanobiphenyl + 4,4-pentyloxy cyanobiphenyl + CO_2, $x_{5OCB}/x_{7OCB} = 1.77 \pm 0.02$ at $P = 4.00$ MPa. N denotes the nematic phase, I the isotropic phase and G the gas phase.**

suitable for CO_2 capture, as the three-phase curve N + I + G is present. The main difference between Figures 18 and 19 is the phase transition temperature of the solid to nematic phase transition. In Figure 18, the solid to nematic phase transition is clearly visible within the range of the *T,x*-diagram, but in Figure 19 it is not. For the binary mixture of 5OCB + 7OCB measured in this study, with $x_{5OCB}/x_{7OCB} = 1.77$, the solid to nematic phase transition is approximately 300 K, whereas the phase transition temperature of pure 5OCB and pure 7OCB are 325 and 327 K, respectively. The S ↔ N phase equilibria of the binary system 5OCB and 7OCB ends in a eutectic point.[10] This behavior is analogous to melting point depression. The N ↔ I phase transition behaves analogous to a zeotropic liquid vapor equilibrium. The liquid crystals are in both the isotropic and the nematic phase miscible at all compositions. For molecules that are very similar in structure, like the mixture of 5OCB and 7OCB, the temperature of the N ↔ I phase transition can be approached by a linear relation between the phase transition temperatures of the two pure liquid crystals. Combining this fact with the "melting point depression," this leads to a larger temperature range of the nematic phase of the binary mixture of two liquid crystals compared to the unary

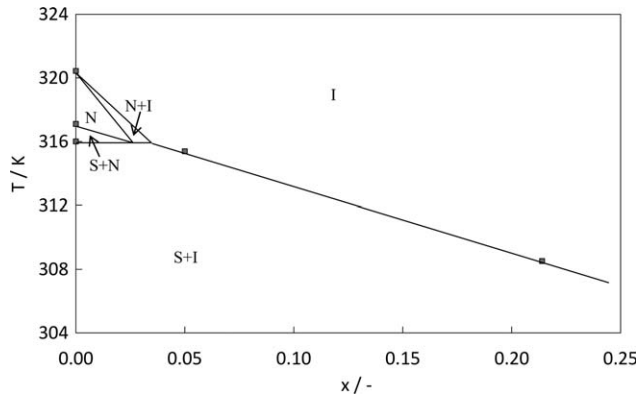

Figure 20. Schematic *T,x*-diagram of the binary mixture 4-propyl-4′-cyclohexylbenzonitrile + CO_2, at $P = 2.00$ MPa. S denotes the solid phase, N the nematic phase I the isotropic phase and G the gas phase.

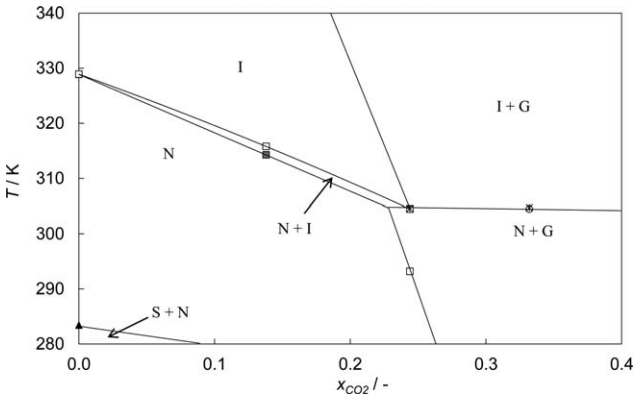

Figure 21. *T,x*-diagram of the ternary mixture 4-propyl-4′-cyclohexylbenzonitrile + 4-heptyl-4′-cyclohexylbenzonitrile + CO_2, $x_{PCH7}/x_{PCH3} = 3.0 \pm 0.1$ at $P = 2.00$ MPa, S denotes the solid phase, N the nematic phase, I the isotropic phase and G the gas phase.

systems. This increases the amount of CO_2 which can be desorbed during one cycle, as the two-phase area N + I becomes wider when more CO_2 is added. Still the maximum amount of CO_2 absorbed and desorbed is small, only 0.008 mol CO_2/mol.

The schematic *T,x*-diagram of PCH3 + CO_2 at $P = 2.00$ MPa is given in Figure 20. The basic idea of this *T,x*-diagram is comparable with the *T,x*-diagram of 5OCB + CO_2 shown in Figure 18. The main difference is that this binary mixture has a smaller temperature range of the nematic phase, leading to an even lower quadruple point concentration, only 0.050 mole CO_2/mole. At a CO_2 concentration at less than 0.050 mole CO_2/mole the N + I + G equilibrium is stable, at higher concentration the three-phase equilibria involving the solid phase are more stable, leading to the conclusion that above this concentration PCH3 cannot be used for CO_2 capture.

The *T,x*-diagram of the ternary mixture of PCH3 + PCH7 + CO_2 at $P = 2.00$ MPa is shown in Figure 21. At this pressure a stable N + I + G equilibrium is measured. Moreover, the solid phase does not interfere with the N + I + G equilibrium. If one would use this mixture for a CO_2 capture process, the maximum amount of CO_2 released during one desorption cycle is 0.013 mol CO_2/mol. Compared with the *T,x*-diagrams of the mixture 5OCB + CO2 and the ternary mixture of 5OCB + 7OCB + CO_2, as given in Figure 18 and Figure 19 respectively, the *T,x*-diagram of the ternary mixture PCH3 + PCH7 + CO_2 and the *P,x*-diagram shown in Figure 21 lead to the conclusion that PCH3 + PCH7 is most beneficial for CO_2 capture. First of all, the Δx value is largest of all the liquid crystals measured. This is in agreement with the phase transition enthalpy of the N ↔ I phase transition: this enthalpy value is significantly higher for the PCH-type molecules. Moreover, the solubility of CO_2 in this material is higher than any of the other mixtures. Second, the mixture is liquid at room temperature, making the handling more easily than the other mixtures.

Conclusions

The combination of PCH3 and PCH7 is in this case more promising for CO_2 capture than 5OCB and 7OCB because the phase transition enthalpy of the first mentioned system is higher. Also, the CO_2 solubility in PCH3 and PCH7 is lower than for 5OCB + CO_2 and 7OCB + CO_2. The drawback of using liquid crystals for CO_2 capture is the low phase transition enthalpy of the N ↔ I phase transition. This leads to a small difference of absorbed CO_2 in the two phases, namely $\Delta x = 0.013$. This Δx value is probably too small to realize a feasible process for CO_2 capture. However, without a proper process design this is difficult to judge.

S + I ↔ I; N + I ↔ N; N + I ↔I; S + N + I; N + I + G; I + G ↔ I. The solid lines are first and second order polynomial fits through the data points.

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