Solubility of the Nematic Liquid Crystal E7 in Supercritical Carbon Dioxide

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The solubility of E7, a nematic liquid crystal mixture, in supercritical carbon dioxide ($scCO_2$) was measured using a static analytical method at (313.15, 323.15, and 333.15) K and at pressures up to 19 MPa. Samples from the CO_2-rich phase were analyzed using a simple but selective reversed-phase high performance liquid chromatographic method. The results indicate unambiguously that $scCO_2$ can fractionate the mixture toward the E7 components at relative low pressures. Due to the lack of thermodynamic data, the solubility data were correlated using the equation of Chrastil. The results obtained are important for the design and development of polymer-dispersed liquid crystals using supercritical fluid technology.

Introduction

The present work is part of a project aimed at the development of polymer-dispersed liquid crystals (PDLC) using supercritical (sc) fluid technology. The application of liquid crystals in display devices has gained increasing interest in the past few years. Their unusual electrooptic properties have resulted in a variety of potential applications ranging from flat panel displays to optical switches for telecommunications.[1−4] Among these materials, special interest has been dedicated to PDLCs (i.e., low molecular mass liquid crystals randomly dispersed as microdroplets in a polymer film).[5] PDLC films typically use nematic liquid crystals that exhibit positive dielectric anisotropy.[6] The liquid crystal E7, a multicomponent nematic mixture, has been widely used due to its high optical anisotropy and large temperature range where it maintains anisotropic characteristics.[7,8] Its nematic to isotropic transition occurs at 58 °C. At room temperature it still exhibits a nematic phase, which easily supercools upon cooling, avoiding crystallization. Thus, its liquid crystalline properties are extended down to the glass transition at −62 °C.[5,9]

Supercritical fluids, especially $scCO_2$, have been identified as prime candidates to develop alternative clean processes. CO_2 is readily available, environmentally acceptable, and no flammable; it has a critical temperature (31 °C) close to ambient temperature and accessible critical pressure (7.4 MPa)[10] and leaves no toxic residues.[11] $scCO_2$ has excellent plasticizing properties and can easily penetrate into polymer films and extract or precipitate substances in those matrixes, simply by manipulating pressure.[12] New materials can be prepared by the impregnation of certain substances into polymeric materials using $scCO_2$ taking advantage of the high diffusivity, low surface tension, and easy recovery of the solvent.[13] To design these processes and especially for scale-up calculations from laboratory experiments, it is important to have a detailed knowledge of phase behavior of the systems involved.

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We have recently reported a new approach for analyzing the liquid crystal E7 by HPLC to quantify its solubility in $scCO_2$.[14] In the present work, the solubility of the liquid crystal E7 in $scCO_2$ was measured up to 19 MPa at (313.15, 323.15, and 323.15) K. The relative mass fraction of each E7 component in the CO_2-rich phase was determined to evaluate the ability of CO_2 to fractionate the liquid crystal (E7) toward its components. Solubility data results were correlated by the Chrastil equation.[15] The Chrastil method does not require the knowledge of thermodynamic parameters as required in the equation of state models. These parameters are not available in the literature for any of the E7 components.[16−18]

Experimental Section

Materials. HPLC Millipore water, HPLC grade methanol from Sigma-Aldrich GmbH (Germany), HPLC grade acetonitrile from Riedel-de-Haën AG (Germany), and 99.998 % pure carbon dioxide from Ar Líquido (Portugal) were used. E7 is the nematic liquid crystal commercially available from Merck, the liquid crystalline mixture (LCM) solubilized in the CO_2 rich-phase is referred as (1) hereafter. Its pure components, 5CB, 4-cyano-4′-*n*-pentyl-1,1′-biphenyl (2); 7CB, 4-cyano-4′-*n*-heptyl-1,1′-biphenyl (3); 8OCB, 4-cyano-4′-*n*-octyloxy-1,1′-biphenyl (4); and 5CT, 4-cyano-4”-*n*-pentyl-1,1′,1″-terphenyl (5), were kindly supplied by Merck KGaA (Darmstadt, Germany). Figure 1 shows the structure and the composition of the four components of this liquid crystal. The mass fraction of commercial E7 according to our previous work is as follows: (50.5 ± 0.2) % of (2); (24.7 ± 0.1) % of (3); (16.8 ± 0.2) % of (4); and (8.0 ± 0.1) % of (5).[14] These values are in agreement with the nominal values indicated by Merck (51 %, 25 %, 16 %, and 8 % respectively).[9,19]

Experimental Procedure. The vapor−liquid equilibrium measurements were undertaken in a high-pressure apparatus, which operates according to the static analytical method already described elsewhere.[20−22] The apparatus was built around a sapphire tube cell, with an internal volume of 35 mL, which allowed full observation of the inside. A new sealing system for this cell was recently improved.[23]

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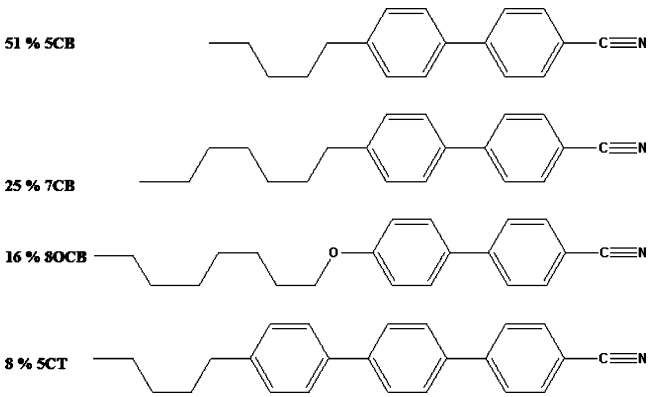

Figure 1. Structure and composition of the four components of the multicomponent nematic mixture E7.

In a typical experiment, the cell was loaded with a known amount of the liquid crystal E7 and then purged with a low CO_2 flow to degas. The CO_2 was introduced by means of a HIP manual pressure generator. Pressure is measured by a pressure transducer Newport M3 (Heize HPO and digital panel INFP100 FS) with scale between (0 and 25) MPa and resolution of 1 kPa. Temperature is measured with a platinum-resistance T (5616 RTD) in contact with the cell, connected to a temperature controller (2100), both from Hart Scientific. The typical temperature stability during experiments is ± 0.01 K at (313 and 323) K and ± 0.02 K at 333 K. After the desired temperature had been reached, the pressure was adjusted above or below the desired equilibrium value, depending on how equilibration changes pressure. By stirring the mixture, the time for equilibration of the phases was reduced, the pressure reaches a plateau, and the equilibration is continued for at least 45 min. Once the equilibrium was achieved, one sample is withdrawn from the vapor phase through a six-port HPLC switching valve, located on the top of the cell, into the sample loop of 500 μL. After sampling, a small pressure drop occurs, typically from 0.06 MPa at 4.5 MPa to 0.6 MPa at 19 MPa. Each sample was expanded into a calibrated volume. The amount of carbon dioxide in the sample was obtained by expansion into a large, well-calibrated volume, followed by measurement of pressure and temperature as a low-pressure gas. The liquid crystal contained in the sample precipitates in a vial. The sampling loop and lines were washed with acetonitrile and with a CO_2 low flow. The solution collected in the vial was then analyzed.

Analytical Method. The collected samples were diluted in acetonitrile to a convenient volume. To determine the amount of the liquid crystalline mixture (LCM) and its components, the resulting solutions were analyzed by HPLC (Merck L-7100) equipped with an UV detector (Merck L-7400) and computer interface (Merck D-7000), according to a previously developed analytical technique.[14] Detection of the E7 compounds was done at 277 nm. Calibration was obtained by using E7 components standard samples with concentrations between $(5.0 \pm 0.6) \times 10^{-6}$ M and $(1.00 \pm 0.09) \times 10^{-4}$ M.

Results and Discussion

In this work, the solubility of E7 components in $scCO_2$ was determined at (313.15, 323.15, and 333.15) K. The solubility of the four E7 components [5CB (2), 7CB (3), 8OCB (4), 5CT (5)] expressed in terms of solute mass per CO_2 volume are given in Table 1. Figure 2 presents the overall solubility of the LCM in CO_2 as a function of pressure and temperature. The effect of pressure on the total solubility follows the expected trend as the solvent capacity increases with pressure at constant temperature while the solubility decreases with increasing temperature. 5CB and 7CB are clearly more soluble in $scCO_2$ than 8OCB and 5CT in the studied pressure range.

The distribution factors (K_i) of the four E7 components (on a CO_2-free mass basis) calculated as the ratios of solute content in the extracted LCM to feed composition are plotted in Figure 3 as a function of pressure for 323.15 K. From this plot it is clear that CO_2 is able to fractionate E7 components according to their molecular masses. 5CB, the

Table 1. Solubilities of Liquid Crystalline Mixture Components[a] 5CB (2), 7CB(3), 8OCB (4), and 5CT (5) in $scCO_2$

p / MPa	ρCO_2[b] / g·L^{-1}	S_2 / g·L^{-1}	S_3 / g·L^{-1}	S_4 / g·L^{-1}	S_5 / g·L^{-1}
		$T = 313.15$ K			
9.0	494.0	0.113	0.025	0.001	0.000
9.8	615.3	0.535	0.137	0.009	0.006
11.0	684.3	1.862	0.635	0.182	0.025
12.1	721.4	2.647	0.929	0.283	0.049
13.0	744.1	3.472	1.320	0.473	0.093
13.6	756.0	5.069	1.853	0.638	0.141
16.4	800.5	7.494	2.912	1.041	0.175
17.6	815.5	8.908	3.479	1.272	0.215
		$T = 323.15$ K			
9.0	284.1	0.004	0.003	0.000	0.000
9.9	369.5	0.017	0.005	0.000	0.000
10.7	469.8	0.095	0.025	0.002	0.000
11.6	558.2	0.490	0.144	0.034	0.001
12.7	623.4	1.176	0.388	0.114	0.001
13.8	666.2	2.019	0.690	0.212	0.008
14.5	687.6	2.902	1.047	0.377	0.068
15.6	714.3	3.466	1.296	0.502	0.095
17.7	752.3	4.760	1.816	0.695	0.110
18.6	766.7	5.456	2.169	0.864	0.141
		$T = 333.15$ K			
8.8	235.3	0.012	0.007	0.002	0.000
9.8	288.5	0.016	0.008	0.002	0.001
10.7	348.2	0.025	0.008	0.001	0.003
11.7	424.9	0.084	0.023	0.003	0.003
12.6	488.3	0.207	0.058	0.011	0.004
13.8	558.3	0.618	0.189	0.046	0.014
14.5	591.3	0.915	0.297	0.086	0.011
15.4	623.1	1.254	0.426	0.140	0.021
16.2	649.4	2.220	0.796	0.293	0.048
17.4	678.4	2.828	1.046	0.392	0.077
18.3	696.3	3.307	1.240	0.475	0.080

[a] 5CB, 4-cyano-4′-*n*-pentyl-1,1′-biphenyl; 7CB, 4-cyano-4′-*n*-heptyl-1,1′-biphenyl; 8OCB, 4-cyano-4′-*n*-octyloxy-1,1′-biphenyl; 5CT, 4-cyano-4″-*n*-pentyl-1,1′,1″-terphenyl. [b] CO_2 densities were calculated using Allprops.[24]

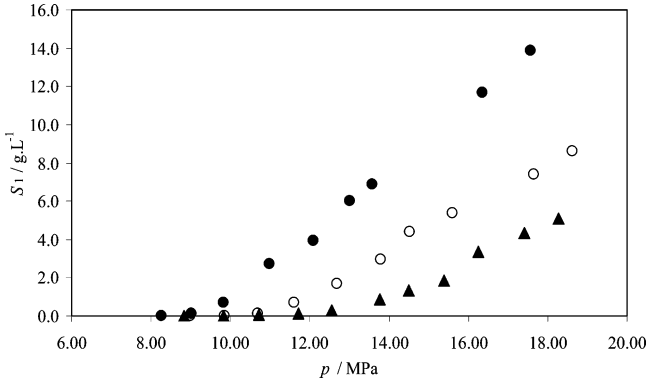

Figure 2. Solubility of liquid crystalline mixture (1) in $scCO_2$ as a function of pressure at ●, 313.15 K; ○, 323.15 K; and ▲, 333.15 K.

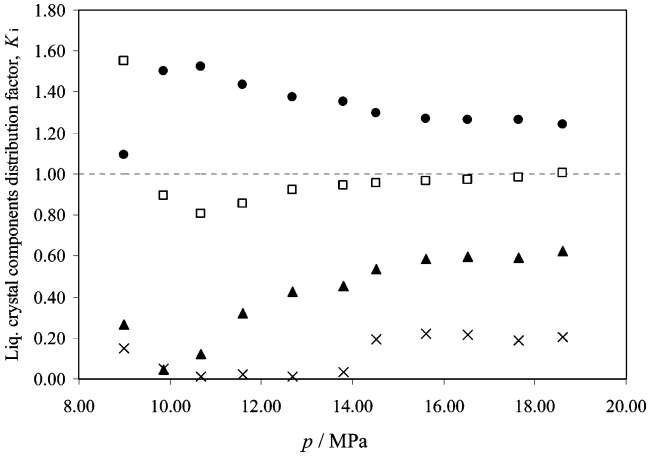

Figure 3. Distribution factors of the liquid crystal components (ratio of each component content in the extracted LCM to feed composition) in $scCO_2$ as a function of pressure at 323.15 K: ●, 5CB (2); □, 7CB (3); ▲, 8OCB (4); and ×, 5CT (5).

lowest molecular mass compound, was concentrated in the CO_2-rich phase as indicated by a distribution factor higher than 1. The distribution factors for 7CB are just less than or equal to 1 depending on the pressure; those for the other two components are smaller as expected due to their higher molecular masses. At around 10 MPa, we observe that the fractionation is more pronounced. When the pressure is increased, the fractionation decreases, and the liquid crystalline mixture extracted by $scCO_2$ tends to a constant mass fraction: (64.6 ± 0.5) % 5CB; (24.6 ± 0.5) % 7CB; (9.2 ± 0.2) % 8OCB; and (1.6 ± 0.2) % 5CT. Comparing with the composition of parent E7 presented earlier in this work, the LCM extracted by $scCO_2$ is richer in 5CB, maintains the relative composition of 7CB, and is poorer in 8OCB and 5CT.

Correlation of Experimental Solubility Data. Because of the lack of information on the thermophysical data of substances, the correlation of solubility data is, in most cases, done using simple empirical correlations such as density-based equations. These empirical models are based on simple error minimization using least-squares methods, and for the majority of them, there is no need to estimate and use thermophysical properties. In this paper the method of Chrastil was used based on the mass-action law by Gonzáles et al.[15] The solubility data of the multicomponent nematic mixture in $scCO_2$ was fitted to the equation of Chrastil derived from a quasi-chemical approach for solubility (S/g·L^{-1}) as a function of the carbon dioxide density (ρ/g·L^{-1}), as shown in eq 1:

$$\ln(S/\text{g·L}^{-1}) = k \ln(\rho/\text{g·L}^{-1}) + a/[T/\text{K}] + b \qquad (1)$$

This equation postulates a linear behavior between the logarithm of the solute solubility and the logarithm of the solvent density. It involves an association reaction of the solute with solvent molecules. The parameter k is the association number, characteristic constant for a given solute−solvent system, and $a = \Delta H/R$, where ΔH is the sum of the solute vaporization enthalpy with the enthalpy of solvation. Parameter b is dependent on the molecular weights of solvent and solutes. For each one of the E7 components, the coefficients k, a, and b were obtained. These coefficients are listed in Table 2 along with ΔH calculated from a. Plots of ln S versus ln ρ can be seen in Figure 4 along with the best-fit line using the same equation. 8OCB and 5CT are bigger molecules than 5CB

Table 2. Optimized Chrastil Solubility Parameters (k) and Calculated Enthalpies for E7 Components in $scCO_2$

compd	M / g·mol^{-1}	k	$a \times 10^{-3}$	b	AARD %[a]	ΔH / kJ·mol^{-1}
5CB	249.4	7.5 ± 0.2	−2.2 ± 0.7	−41 ± 2	17.6	−18
7CB	277.4	9.5 ± 0.3	−4.7 ± 0.6	−47 ± 2	11.8	−39
8OCB	307.4	12.0 ± 0.3	−6.4± 0.7	−60 ± 2	17.7	−53
5CT	325.0	16.0 ± 1.0	−7.0 ± 1.0	−84 ± 6	21.6	−56

[a] AARD = $100/n\sum_1^n |(S_{cal} - S_{exp})/S_{exp}|$.

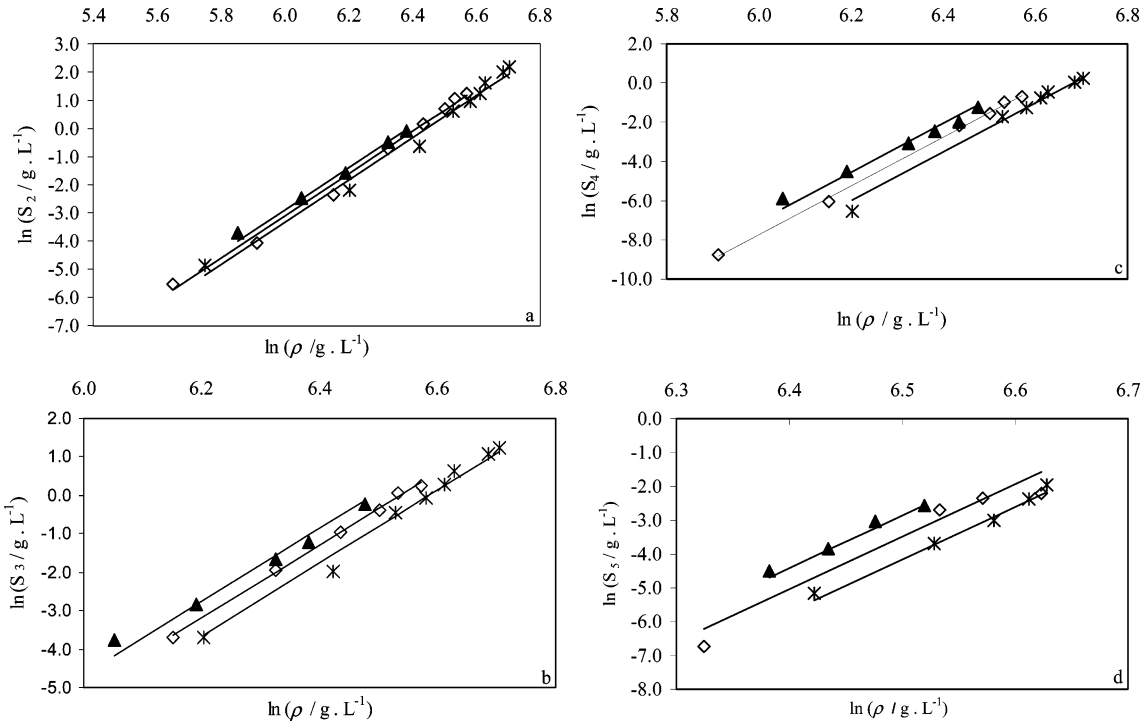

Figure 4. Logarithmic relationship between the solubility of each E7 component and the density of CO_2 for (a) 5CB (2); (b) 7CB (3); (c) 8OCB (4); and (d) 5CT (5), along with the best-fit line given by eq 1 at ▲, 313.15 K; ◇, 323.15 K; and ∗, 333.15 K.

and 7CB. Their molecular weights are included in Table 2. The values of k are roughly proportional to the molar masses of the four forms, a reasonable result for association numbers for chemically similar solutes.

The Chrastil model was applied independently for each E7 component. Although the liquid crystal under study is a multicomponent system, experimental data were well-correlated by fitting the solubility of each component with carbon dioxide density. This result was expected since the solution is diluted in the vapor phase. Thus, we can consider that each molecule is mainly surrounded by carbon dioxide molecules. This is validated since experimental data could be satisfactorily correlated by the Chrastil model with an average absolute relative deviation (AARD) between 11 % and 22 %, as can be seen in Table 2. The Chrastil model has been adapted by other authors when a cosolvent is used. However in these cases the cosolvent contribution cannot be neglected in the solvent density since molar percentages of (2 to 10) % are usually used.

Conclusions

The equilibrium solubilities of E7 and its components in $scCO_2$ were measured using a static analytical method at (313.15, 323.15, and 333.15) K and at pressures up to 19 MPa. CO_2 is able to fractionate E7 components according to their molecular masses. When the pressure is increased, the fractionation decreases, and the liquid crystalline mixture extracted by $scCO_2$ tends to a constant composition richer in 5CB than the parent E7. Experimental data were satisfactorily correlated using the Chrastil model for all the E7 components. The results obtained are important for the design and development of polymer-dispersed liquid crystals using supercritical fluid technology.

Literature Cited

(1) Schadt, M. Liquid crystal materials and liquid crystal displays. *Annu. Rev. Mater. Sci.* **1997**, *27*, 305−379.

(2) Doane, J. W. *Liquid Crystals—Application and Uses*, Vol. 1; World Scientific: Singapore, 1990.

(3) Khoo, I. C.; Wu, S. T. *Optics and Nonlinear Optics of Liquid Crystals*; World Scientific: Singapore, 1993.

(4) Drzaic, P. S., *Liquid Crystal Dispersions*; World Scientific: Singapore, 1995.

(5) Viciosa, M. T.; Nunes, A. M.; Fernandes, A.; Almeida, P. L.; Godinho, M. H.; Dionísio, M. D. Dilelectric studies of the nematic mixture E7 on a hydroxypropylcellulose substrate. *Liq. Cryst.* **2002**, *29*, 429−441.

(6) McKenna, L.; Miller, L. S.; Peterson, I. R. Polymer dispersed liquid crystal films for modulating infra-red radiation. *Polymer* **2004**, *45*, 6977−6984.

(7) Wu, S. T.; Yang, D. K. *Reflective Liquid Crystal Displays*; Wiley: New York, 2001.

(8) Godinho, M. H.; Figueirinhas, J. L.; Martins, A. F. Novel PDLC type display based on cellulose derivatives. *Liq. Cryst.* **1996**, *20*, 373−376.

(9) Maschke, U.; Benmouna, M.; Coqueret, X. Electro-optical properties of polymer-dispersed liquid crystals. *Macromol. Rapid Commun.* **2002**, *23*, 159−170.

(10) International Thermodynamic Tables of the Fluid State Carbon Dioxide. In *IUPAC*, Vol. 3; Angus, S., Amstrong, B., Reuck, K. M., Eds.; Pergamon Press: New York, 1976.

(11) Tomasko, D. L.; Li, H.; Liu, D.; Han, X.; Wingert, M. J.; Lee, L. J.; Koelling, K. W. A review of CO_2 applications in the processing of polymers. *Ind. Eng. Chem. Res.* **2004**, *42*, 6431−6456.

(12) Woods, H. M.; Silva, M. M. C. G.; Nouvel, C.; Shakesheff, K. M.; Howdle, S. M. Materials processing in supercritical carbon dioxide: surfactants, polymers and biomaterials: A review, *J. Mater. Chem.* **2004**, *14*, 1663−1678.

(13) Kikic, I.; Vecchione, F. Supercritical impregnation of polymers: a review current opinion.*Solid State Mater. Sci.* **2003**, *7*, 399−405.

(14) Brás, A. R. E.; Henriques, S.; Casimiro, T.; Aguiar-Ricardo, A.; Sotomayor, J.; Caldeira, J.; Santos, C.; Dionísio, M. D. Characterization of a nematic mixture by reversed-phase HPLC and UV spectroscopy: application to phase-behavior studies in liquid crystal-CO_2 systems. *Electron. Liq. Cryst. Commun.* **2005**, March, 28.

(15) Gonzáles, J. C.; Vieytes, M. R.; Botana, A. M.; Vieites, J. M.; Botana, L. M. Modified mass action law-based model to correlate the solubility of solids and liquids in entrained supercritical carbon dioxide. *J. Chromatogr. A* **2001**, *910*, 119−125.

(16) Chrastil, J. Solubility of solids and liquids in supercritical gases. *J. Phys. Chem.* **1982**, *86*, 3016−3021.

(17) Matias, A. A.; Nunes, A. V. M.; Casimiro, T.; Duarte, C. M. M. Solubility of coenzyme Q10 in supercritical carbon dioxide, *J. Supercrit. Fluids* **2004**, *28*, 201−206.

(18) Duarte, A. R. C.; Coimbra, P.; de Sousa, H. C.; Duarte, C. M. M. Solubility of acetazolamide in supercritical carbon dioxide in the presence of ethanol as a cosolvent. *J. Chem. Eng. Data* **2005**, *50*, 216−220.

(19) Information from Merck KGa, Darmstadt, Germany.

(20) Gourgouillon, D.; Nunes da Ponte, M. High-pressure phase equilibria for poly(ethylene glycol)s + CO_2: experimental results and modeling, *Phys. Chem. Chem. Phys.* **1999**, *1*, 5369−5375.

(21) Casimiro, T.; Montilla, F.; Garcia, S.; Avilés, T.; Shariati, A.; Raeissi, S.; Peters, C. J.; Nunes da Ponte, M.; Aguiar-Ricardo, A. Phase behaviour of the catalyst dicarbonyl (η^5-cyclopentadienyl)-cobalt in carbon dioxide. *J. Supercrit. Fluids* **2004**, *31*, 1−8.

(22) Casimiro, T.; Shariati, A.; Peters, C. J.; Nunes da Ponte, M.; Aguiar-Ricardo, A. Phase behavior studies of a perfluoropolyether in high-pressure carbon dioxide. *Fluid Phase Equilib*. **2004**, *224*, 257−261.

(23) Duarte, C. M. M.; Crew, M.; Casimiro, T.; Aguiar-Ricardo, A.; Nunes da Ponte, M. Phase equilibrium for capsaicin + water + ethanol + supercritical carbon dioxide. *J. Supercrit. Fluids* **2002**, *22*, 87−92.

(24) *Allprops—Thermodynamic Properties of Fluids*; Program from C.A.T.S.—Center for Applied Thermodynamic Studies, College of Engineering, University of Idaho, 1991.

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