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Characterization of a nematic mixture by reversed-phase HPLC and UV spectroscopy: an application to phase behaviour studies in liquid crystal–CO_2 systems

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In the present work a simple but selective reversed-phase high performance liquid chromatographic method (HPLC) was developed for the analysis of the nematic liquid crystal mixture E7 to determine precisely the composition of the liquid crystal mixture used in PDLC film preparation. Ultraviolet absorption spectrophotometry experiments were carried out to determine the HPLC detection wavelength and to characterize the absorptivity constants of E7 constituents. The technique developed is applied in the case of equilibrium solubility studies for E7 in supercritical carbon dioxide ($scCO_2$). The results indicate unambiguously that $scCO_2$ can fractionate the mixture towards the E7 components. The four single component peaks of the E7 mixture were distinctively separated by this method, which enabled the determination of the solubility of E7 constituents in the $scCO_2$.

1. Introduction

Liquid crystals have been widely studied due to their unique electro-optical properties, which has resulted in a variety of potential applications ranging from flat panel displays to laser beam steering and optical switches for telecommunications [1–4].

Among liquid crystals, a multicomponent nematic mixture, E7, has been widely used [5–7] due to a high optical anisotropy [8] and a large temperature range in which it maintains anisotropic characteristics. Its nematic to isotropic transition occurs at 58°C [9]. 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 $-62°C$ [9, 10]. Most applications rely on the specific nature of electro-optical response functions together with the possibility of controlling the phase behaviour/miscibility and thermophysical properties of these systems.

The present work is part of a research project on the development of polymer-dispersed liquid crystals, PDLCs, using supercritical fluid technology. Supercritical CO_2 $scCO_2$ has excellent plasticizing properties; it can easily penetrate polymer films and extract or precipitate substances in those matrices under the manipulation of pressure [11, 12]. The challenge is to control the morphology of the PDLC, i.e. to generate porosity and to control the pore sizes and surface area in the materials. This can be rationalized by considering the variation in solvent quality as a function of CO_2 density and the resulting influence on the mechanism of phase separation, aggregation and pore formation [13]. In order to design these processes, and especially for scale-up calculations from laboratory experiments, a detailed knowledge of phase behaviour is important [14, 15]. In the present work, a simple analytical technique was developed to determine the solubility of E7 in $scCO_2$ and to identify the partitioning of the E7 components into the CO_2 rich phase as a function of pressure and temperature.

The E7 mixture was studied by both UV absorption spectroscopy and high performance liquid chromatography (HPLC) in order to determine its composition and find a suitable method to quantify its solubility in supercritical CO_2. The UV spectra also provided the respective molar absorptivities (ε) and the choice of adequate wavelength for the HPLC assays. UV and HPLC analytical techniques allowed the identification of each E7 component and the determination of E7 solubility in supercritical CO_2.

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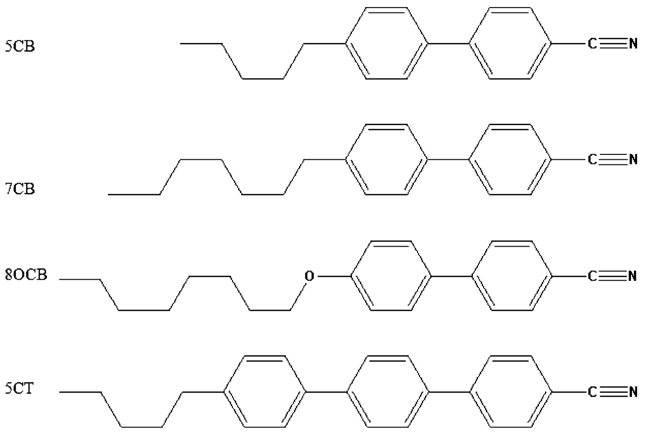

Figure 1. Structures of the components of the nematic liquid crystal mixture E7.

2. Experimental results

2.1. *Reagents*

HPLC Milipore water and methanol CHROMASOLV® for HPLC were supplied by Sigma-Aldrich GmbH (Germany); acetonitrile E CHROMASOLV® for HPLC was from Riedel-de-Haën AG (Germany), and carbon dioxide from Soc. Port. do Ar Líquido, 'ARLÍQUIDO', S.A. (Portugal). The nematic liquid crystal E7 and its pure components (see figure 1), 4-cyano-4′-*n*-pentyl-1,1′-biphenyl (5CB), 4-cyano-4′-*n*-heptyl-1,1′-biphenyl (7CB), 4-cyano-4′-*n*-octyloxy-1,1′-biphenyl (8OCB) and 4-cyano-4″-*n*-pentyl-1,1′,1″-terphenyl (5CT) were kindly supplied by Merck KGaA (Darmstadt, Germany). All the products were used as received.

2.2. *Sample preparation*

E7 liquid crystal is a highly viscous liquid, as are 5CB and 7CB; 8OCB and 5CT are solids at room temperature. Solutions of E7 and its pure components within the concentration range 4.0×10^{-6} and 7.5×10^{-4}M were prepared by weighing and dissolving in HPLC grade acetonitrile. The averaged molar mass of E7, $\overline{M_{\mathrm{M}}}$, was calculated from the weighted sum of the individual molar masses M_{M_i} of the E7 pure components and their molar fractions, x_i, ($\overline{M_{\mathrm{M}}}=\sum_i x_i M_{\mathrm{M}_i}$). The following composition (w/w) was assumed: 51% of 5CB (M_{M}= 249.36 g mol^{-1}), 25% of 7CB (M_{M}=277.41 g mol^{-1}), 16% of 8OCB (M_{M}=307.44 g mol^{-1}) and 8% of 5CT (M_{M}=325.45 g mol^{-1}).

2.3. *UV spectroscopy*

UV spectrophotometry spectra of samples in HPLC grade acetonitrile were recorded with a Shimadzu UV-2501 PC, UV-Vis spectrophotometer at room temperature. The absorption spectra of E7 and its components in acetonitrile solutions were measured between 190 and 400 nm. Figure 2 presents the obtained molar absorptivity (ε) spectra obtained in the range 220–350 nm. The observed absorption band corresponds to a π–π* transition as found in single liquid crystals, with a maximum wavelength located at 281 nm.

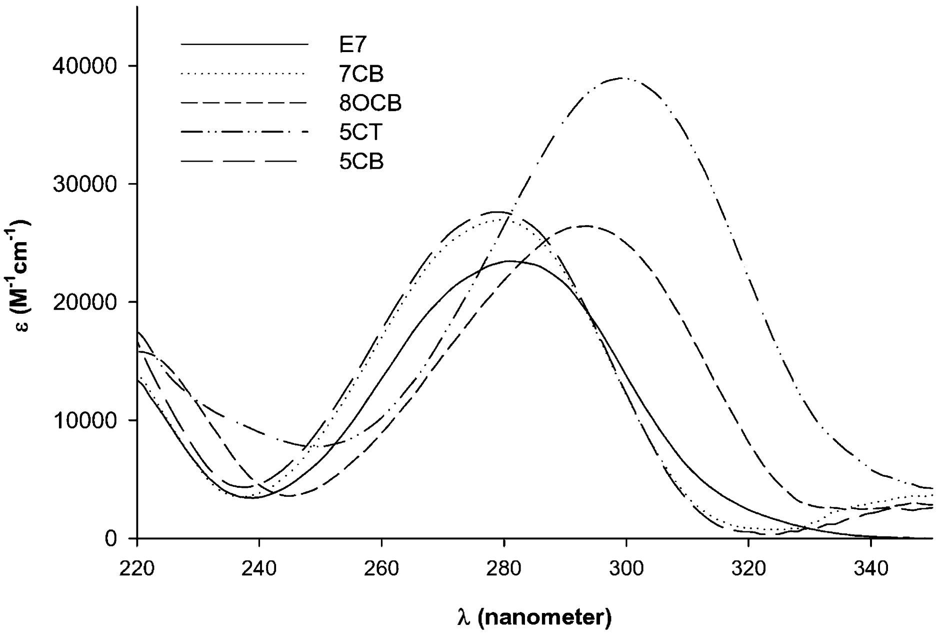

Figure 2. Molar absorptivity spectra of E7 and its components (see legend).

Table 1. Molar absorptivity (ε) values of E7 mixture and its components diluted in acetonitrile.

Component	$\lambda_{\text{máx}}$/nm	ε/$M^{-1}\,cm^{-1}$
E7	281	23.4×10^3
5CB	279	27.6×10^3
7CB	279	26.9×10^3
8OCB	294	26.4×10^3
5CT	299	38.9×10^3

Two additional bands are reported in the literature, both below 220 nm, due to $\sigma \rightarrow \sigma^*$ and a first π–π^* transition [16, 17]. These bands are not shown in the spectrum since they are located in the cut-off region of the solvent.

The 5CB spectrum presents a maximum absorption wavelength located at 279 nm, in agreement with $\lambda_{\max}$ reported in the literature [16], as well as 7CB. The $\lambda_{\max}$ of both 8OCB and 5CT shifts to higher wavelength (see table 1) due to the presence of, respectively, the oxygen atom and the third conjugated phenyl ring. The molar absorptivities (ε) at the maximum wavelength for the E7 mixture and its constituents were also obtained according to Beer's law within the previous concentration range. The obtained values, ε and $\lambda_{\max}$ are listed in table 1.

The UV spectrum presented in figure 2 shows negligible absorptivity of E7 at wavelengths higher than 365 nm, the wavelength of either the pulsed laser beam used in the liquid crystal deposition or the UV light used for curing sealant in liquid crystal devices [18]. Thus, these results in acetonitrile media appear to confirm the reported stability of pure E7 to photodegradation [19], even in solutions stored for periods as long as six months.

2.4. *HPLC analysis*

Chromatographic analysis was carried out using a Merck L-7100 HPLC instrument equipped with an

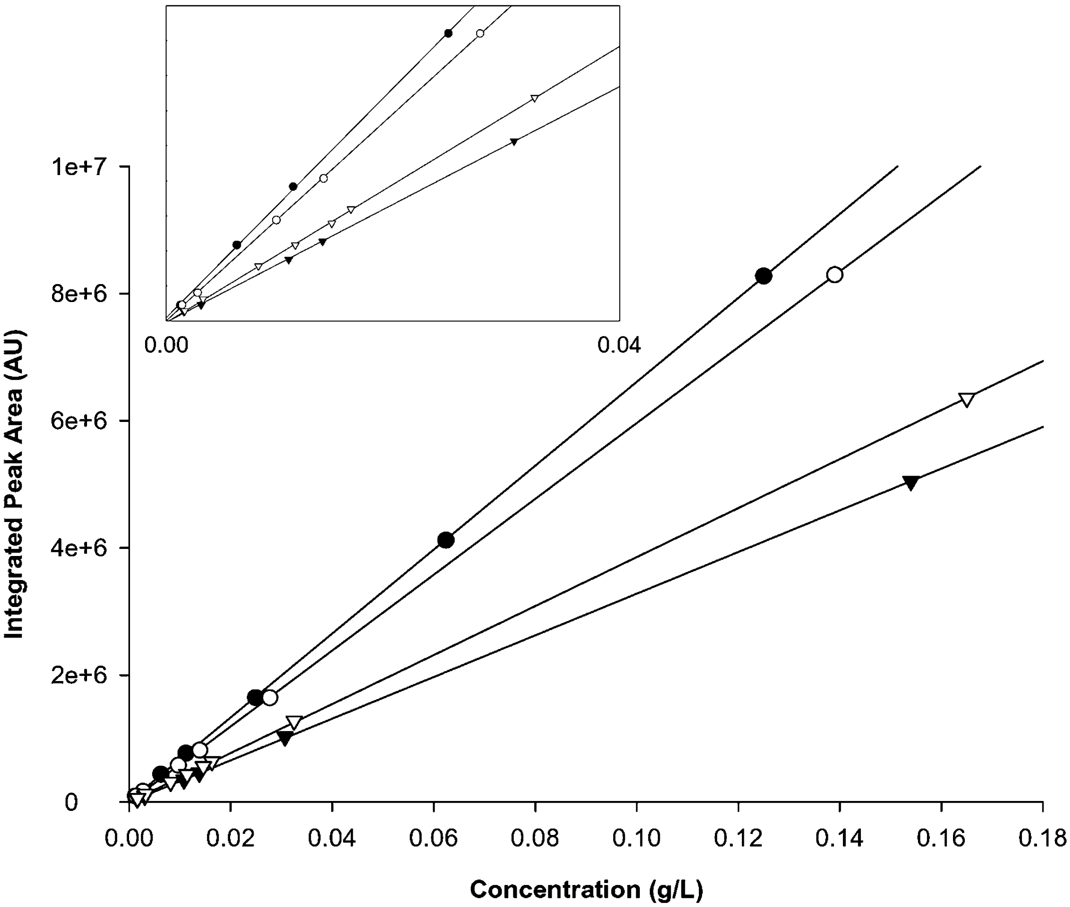

Figure 3. Calibration curves (integrated HPLC peak area vs. concentration) for E7 constituents (5CB—full circles, $y=6.60 \times 10^7x+1.08 \times 10^3$; 7CB—open circles, $y=5.97 \times 10^7x-6.29 \times 10^3$; 8OCB—full triangles, $y=3.28 \times 10^7x+2.57 \times 10^3$ and 5CT—open triangles, $y=3.85 \times 10^7x+3.85 \times 10^3$. All $r^2=0.9999$ or better). The inset amplifies the region of lowest concentrations.

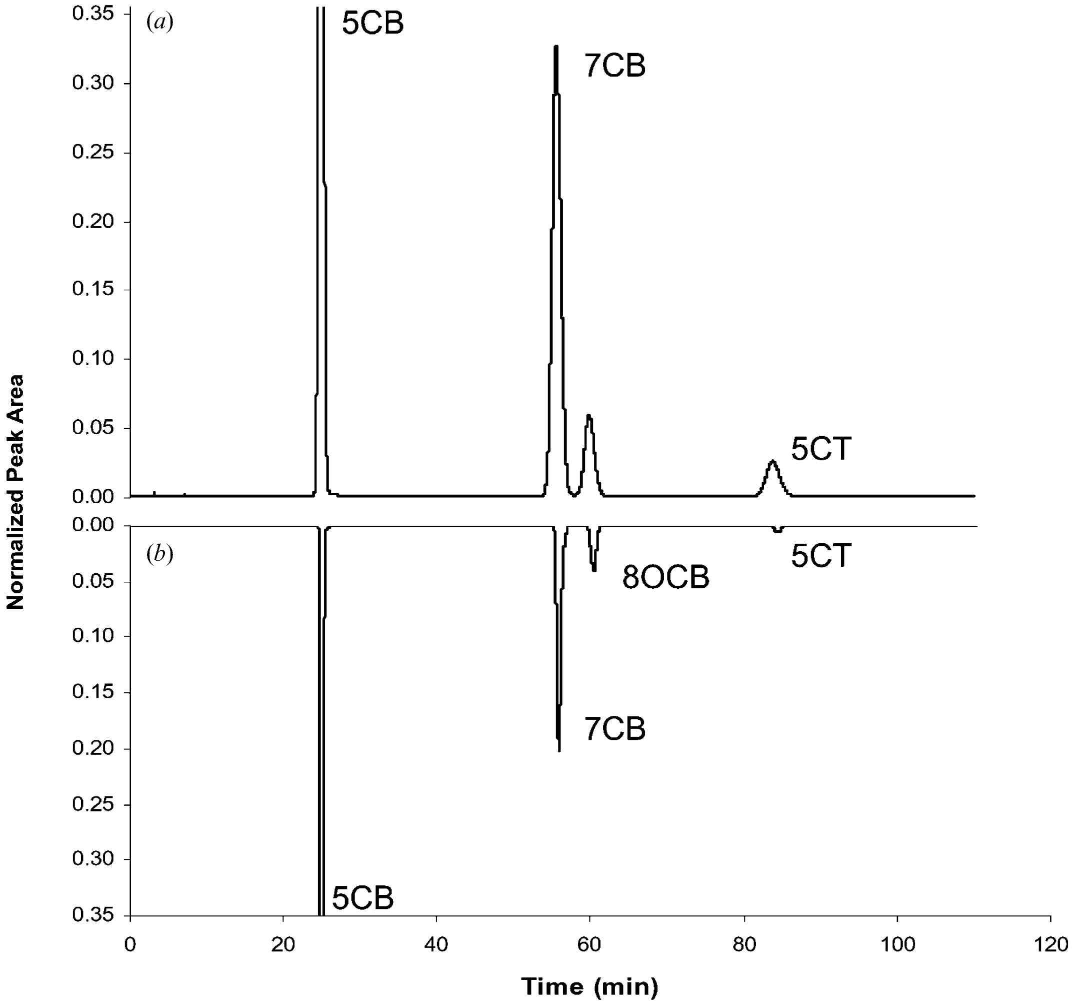

Figure 4. HPLC chromatograms of E7: A, mixture commercially available; B, mixture from VLE sample (experiment at 40°C and 13.59 MPa). The peaks were normalized to the 5CB peak and are represented in this scale for a better viewing of the smaller peaks.

L-7400 UV detector and D-7000 computer interface. Compounds were detected at 277 nm. Elution was performed with 79% methanol (HPLC grade)/21% water (Milipore) with a flow rate of 1 ml min^{-1}, using a water jacket thermostated at 25°C. A Purospher® 100 STAR RP-18e column (250 × 4 mm, 5 µm particle) from Merck KGaA (Darmstadt, Germany) was used. Quantitative determinations were performed with an injection loop of 20 µl, in a time-synchronized autosampler (Marathon) from standard compounds dissolved in acetonitrile or from supercritically extracted solutions. Baseline resolution for all the components including the 7CB and 8OCB critical pair [20], was achieved under these conditions.

The retention times of commercial E7 were 25.57, 55.45, 59.71 and 84.09 min respectively for 5CB, 7CB, 8OCB and 5CT. The attribution of the peaks to the different single components was accomplished by measuring the pure liquid crystals separately under the same conditions. Through the calibration curves, figure 3, it was possible to achieve a relationship between peak areas and the single component concentrations, which enabled us to determine the exact E7 composition.

2.5. *Equilibrium solubility measurements*

The equilibrium solubility measurements were undertaken in a high pressure apparatus, which operates according to the static analytical method already described elsewhere [21, 22]. This apparatus operates between 290 and 345 K and at pressures from atmospheric pressure up to 30 MPa [23]. The central part of the apparatus is a sapphire tube cell of 35 ml useful internal volume, allowing full observation of the inside. In a typical experiment, the cell is loaded with a known amount of E7 and then purged with a low CO_2 flow to

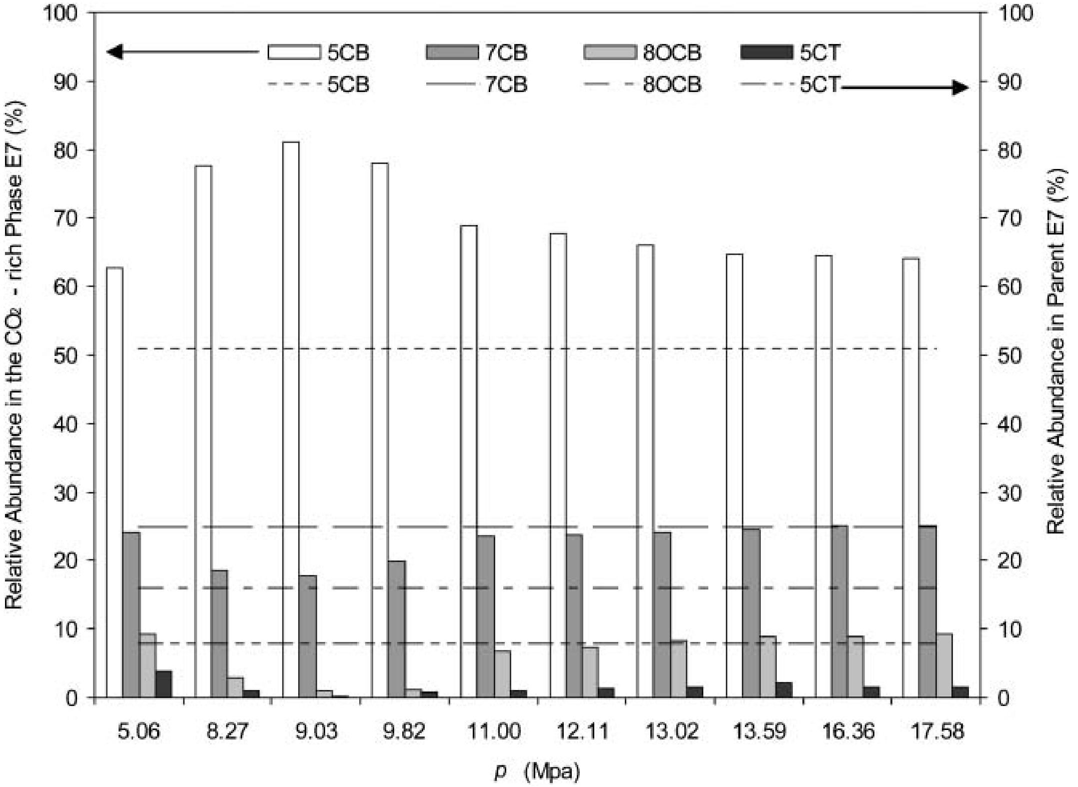

Figure 5. Relative abundance of each E7 component relative to total E7 in the CO_2-rich phase and relative to the initial parent E7, at 313.15 K.

degas. The CO_2 is 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). The temperature is measured with a platinum resistance thermometer (5616 RTD) in contact with the cell, connected to a temperature controller (2100), both from Hart Scientific. Typical temperature stability is ± 0.01 K, at 313.15 K.

After the desired temperature is reached, the pressure is adjusted to the desired value. By stirring the mixture, the time for equilibration of the phases is reduced, the pressure reaches a plateau, and the equilibration is continued for at least 40 min. Once equilibrium is achieved one sample is withdrawn from the CO_2-rich phase through a six-port valve located on the top of the cell, into the sample loop. The gas in each sample is quantified by expansion into calibrated volumes and the amount of CO_2 calculated from measurement of the pressure increase at the working temperature. The sampling loop is cleaned with a low flow of CO_2, after washing the lines with the chosen solvent acetonitrile. In this work, gaseous samples of the vapor–liquid equilibrium system were collected at pressures in the range 5–18 MPa and at 313.15 K.

3. Results and Discussion

The HPLC results allowed the determination of commercial E7 composition: $(50.5 \pm 0.2)\%$ 5CB; $(24.7 \pm 0.1)\%$ 7CB; $(16.8 \pm 0.2)\%$ 8OCB and $(8.1 \pm 0.1)\%$ 5CT. These values are in agreement with the nominal values indicated by Merck (51%, 25%, 16% and 8%, respectively) [7, 24]. As far as we know this is the first report of an accurate analytical determination of E7 composition. The four single peaks corresponding to the individual E7 components were clearly identified in the HPLC chromatogram (figure 4A). This work represents an improvement on other previously reports liquid crystal mixture separation methods [20, 25] where shoulders and poor peaks were observed, using equipment available in most laboratories.

The separation efficiency achieved and the agreement of the determined composition with data furnished by suppliers, allow us to conclude that the proposed reversed-phase HPLC method is valid for accurate analysis of E7 under different conditions. Therefore, the method was applied to the determination of the equilibrium solubility of E7 and its components in $scCO_2$. Samples of liquid crystal mixture collected from the CO_2-rich phase were diluted in acetonitrile to a

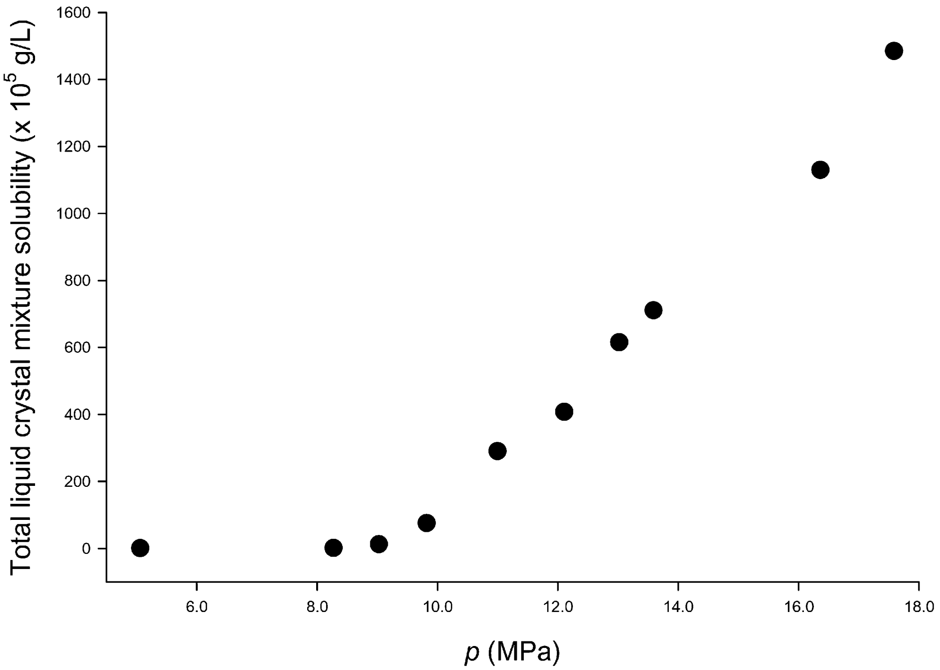

Figure 6. Total liquid crystal mixture solubility as a function of pressure in supercritical CO_2 at 313.15 K.

convenient known volume. The resulting solutions were then analysed by HPLC.

HPLC chromatograms of commercially available E7 and of the liquid crystal mixture obtained from equilibrium solubility measurements at 313.15 K and 13.59 MPa are compared in Figure 4A and B, respectively. The detailed analysis of the chromatograms shows that the ratio between the sample peaks areas obtained in the solubility measurements is different from the observed ratio in the neat E7.

Using the calibration curves, concentrations of the E7 components were determined for each solubility measurement. In figure 5, the relative abundance of each component relative to the total solubilized E7 is represented as a function of pressure, at 313.15 K. Horizontal lines in this figure indicate the composition of 5CB, 7CB, 8OCB and 5CT in parent E7. From this plot it is clear that CO_2 can fractionate the E7 components. The 5CB and the 7CB are clearly more soluble in $scCO_2$ than are 8OCB and 5CT, in the pressure range studied. Additionally, the composition of the liquid crystal mixture solubilized in the CO_2-rich phase tends to a constant value at pressures higher than 13.0 MPa: 64.1%5CB, 25.1% 7CB, 9.2% 8OCB and 1.55% 5CT.

The overall solubility of E7 in CO_2 is presented in figure 6 as a function of pressure, at 313.15 K. The effect of pressure on the total E7 solubility follows the expected trend as the solvent capacity increases with pressure at constant temperature.

4. Conclusions

This analytical reversed-phase HPLC method permits the quantitative determination and resolution of all E7 components in a reproducible manner, using conventional instrumentation. Furthermore, parallel UV studies provided the molar absorptivities and maximum absorption wavelengths of E7 and all its constituents, in diluted acetonitrile solutions.

The HPLC procedure meets the demands of the analytical determination of E7 mixture components since some of their applications can induce composition variation. This is evident in selective miscibility relative to the polymer matrix of some PDLC devices, or in the studied example of differential extraction with a supercritical fluid, namely $scCO_2$. It was demonstrated that selective solubility of E7 occurs in $scCO_2$, enriching the extracted samples in 5CB and 7CB components and approaching an invariant composition for pressures higher than 13.0 MPa. To our knowledge, this is the first evidence for the ability of supercritical CO_2 to fractionate E7.

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