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Submitted date: 04/12/2017 • Posted date: 05/12/2017
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Citation information: Serrano, Luis A; Fornerod, Maximiliano J; Yang, Ye; Gaisford, Simon; Stellacci, Francesco; Guldin, Stefan (2017): Phase behaviour and applications of a binary liquid-liquid mixture of methanol and a thermotropic liquid crystal. ChemRxiv. Preprint.

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Phase behaviour and applications of a binary liquid-liquid mixture of methanol and a thermotropic liquid crystal

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Herein, we report on the phase behaviour of a binary liquid-liquid mixture composed of methanol (MeOH) and the thermotropic liquid crystal 4-Cyano-4'-pentylbiphenyl (SCB). The corresponding phase diagram combines features of a conventional liquid-liquid mixture with characteristics that are particular to the nematic liquid crystal. We observe four arrangements as a function of composition and temperature, namely monophasic isotropic, monophasic nematic, biphasic isotropic-isotropic and biphasic isotropic-nematic, with an upper critical solution temperature of 298 K. The interplay of nematogenic and non-nematogenic species offers a number of applications. Dilution of mesogens with MeOH allows to control the isotropic-to-nematic phase transition of SCB over a range of 35 K. The tunability of phase mixing and phase composition in an accessible temperature window provides novel routes for the extraction of target compounds, here shown for Eosin Y, Doxorubicin, Crystal Violet and Sudan IV.

Introduction

The phase behaviour of a binary liquid mixture is generally described by the Gibbs free energy of mixing. A phase diagram for partially miscible mixtures may be presented as a function of composition $\Phi$ and temperature $T$ where the coexistence curve separates the monophasic and biphasic regions.\textsuperscript{1} The upper critical solution temperature (UCST) distinguishes the temperature above which the two liquids are completely miscible for all compositions from where phase separation occurs for certain compositions. The lower critical solution temperature (LCST) is referred to in an opposite scenario, where a single phase exists for all compositions below a certain temperature. An example of a binary mixture with an UCST is nitrobenzene and hexane, whereas an example of a liquid-liquid mixture with LCST is water and triethylamine.\textsuperscript{2} We refer to a monograph by Francis for a comprehensive overview of binary liquid mixtures and their critical solution temperatures.\textsuperscript{3}

Such binary liquid mixtures are of great importance for separation processes. Aqueous-organic systems find industrial applications ranging from water pollution abatement to removal of waste petroleum and pesticides from soil.\textsuperscript{4} In contrast, aqueous two-phase systems (ATPS) are formed of two aqueous phases and offer advantages related to their environmental sustainability and compatibility with biological media. ATPS are typically composed of an upper phase that contains a high concentration of a more hydrophobic polymer such as polyethylene glycol and a lower phase with denser and more hydrophilic polymer such as dextran.\textsuperscript{5,6} Other phase configurations include polymer-salt, salt-salt and combinations with ionic liquids.\textsuperscript{7,8}

Binary liquid-liquid mixtures with an LCST are a promising material system for artificial microswimmers. In a recent study, a media composed of a mixture of water and lutidine enabled to trigger active Brownian motion by spatially confined phase separation through local heating by a light stimulus.\textsuperscript{9} These findings prompted a number of interesting concepts towards active soft matter.\textsuperscript{10}

In this work, we study the behaviour of a thermotropic liquid crystal (LC) in liquid-liquid binary mixtures. LCs are an important class of soft materials with broad applications in optoelectronic and biomedical devices.\textsuperscript{11-14} Thermotropic LCs display temperature-dependent liquid crystalline mesophases with a characteristic orientation of mesogens, the most common being nematic, smectic, and chiral.\textsuperscript{15} In a nematic arrangement, the mesogens exhibit orientational order along a common director without positional order. A widely used nematic LC is 4-Cyano-4'-pentylbiphenyl (SCB), which was first synthesised by Gray et al. in 1973.\textsuperscript{16} SCB undergoes a transition from crystalline to nematic at 18 °C and from nematic to isotropic at 35 °C.\textsuperscript{17}

The mixing of nematic LCs with non-nematogenic species, in particular polymers and nanoparticles, has been studied in both theory and experiments.\textsuperscript{18-24} Early work focused on elucidating the effect of non-nematogenic doping on the isotropic-to-nematic phase transition temperature $T_{NC25}$ The phase behaviour of binary mixtures of low molecular weight nematic LCs and non-nematogenic species is typically well described by hybrid mean field models that take into account aspects of the Maier-Saupe as well as the Flory-Huggins theory.\textsuperscript{26-30} For a binary liquid mixture of a nematic LC and an isotropic liquid, the consideration of nematohydrodynamics enables to predict kinetic effects of the phase separation.\textsuperscript{31}

Herein, we report on the phase behaviour of a binary liquid-liquid mixture composed of MeOH and the nematic LC SCB. This binary mixture is an important model system that deserves detailed study. First, SCB is a common nematogenic LC that exhibits its mesophase transitions near ambient conditions. Second, MeOH is a common organic solvent with minimal molecular weight and thus ideally suited for studying dilution effects with non-nematogenic species. Furthermore, the

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Electronic Supplementary Information (ESI) available: see separate file.
interplay of MeOH as a versatile organic solvent and 5CB as a thermotropic LC solvent promises avenues of temperature-driven liquid-liquid extraction.

Experimental

Reagents: The LC 5CB was obtained from Synthon Chemicals (99.5% (GC)). Eosin Y (99%), doxorubicin hydrochloride (98-102%, HPLC), rhodamine 6G (99%), crystal violet (for microscopy (Bact., Bot., Hist., Vit.), sudan IV (>80%), and MeOH (HPLC grade) were purchased from Sigma Aldrich. All compounds were used without further purification.

Phase diagram: The T-Φ phase diagram was experimentally mapped as follows. Corresponding volumes of 5CB and MeOH were placed in a 3.5 ml quartz cuvette with a small magnetic stir bar and sealed with a cap. The mixtures were then heated to 40 °C and stirred at 1000 rpm for 10 min to ensure that the solution was clear and homogeneous. Then, the solution was cooled down from 40 °C to 2 °C in steps of 5 °C and a dwell time of 3 min. Once a first estimate was established by the cloud point method, the experiment was repeated but with intervals of 1 °C. The temperature and stirring were controlled by a Peltier-regulated sample compartment (Quantum Northwest, QPod 2e). Videos were recorded with a digital microscope (Dino-Lite) that was attached to the optical port of the compartment.

Absorbance measurements: The optical set-up included a broadband laser-driven light source (Energetiq, EQ-99XFC), a temperature-controlled cuvette holder (Quantum Northwest, QPod 2e) and a high-sensitivity spectrometer (Ocean Optics, QE Pro). Optical fibres with a core diameter of 1000 μm (Ocean Optics) were used for light transmission. Disposable polystyrene 4.5 ml cuvettes (Fisher Scientific) served as sample compartments. The concentration of the molecules was 10μM except for Crystal Violet (SuM) and for Sudan IV (20μM).

Extraction experiments: The standard protocol consisted of dissolving a compound in MeOH, adding an equal volume of 5CB, heating at 40 °C for 5 min, manually shaking the vial to mix both phases and then leaving the mixture at 40 °C for 1 min. Afterwards, the vial was cooled down to the desired temperature. Each of the phases was subsequently extracted and their absorbance was measured using the optical set-up described above.

Compositional analysis of MeOH 5CB mixtures: solutions of LC in MeOH were prepared with the concentration of 5CB ranging from 5x10^{-7} M to 5x10^{-5} M. The absorbance of the respective solutions was measured at 297nm where the absorbance of MeOH the absorbance of MeOH was found to be negligible. The absorbance of the different solutions was used to compose the calibration curve shown in the Supplementary Information (Figure S2, right). In order to further validate the phase diagram regarding its phase composition, solutions with an equal volume of 5CB and MeOH were heated and then cooled to respective temperatures. The solutions were diluted (10^5x) with MeOH to ensure that the concentration of 5CB would fall in the range of the calibration curve. Then, the absorbance of the diluted samples was measured and used to calculate the actual amount of 5CB in the sample. The errors shown in Table S2 (see Supplementary Information) correspond to the difference in the percentage of 5CB found in the sample with respect to the percentage of 5CB predicted from the phase diagram.

Differential scanning calorimetry (DSC): A Multi-Cell DSC (TA Instruments) was used in the DSC analysis. 0.4 ml mixtures of 5CB with MeOH of 0, 3, 6, 9, 12, 15 and 50 vol% were characterised in 1.0 ml capacity ampoules with an empty cell as reference, respectively. The samples were heated to 50 °C before a cooling scan to -30 °C at a ramp rate of 0.1 °C/min. The results in the temperature range of isotropic-to-nematic transition are presented in Figure S3 (see Supplementary Information) to highlight the evolution of 5CB transition temperature at different MeOH compositions.

Results

In order to study the phase behaviour of mixtures containing 5CB and MeOH, it is important to identify the minimum amount of required parameters. The Gibbs phase rule (eq. 1) defines the intensive variables that are necessary to describe the system, where $F = C - P + 2$ (Eq. 1).

$$F = C - P + 2$$

where F is the number of degrees of freedom, C is the number of components, and P is the number of states of matter. In the present study, the system was a binary liquid mixture, thus $C = 2$, and $P = 1$. Therefore, $F = 3$, i.e. 3 intensive variables are needed to describe the system: composition of the mixture, temperature, and pressure. With the reasonable assumption that the pressure is constant and equal to 1 atm (condensed phase rule), the problem can be simplified and the binary system may be described by plotting the composition of the mixture (Φ) against the temperature (T).

The experimental determination of the coexistence equilibrium point as a function of composition was based on the cloud point method. Cooling of the monophasic solution was carried out until a cloudiness was observed, which was then related to microscopic heterogeneity evidenced by light being scattered by the refractive index contrast of the microphases. A typical temperature-dependent phase behaviour of a binary mixture of 50 vol% 5CB and 50 vol% MeOH is shown in Figure 1. At 40 °C, the mixture was fully miscible and the system showed a single clear phase that remained monophasic over time (Figure 1a). Upon cooling, the system eventually reached a cloud point at 25 °C (Figure 1b). When the solution was settled below the cloud point, the system subsequently separated into two clear phases (Figure 1c). Finally, once cooled below -1 °C, the bottom phase became cloudy again, indicating a change of mesogen orientation to the nematic state. 33
While the phase separation induced a temporary cloudiness related to a transient emulsification of the mixture, the cloudiness related to the isotropic-to-nematic transition remained. The isotropic-to-nematic phase transition in 5CB is further illustrated in Figure S1 in the Supporting Information. It is worth noting that when reheating the biphasic 5CB-MeOH mixture to just above the cloud point (i.e. from 25 °C to 26 °C) under stirring, the mixture became a single phase and cleared within seconds.

Different mixtures of 5CB and MeOH were studied, and the results are summarised in a T-Φ phase diagram shown in Figure 2. Alongside the diagram, all observed configurations are illustrated in a schematic. The phase diagram depicts four well defined regions. The red diamonds represent the experimental results for phase separation. A phase coexistence curve with an upper critical solution temperature of 24.4±0.5 °C was then derived by a second-degree polynomial interpolation of the experimental results. The black circles separate conditions where a nematic phase was observed from conditions that generated only isotropic configurations. Above the phase coexistence curve, a single isotropic phase (I) was found for all compositions with MeOH > 13 vol%. For a lower MeOH content and temperatures above the phase coexistence curve, a single nematic phase (N) was observed. Below the phase coexistence curve, two biphatic regions were found, an isotropic-isotropic (I+I) and a nematic-isotropic (N+I) arrangement. In the I+I region, two isotropic phases coexisted, namely MeOH enriched with 5CB and isotropic 5CB enriched with MeOH, while in the N+I region the 5CB-rich phase displayed a nematic orientation. In the course of this study, we did not experimentally observe the co-existence of three phases which was expected at around 1 °C and 13 vol% MeOH.

The phase diagram was further validated by comparing the expected phase composition from applying the level rule to the actual composition of the phase separated sample for a given temperature. As shown in the Supplementary Information (Figure S3), 5CB exhibits a characteristic absorbance at 297 nm, which allows to quantify the composition of each phase via multiple dilution steps with MeOH alongside absorbance measurements. In all cases the determined phase composition was within 5% of the predicted composition based on the phase diagram (Table S2, see Supporting Information).

Figure 1: Phase behaviour of a mixture of 50 vol% MeOH and 50 vol% 5CB. Side-views of the mixture are shown a) above the UCST, b) at the cloud point (25 °C), c) below the UCST and d) below -1 °C, respectively. Note that a white screen was placed behind the sample for clarity.

The phase diagram exhibits a number of interesting aspects. As indicated by the black circles, the isotropic-to-nematic phase transition (T_{in}) is highly dependent on the MeOH content for compositions below 13% MeOH. We were able to tune the transition temperature systematically from 35 °C to 1 °C by an increasing addition of MeOH. These results are in line with differential scanning calorimetry experiments shown in the Supplementary Information. The observed behaviour is attributed to the so-called dilute effect of the nematic mean field ordering.22 Early work on the effect of solvents on the properties of nematic LCs reported a linear decrease at low solvent content.23 Doping with non-nematogenic solvent species was later proposed as a method to bi-directionally tune T_{in} within a limited temperature range: lowering T_{in} by dilution as well as increasing T_{in} through donor-acceptor interactions of nematic mesogens and solvent molecules.35 In comparison to previous reports, the dilution effect is particularly pronounced in our study, enabling to tune T_{in} over a wide temperature range. For a MeOH composition of 13 vol% and above, no further decrease was observed. Any additional increment in the MeOH content resulted in a phase separation from the nematic phase. It is worth pointing out that despite the fact that the nematic-to-solid crystalline transformation of pure 5CB typically occurs around 18 °C, no solidification in the presence of MeOH was observed herein for the studied range of temperatures (-5 °C to 40 °C).
The general shape and arrangement of the phase diagram is of further interest. The phase coexistence curve resembles a conventional symmetric shape of a binary liquid-liquid mixture with partial miscibility. An asymmetry was only observed for a 5CB content above 87 vol%, then resulting in the already discussed gradual increase of $T_{N-I}$. These experimental results are well aligned with earlier theoretical work on binary mixtures of nematic LCs with non-nematicogenic solvents that was derived from a combined model of Flory-Huggins and Maier-Saupe.\textsuperscript{30}

This is in contrast to most studies involving the mixture of nematic LCs with nanoparticles or polymers, where the reported phase space was typically highly asymmetric and did not resemble an inverse parabolic shape around its 50-50 vol% axis.\textsuperscript{21,20,23} While possible enthalpic and entropic effects that lead to an asymmetry of the coexistence curve may be most pronounced for LC blends with polymers or nanoparticles, enthalpic effects with solvents may also render LC-solvent binary mixtures asymmetric.\textsuperscript{35} The fact that we see a near linear decrease of the isotropic-to-nematic phase transition of 5CB at a lower and a fully symmetric phase coexistence curve at higher MeOH content suggests that the extremely low molecular weight MeOH acts as an ideal diluant of 5CB. At low volume content, it homogeneously blends and dilutes the nematic ordering. Above 13 vol% MeOH, both components act as near ideal mixture with full symmetry around an equal volume composition.

Based on our findings of temperature-dictated phase behaviour and compositional tuning as well as the complex properties of LCs as solvents, the potential of using a 5CB – MeOH binary mixture for temperature-driven liquid-liquid extraction was further explored. A series of molecules with different degrees of planarity, ranging from food colourants to chemotherapeutic drugs, were therefore chosen for a first study as shown in Figure 3.

A typical phase transfer experiment was carried out as follows: the compounds were individually dissolved in MeOH (1ml) and the solution was then transferred to a vial containing an equal volume of 5CB. The vials were then placed in an oven at 40 °C for 5 min, manually shaken for 5 seconds and further heated in the oven for 1 min. Subsequently, the vials were placed in a fridge ($T = 3.5 \degree C$) for 10 min in order to allow the phases to separate and reach equilibrium. Finally, both the upper phase (MeOH-rich) and the bottom phase (5CB-rich) were extracted, and the absorbance of each of the phases was measured in order to calculate the partition coefficients. This was done by comparing the maximum in absorbance of the molecules in each phase with the maximum in absorbance of the compounds in the phase-pure solution of MeOH and 5CB, respectively. It is worth mentioning that the maximum in absorbance would typically be shifted (5-10nm) to longer wavelengths in 5CB with respect to MeOH. See Figure S4 in the Supporting information for photographs of the vials at each step of phase transfer experiment.

The results of the partitioning experiments are summarised in Figure 4. Eosin Y and doxorubicin showed a partitioning predominantly into the MeOH phase with ratios of 4.9:1 and 3.2:1, respectively. Rhodamine 6G was found in equal amount in both phases (1:0:1). In contrast, crystal violet and sudan IV showed a strong tendency towards 5CB, with partitioning ratios of 2.6:1 and 30:1, respectively. These results demonstrate that the chemical structure of the molecules had a dramatic effect on the partitioning between the 5CB-rich and the MeOH-rich phases. When rationalising the behaviour based on the molecular structures shown in Figure 3, two molecular properties come to mind, namely the polarity and the ability for π-π stacking. Polarity is not likely to be the main driving force as only two compounds contained charges among the five chosen ones, namely eosin Y and doxorubicin, which displayed opposite behaviour in terms of their distribution between the 5CB and the MeOH phase.

![Figure 3: Molecular structure of model compounds for phase extraction. From left to right: Eosin Y, doxorubicin, rhodamine 6G, crystal violet and sudan IV.](image)

![Figure 4: Partitioning of model compounds. Percentage of eosin Y (EO), doxorubicin (DOX), rhodamine 6G (RH), crystal violet (CV) and sudan IV (SU)., extracted into the 5CB and MeOH phase at 3.5 °C.](image)
On the other hand, the ability for π-π stacking is associated with aromaticity and Huckel’s rule. The criteria for Huckel’s rule were met by the five molecules in this study, as they all displayed at least one benzene moiety. Therefore, it is reasonable to assume that the affinity of the molecules for either the 5CB or the MeOH phase was related to their tendency for π-π stacking. The molecule that showed the highest affinity for the 5CB phase was sudan IV. It is not only a planar molecule, but also the only one that contains an aromatic moiety (napthalene) bigger than benzene. Thus, this molecule is the most likely to form π-π stacking. While crystal violet is not completely planar due to the steric hindrance of its aromatic rings, it still displayed the second highest affinity for the 5CB-rich phase. It is worth noticing that both sudan IV and crystal violet contain electron-rich aromatic rings due to their azo and amino substituents, respectively. This is likely to enhance their affinity for 5CB, since the aromatic core of 5CB is expected to be slightly electron deficient due to the electron withdrawing character of the carbonitrile group. Interestingly, rhodamine 6G was distributed in equal amount in both phases. This molecule exhibits an orthogonal substituent which disrupts the ability of the molecule to form π-π stacking. This distortion is enhanced since the orthogonal aromatic ring contains an ortho-substituent. Following this trend, doxorubicin is substituted with a bulky sugar ring, disrupting even more its ability to form π-π stacking. Finally, eosin Y was found to have the highest affinity for the MeOH phase. This molecule is completely orthogonal and therefore very unlikely to π stack.

According to the phase diagram of the binary mixture, the composition of both phases upon cooling and phase separation is highly temperature-dependent. Studying the effect of temperature on the partitioning of target molecules was therefore of great interest. For this purpose, eosin Y and sudan IV were chosen as they exhibited the most prominent affinity for the MeOH-rich and 5CB-rich phase, respectively. The phase transfer experiments were carried out as described above, but the cooling temperature was systematically varied from -5°C to 23°C. The results presented in Figure 5 show that as the temperature of the phase transfer was decreased, the selectivity for each phase increased. As an example, the MeOH-rich phase contained 34 vol% 5CB at 20°C and only 12 vol% at 0°C. In this particular example of eosin Y and sudan IV, the difference in affinity for the two phases and thus the partitioning was maximised when the phase transfer was carried out at the low temperatures, and minimised when the phase transfer was performed at the highest temperatures of the observed range. While our findings suggest that the extraction is most efficient at highest contrast in composition, we want to point out that the herein reported control over phase composition, by temperature variation within an accessible range, represents a useful tool for a number of applications. For phase transfer-based sensing, the availability of results at various temperatures increases experimental redundancy and thus may allow to reliably determine weakly selective sensing events with greater accuracy. One may also envision a situation where a multi-stage extraction of a number of compounds at different temperatures may allow greater versatility.

**Conclusions**

In conclusion, we report on the phase behaviour and possible applications of a binary liquid-liquid mixture of MeOH and the thermotropic LC 5CB. Four different phases were observed as a function of temperature and composition, namely monophasic isotropic, monophasic nematic, biphasic isotropic-isotropic and biphasic isotropic-nematic. At a MeOH volume content below 13%, the non-nematogenic dilution allowed to finely tune the isotropic-to-nematic transition temperature from 35°C to 1°C. Above 13 vol% MeOH content, a binary mixture with an upper critical solution temperature of 24.4±0.5°C was obtained, where the cooling temperature dictated the composition of both phases. We anticipate these findings to be relevant for a number of applications. The use of MeOH promises highly controllable dilution-based manipulation of the mesophase temperature window of 5CB. Furthermore, the combination of LC-related complex solvation properties and temperature-induced compositional tuning offers novel routes for the extraction of target molecules.

**Conflicts of interest**

There are no conflicts to declare.
Acknowledgements

This project received funding from the European Union’s Horizon 2020 research and innovation programme under grant agreement No 633635 (DIAChemO). YY acknowledges University College London for an Overseas Research Scholarship. SG is grateful for support by a start-up fund from the Department of Chemical Engineering at University College London.

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Supplementary information

Phase behaviour and applications of a binary liquid-liquid mixture of methanol and a thermotropic liquid crystal

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Figure S1: Thermotropic transformation of the liquid crystal SCB; a) Isotropic phase at 36 °C, b) Nematic phase at 35 °C.
Table S1: Phase separation and isotropic-to-nematic transformation temperatures obtained for a range of SCB-MeOH mixtures.
Figure S2: Absorbance spectra of different amounts of 5CB in MeOH (left). Calibration curve using the absorbance at 297nm (n=3) (right).

Table S2: Errors on the quantification of 5CB in MeOH solutions (based on the 5CB% found in a solution at a given phase separation temperature VS the predicted value from the phase diagram)
Figure S3: DSC characterisation of isotropic-to-nematic transition: The heat power versus temperature (°C) plots for cooling different 5CB-MeOH mixtures at 0.1 °C/min ramp rate.

Figure S4: Different compounds before phase mixing (top), after phase mixing (middle), and after phase separation (bottom).

Supplementary Information:
Phase behaviour and applications of a binary liquid-liquid mixture of methanol and a thermotropic liquid crystal
