

Cholesteric liquid crystals for detection of organic vapours

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Abstract

Studies on the use of cholesteric liquid crystals (CLCs) as sensing phase for detection of organic vapours in air are described. Stock solutions of 1.0% (w/v) cholesteryl nonanoate (CN) and cholesteryl chloride (CC) were prepared in tetrahydrofuran. Binary mixtures, with compositions ranging from 0.18 to 0.25% of CC and 0.82–0.75% of CN, respectively, were prepared by appropriate mixing of the stock solutions. Films were cast by pipetting three 10 μ l aliquots of the CLC solution mixture onto a glass disk, whose reverse side was made black to absorb unscattered light. The glass disk was adapted to the common end of a bifurcated optical fibre bundle and placed in a glass vial, which provided a headspace of organic vapours. Measurements were carried out at 27 ± 1 °C, a temperature in which the CLC mixtures maintain their liquid crystalline properties. The responses of the CLC mixtures to vapours of ethanol, acetone, benzene, pyridine and hexane were investigated. The colour of the sensing phases depended on their compositions and exposure to organic vapours gives rise to a change in the optical characteristics of liquid crystals. It was found that the CLC layers containing 0.23–0.25% of CC had no significant change in optical properties when exposed to organic vapours and that ethanol did not cause any optical changes in the liquid crystal layers. Benzene as well as hexane always turned all the coloured liquid crystalline layers to colourless. The CLC layers exhibited different behaviours to vapours of acetone and pyridine. For example, the wavelengths of maximum scattering for the 0.19% CC layer were 530 nm in air, 545 nm in pyridine and 580 nm in acetone. The CLC layers showed reversibility. The lifetimes of these layers (interval of time in which the liquid crystalline phase exists, before crystallisation) were investigated by employing acetone and *n*-hexane vapours. Average lifetimes of 14–15 min were found for films in contact with these vapours, while a lifetime of 205 min was possible when the CLC film was exposed to air.

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Keywords: Liquid crystals; Cholesteric liquid crystals; Organic vapours; Optical sensor

1. Introduction

Organic solvents are widely used in industry and are found extensively on a smaller scale in laboratories world wide. Almost all these compounds have been found to have detrimental effects on health when certain levels of exposure are exceeded. The effects vary widely from solvent to solvent, but range from the relatively minor, such as dermatitis, to the more serious, such as damage to the nervous system and brain damage. Another hazard associated with organic solvents is that the majority are considered to be highly flammable and can form explosive mixtures with air. This combination of properties means that the use of organic solvents must be rigorously monitored and the levels that are allowed to form in the immediate atmosphere quantified. Safe levels of exposure, enforceable by law, have been

defined by governments around the world and by groups such as the World Health Organisation. It is therefore imperative, both from a legal point of view but also from a health aspect, that levels of solvent vapour in the atmosphere are monitored.

Although most of the methods for determination of organic vapours in air are based on gas chromatography and infrared spectroscopy, electrochemical [1–3] and optical sensors [4–11] have also been used to perform this task. Electrochemical sensors, including electronic noses, are usually based on metal oxide and conducting polymer resistive materials [1] and have been frequently described in the literature. Similarly, an increasing interest on optical sensors for organic vapour detection can be perceived in the literature. Bariáin et al. [4] have developed a vapochromic material, whose colour and refractive index changes in the presence of organic vapours. Films of co-ordination polymer have been prepared by Casalini et al. [5] for detection of benzene, acetonitrile, ethanol and toluene using surface plasmon resonance and admittance spectroscopy. Beenen and Niessner [6] have developed a photoacoustic sensor system for on-line monitoring of benzene, toluene and

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xylylene, employing near-infrared laser diodes. An array of optical fibre sensors containing fluorescent solvatochromatic dyes has been proposed by Walt et al. [7] for organic vapour recognition. A system for discrimination and determination of organic vapour based on a cataluminescence sensor which can measure the spectroscopy images generated by catalytic oxidation of combustible gas, has been developed by Nakagawa et al. [8]. Films of substituted phthalocyanines containing copper or nickel as the central metal ion have been prepared for detection of toluene vapour based on surface plasmon resonance [9]. Brehmer et al. [10] have proposed the use of fluorocyclorhizands as sensing reagent for determination of organic vapours by fluorescent measurements, while Sutter and Jurs [11], based on the same technique, employed a sensor array with immobilised dye in polymer matrices for classification and quantification of organic vapours.

Liquid crystals are compounds that exhibit an intermediate state between liquid and solid being described as anisotropic fluids. In the cholesteric liquid crystals (CLCs), properly known as chiral nematic liquid crystals, the molecules are arranged in layers that are twisted in relation to each other, in a helical pattern. A complete period of rotation is called pitch and the length of the pitch brings interesting properties to the CLC. The temperature affects directly the length of the pitch, as long as there is a temperature range in which these compounds behave as liquid crystals (below a given temperature they are solids and above another temperature they are liquids). If the pitch length of the CLC is around the wavelength of the visible radiation, its colour depends on the temperature, for example, showing a shift from blue to red when the temperature is raised as the pitch length increases. This property of the CLC has been used to develop commercial thermometers. Organic vapours can be incorporated between the layers of a CLC, changing its pitch length and, therefore, its colour. As a consequence, CLCs can be employed for detection of organic vapours in air and some contributions have been described in the literature [12–16]. One of the most recent work on this subject was published by Dickert et al. [12] in 1994, who employed a mixture of cholesteryl esters for determination of aromatic and halogenated hydrocarbons. The authors concluded that the optical properties of the sensing phase can be tuned by changing the composition of the CLC mixture, altering the sensitivity and selectivity for different organic vapours. In addition, it was stated that new perspectives would arise as a result of the development of chemometric methods, such as neural networks and fuzzy logic.

Although some contributions on detection of organic vapours by CLC have been described in the literature, no efforts have been made to develop an optical fibre chemical sensor based on this kind of compounds. Therefore, this work describes preliminary studies on the use of CLCs as sensing phase for detection of organic vapours in air. Films of mixtures of cholesteryl nonanoate (CN) and cholesteryl chloride (CC) were prepared and their optical properties

were studied under atmospheres of ethanol, acetone, benzene, pyridine and hexane.

2. Experimental

2.1. Reagents and solutions

All reagents were of analytical grade. Solvents (ethanol, acetone, benzene, pyridine and hexane) and reagents were employed as purchased, without any further purification. Stock solutions of 1.0% (w/v) CN and CC were prepared in tetrahydrofuran. Binary mixtures, with compositions ranging from 18 to 25% (v/v) of CC solution were prepared by appropriate mixing, resulting in solutions containing 0.18–0.25% (w/v) of CC and 0.82–0.75% (w/v) of CN, respectively.

2.2. Sensor probe

A glass disk (1.0 mm high, 4.5 mm diameter) was used as substrate for preparation of the CLC films. Its reverse side was made black to absorb unscattered light, which would impair the analytical signal. The glass disk was then affixed to a plastic screw, allowing its adaptation to the common end of a bifurcated optical fibre bundle in a probe as previously described [17].

2.3. Procedure

Films were cast by pipetting three 10 μ l aliquots of the CLC solution mixture onto the glass disk. A period of 15 min was allowed for the solvent to evaporate before applying the next aliquot. Then, the disk was placed 1 mm apart from the optical bundle and the probe was put in a 20 ml air tight vial, containing 1.0 ml of organic solvent. The system was maintained at 27.0 ± 1.0 °C in a controlled environmental chamber (Thermotron, Holland, MI, USA) and spectra were recorded after 3 min, from 400 to 800 nm, employing a CCD based multichannel spectrophotometer (Ocean Optics PC 1000, Dunedin, FL, USA).

2.4. Immobilisation of liquid crystals in polymers

The immobilising agents used were PVC and silicone rubber (Dow Corning RTV 734). Solutions of the 18 CC:82 CN solutions were prepared. The solutions were split into groups of three and were made with 0.1, 0.2 or 0.5% (w/v) of dry PVC powder added. The solutions were then thoroughly mixed using an ultrasonic bath. The same procedure was employed to prepare solutions containing silicone rubber. The silicone rubber used was of the room temperature vulcanisation type, eliminating the need for a cross-linking agent for curing to take place. The films were prepared as described above and then cured at 50 °C for 15 min. Measurements were then taken as described in the procedure and the effects of acetone were investigated.

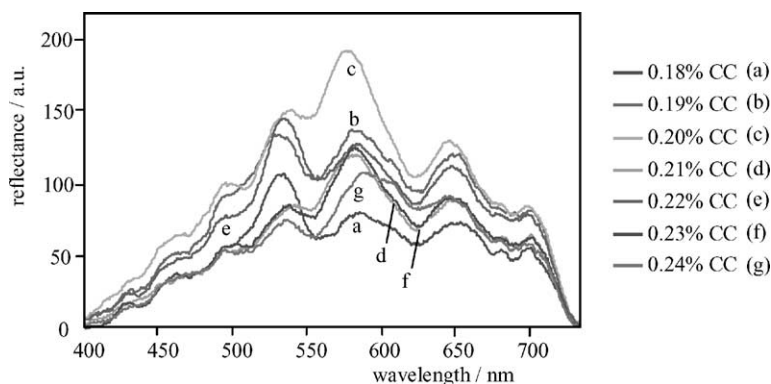


Fig. 1. Reflectance spectra of the CLC films obtained in air.

3. Results and discussion

Temperature affects directly the cholesteric liquid crystalline phase, which can exist in a given range determined by the composition of the CLC system. The binary mixtures of CC and CN form liquid crystalline phases around 27 °C, which was, therefore, employed in all measurements.

Preliminary experiments using films cast from 5.0 and 10% (w/v) stock solutions of CLC showed signal intensities higher than those prepared from 1.0% solutions, however, they entered the solid phase faster. Therefore, all films were prepared from 1.0% stock solutions. Furthermore, films prepared from 0.25% (w/v) CC plus 0.75% CN (w/v) solution showed no significant changes in their optical properties when exposed to organic vapours and ethanol did not cause any optical changes in the liquid crystal layers.

The composition of the films affects directly their optical properties, due to the changing of the pitch length of the mesophase, which causes light to be scattered at different wavelengths. Fig. 1 shows the reflectance spectra of films with different compositions under atmosphere of air. The effects of solvent vapours upon these liquid crystalline films were studied and, as expected, different behaviours for these layers under atmosphere of different organic vapours were verified.

Fig. 2 shows the effect of the solvents on the reflectance spectra of the 0.18% CC:0.82% CN film. Acetone shifts the peak present at 530 nm to a slightly longer wavelength of 540 nm, brightening the green colouration of the film. Pyridine has the most pronounced effect, intensifying the green colouration of the layers, indicated by the presence of large peak at 535 nm. Both hexane and benzene caused the same effect upon the 0.18% CC films, reducing the intensity of the scattered light at 530 nm and making the films appear colourless.

The spectra showing the effect of acetone, pyridine, hexane and benzene vapour upon the 0.19% CC:0.81% CN films are depicted in Fig. 3. As can be seen, interaction between these films and acetone vapour causes light to be scattered at 580 nm, pyridine causes the peak at 530 nm to shift to the longer wavelength of 545 nm, while benzene and hexane reduce the overall intensity of the spectrum, causing the layers to become colourless.

The spectral behaviours of the 0.20% CC:0.80% CN films submitted to the organic vapours are shown in Fig. 4. The spectrum taken when the 0.20% CC film was exposed to air shows that it is an intense green/yellow colour. Interaction between the layers and acetone vapour results in the films adopting a much less intense yellow/red colouration. Exposure of the films to pyridine vapour results in a bright yellow

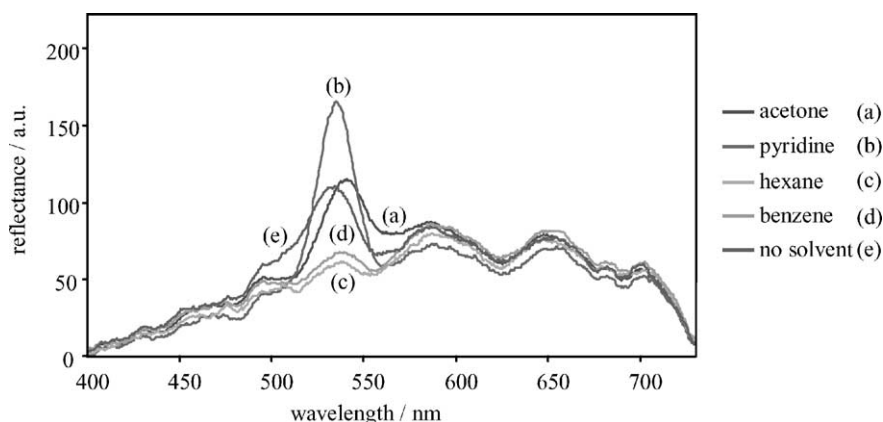


Fig. 2. Effect of the solvents on the reflectance spectra of the 0.18% CC:0.82% CN films.

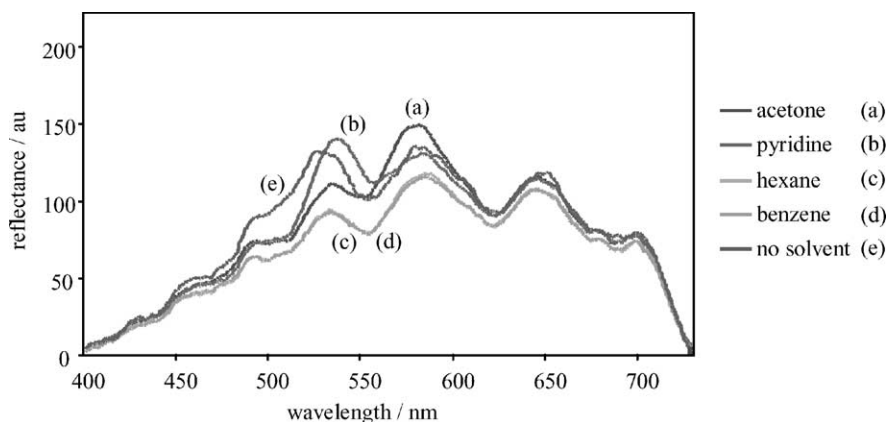


Fig. 3. Effect of the solvents on the reflectance spectra of the 0.19% CC:0.81% CN films.

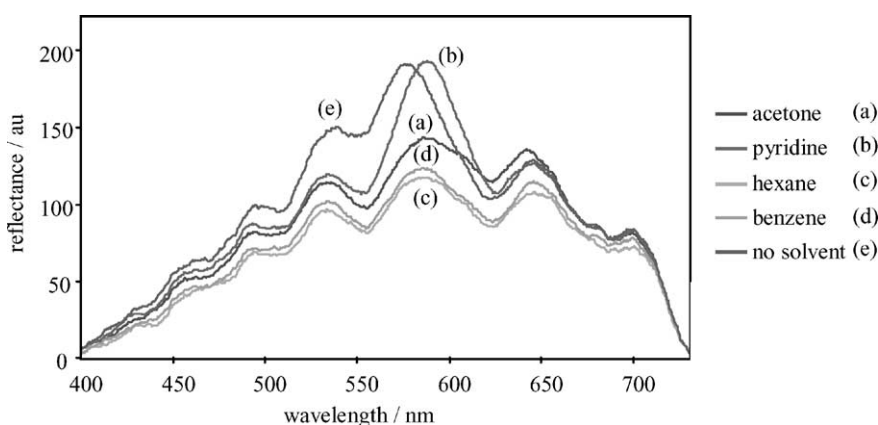


Fig. 4. Effect of the solvents on the reflectance spectra of the 0.20% CC:0.80% CN films.

colour, while exposure to benzene or hexane vapour results in the films becoming colourless.

The result of exposing the 0.21% CC:0.79% CN liquid crystalline films to acetone vapour is that the scattered light shifts from 585 to 615 nm, causing a yellow/orange colouration, as shown in Fig. 5. This can be seen from the broad peak in the acetone spectra ranging from 550 to 650 nm. Exposure

to pyridine vapour causes the intensity of the scattered light to increase slightly and a shift of the band to a slightly longer wavelength of 588 nm. Hexane or benzene vapours cause the same effect as before, resulting in colourless films.

Exposure of the 0.22% CC films to acetone had the effect of shifting the scattered light from 535 to 590 nm. The same effect, albeit less intense, is produced when the films are

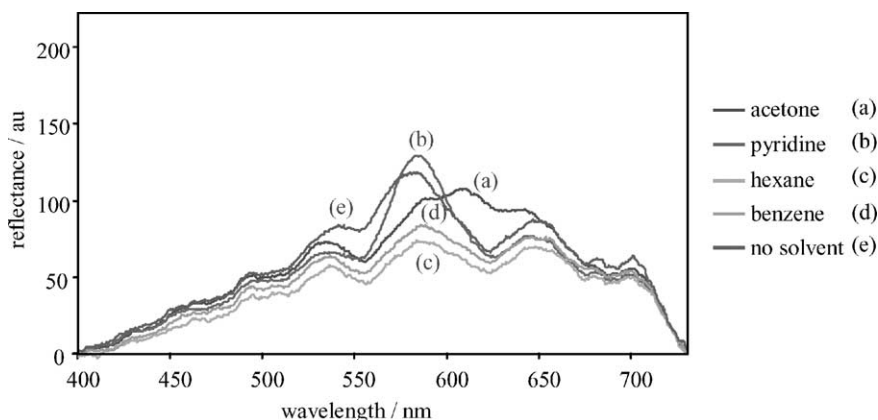


Fig. 5. Effect of the solvents on the reflectance spectra of the 0.21% CC:0.79% CN films.

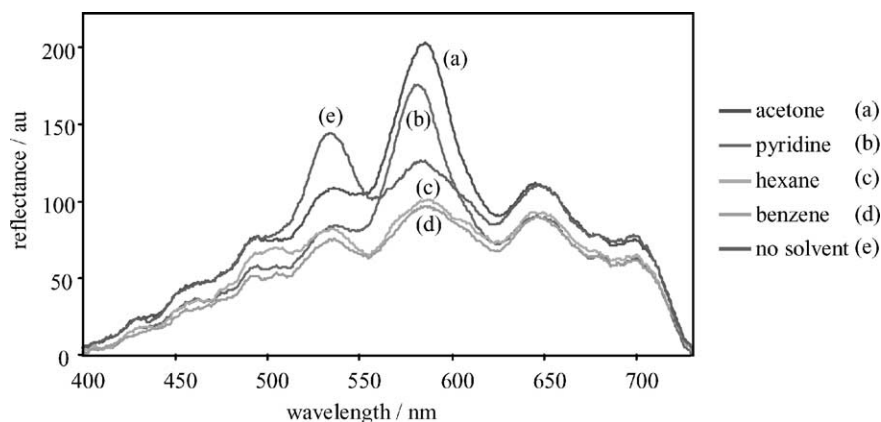


Fig. 6. Effect of the solvents on the reflectance spectra of the 0.22% CC:0.78% CN films.

exposed to pyridine vapour. Exposure to benzene or hexane vapour causes the green colour to recede, leaving the films colourless. Fig. 6 shows the behaviour of the film when exposed to these solvents.

The four solvents have no significant effect upon the optical characteristics of the 0.23% CC:0.77% CN films. Acetone vapour causes a decrease in the intensity of light scattered at 585 nm, while increasing the intensity of light scattered at 650 nm, which causes the films to appear red in colour. Interaction between the films and pyridine has the effect of reducing the overall intensity of scattered light. Benzene vapour reduces the overall intensity of the scattered light from the films, making them appear colourless, as does hexane.

The 0.24% CC films are virtually colourless before being exposed to any of the solvent vapours, which cause minimal differences in their optical characteristics and, therefore, will not be discussed in this paper.

As can be noted, the composition of the CLC film can be changed in order to provide different sensitivity and/or selectivity to the organic solvents. Furthermore, as the films usually show distinct responses for the solvents, chemometric methods, such as artificial neural networks [18], can be employed for identification and quantification of organic solvents in air.

As pointed out above, a problem noted during this work was that the liquid crystal layers had varying lifetimes, dependent upon composition, temperature and previous history, i.e. if the film has been heated and cooled and to what type of organic solvents the layers have been exposed. The lifetime of the mesophase for layer of each composition was investigated, along with the lifetimes of the films when in an atmosphere containing acetone or hexane vapours, which represent both polar and non-polar compounds, respectively. Three layers were used for each measurement, based on the standard layers employed throughout the work. The time taken for crystallisation was based on the spectrum for each film becoming identical to a spectrum of a solid phase film. The average lifetime of the films in air was

205 min, with a standard deviation of 7 min. The average time taken for the films to leave the mesophase in an atmosphere containing acetone was 16 min, with a standard deviation of 2 min. When exposed to hexane, the average time taken before crystallisation occurred was 14 min, with a standard deviation of 3 min. As can be seen, organic solvents intensely affect the lifetime of the liquid crystalline phase.

In order to overcome the drawback concerning the lifetime of the mesophases, the liquid crystal films were immobilised in PVC and silicone rubber, based on the fact that CLC is maintained in small clusters dispersed in the polymeric film. It was found that all the immobilised 0.18% CC:0.82% CN films exhibited an effect when exposed to acetone vapour. However, the response time of the films was dependent upon the amount of polymer used in the immobilisation. Whereas 3 min was sufficient to measure the optical changes caused by the solvent vapours for the pure liquid crystal layers, longer time was needed to observe the same changes in the immobilised films. The results of times measured for the optical changes to cease when exposed to acetone vapour for the layers immobilised in PVC and silicone rubber are presented in Table 1. Silicone rubber shows slightly better results when compared with PVC films. The immobilisation of CLC in polymer films extended the lifetime of the mesophase and, as can be noted in Table 1, films prepared from the 0.1% polymer solutions show a response time very close to those obtained with the “pure” film.

Table 1
Response time of the CLC immobilised in polymeric films to acetone vapours

Polymer concentration (%)	Time for response to acetone vapour to cease (s)	
	PVC	Silicone rubber
0.010	233	226
0.020	391	382
0.050	646	555

4. Conclusions

Results obtained in this work show that CLCs can be employed as sensing phase for detection and determination of organic vapours in air. Furthermore, the sensitivity and selectivity of the sensing phase can be tuned by changing its composition. Finally, as the CLC mixture responds differently to different organic vapours, chemometric methods can be employed in a multivariate calibration, providing a method for simultaneous determination of organic vapours in air. Such investigations are currently being undertaken.

Acknowledgements

I.M. Raimundo Jr. kindly acknowledges FAPESP for the fellowship (process no. 98/3111-6) and CNPq (process no. 450073/02-5) for the financial support to attend Europt(r)ode VI Conference.

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R. Narayanaswamy is currently a Reader in DIAS at UMIST. He obtained his PhD in 1972 (Imperial College, University of London, UK) in analytical chemistry and his DSc in 1995 (University of London) in analytical science. Previously he was a lecturer in chemistry at the University of Sri Lanka, Peradeniya, Sri Lanka (1967–1978), and a postdoctoral research fellow at the University of Southampton, UK (1978–1981) and the University of Warwick, UK (1982). He joined DIAS, UMIST, UK in 1983 as a senior postdoctoral research associate and became the manager of the Optical Sensors Research Unit (1984–1987) and lecturer in instrumentation and analytical science (October 1984–July 1990). He leads the research group in DIAS that deals with the fundamental and applied studies in molecular spectroscopy and in optical chemical sensors, biosensors and instrumentation. He is the recipient of the 1997 Industrially sponsored Silver Medal for his work on analytical reactions and analytical reagents in the field of optical sensors, awarded by the Royal Society of Chemistry, London, UK (in 1998).

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