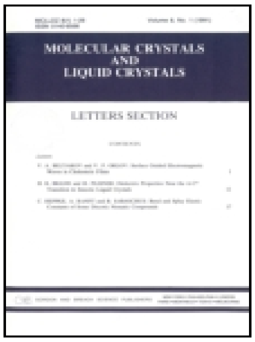

Molecular Crystals and Liquid Crystals

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Liquid Crystalline Compositions as Gas Sensors

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Droplets and films of liquid crystalline mixtures were studied as promising detectors of volatile organic compounds (VOCs) in the air. Under increasing concentration of VOC in the air the detection may rely on each of the following effects sequentially observed one after the other: i. slight changes in orientation and order parameter of liquid crystal, ii. formation of bubbles on the top of the liquid crystalline droplet, iii. complete isotropisation of the liquid crystal. All three stages can be easily monitored by optical microscopy. Detection limits corresponding to the first stage are typically lower by a factor of 3–6 than detection limits corresponding to isotropisation. The qualitative model is presented to account for the observed changes.

Keywords gas; VOC; detection; liquid crystals; nematic; cholesteric

1. Introduction

The detection of biological and chemical agents by means of liquid crystals became an important topic of research in recent years [1–3]. Much effort was dedicated to solve the problem of the detection of biological molecules in aqueous media by analyzing morphological changes in free standing low molar mass liquid crystalline films and droplets [1], or films deposited on functionalized surfaces. Liquid crystalline polymers and polymer networks were also explored for detection of organic solvents [2], pH changes in water and amino acids [3]. The following short overview mostly focuses its attention on the use of liquid crystals (LCs) as gas sensors.

One of the first attempts to use LCs as simple visual gas sensors is described in [4], where different LCs were tested as detectors of a number of volatile organic compounds (VOCs). The effect of lowering the temperature of nematic-isotropic transition while absorbing the molecules of VOC was explored for designing sensors based on nematic LCs. It was determined that one of the most sensitive compounds in a class of nematic LCs was MBBA (4-Methoxybenzylidene-4-butylaniline) or its mixtures with other derivatives of butylaniline. In [5], the discotic liquid crystals based on phthalocyanines were used to detect low concentration of nitrogen oxide. Functionalized cholesterol derivatives forming cholesteric films were studied in [6] as promising sensors for detecting amine vapors. The

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detection effect manifested itself as a spectral shift of the selective reflection band position. The use of cholesteric liquid crystals for monitoring gas concentration was also considered in [7] where reactive chiral dopants changed helical twisting power and, therefore, the position of the selective reflection band as well as the sample color by reacting with carbon dioxide. Cholesteric liquid crystals with the selective reflection band changing its position in gases were further explored in [8] for sensing such volatile compounds as methanol, ethanol, tetrahydrofuran, etc. The cholesteric material was shown to be the most responsive to polar solvents; the sensitivity threshold for ethanol was determined to be c.a. 0.5% of solvent in the air. Cholesteric liquid crystals doped with dodecylamine were used for visual detection of aldehyde vapors in [9]. The major mechanism of detection was based on a chemical reaction between amine and aldehyde groups. The similar principle (i.e. the reaction between butylamine and lauric aldehyde) was recently employed in [10] for a nematic film changing its orientation during the reaction. Optical detection by means of cholesteric liquid crystals formed by mixtures of chiral cyanobiphenyl derivatives and carbon nanotubes were recently studied in [11–12]. The prototype for estimation of acetone vapor concentration in the range 250–550ppm was built and tested.

This work is mostly focused on systematic study of the optical response of low molar mass liquid crystals to different volatile organic compounds (VOCs) before the transition of liquid crystal to isotropic state. The monitoring of the interference pattern allowed us to decrease the detection limit of different VOCs by a factor of 3–6 depending on the chemical structure of particular VOC.

2. Experimental

A gas atmosphere was created inside a sealed Petri dish (container) that was placed on a microscope table. A LC sample was placed inside the container and a few microliters of VOC liquid were injected through a small hole made in the upper plate. Immediately after the injection the hole was sealed by aluminum tape. The rapid evaporation and a uniform gas atmosphere inside the container were facilitated by the installation of a small fan inside. A tin dioxide gas sensor was also installed inside the container. All observations and measurements were performed through the microscope with illumination of the sample either from the top or from the bottom of the container. The photos were taken by a photo camera (Samsung MV800 with CMOS sensor) attached to the microscope. Different types of nematic liquid crystals were used in experiments (MBBA, pentylcyanobiphenyl, and mixtures of these nematic LCs with chiral perillyl alcohol and ethylbenzylamine). All chemicals were purchased from Sigma-Aldrich and used as received. The droplets were placed on the glass slide either by using a micropipette or a lengthy needle. Nematic droplets were put on microscope slides covered with polyimide layers promoting planar orientation; chiral droplets were placed on microscope slides covered with sodium dodecyl sulfate promoting homeotropic orientation of LCs and, therefore, a formation of fingerprint structure.

3. Results and Discussion

In case of nematic liquid crystal the droplets were deposited on a microscope glass slide with the surface treated for planar or homeotropic orientation. After injection of VOC liquid, its evaporation starts immediately, its concentration rapidly rises and reaches a saturation at approximately one minute after the injection. The typical concentration dependence on time

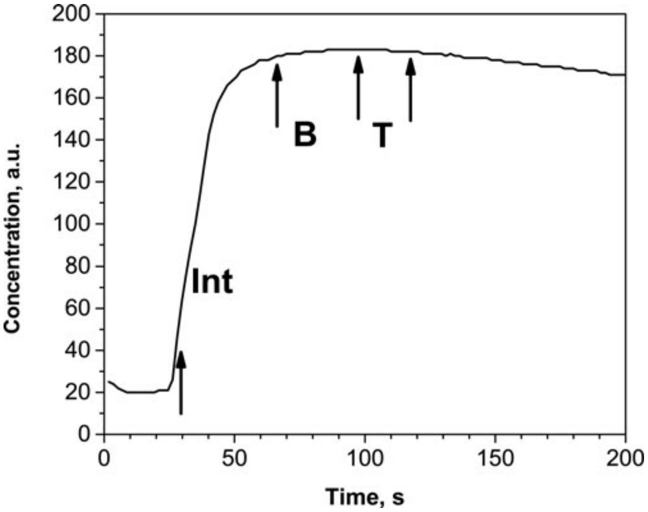

Figure 1. Typical dependence of ethanol concentration in the container as a function of time (measured by tin dioxide sensor). Area “T” corresponds to isotropisation, area “B” corresponds to bubbles formation, area “Int” corresponds to changes in interference pattern. Injection of ethanol occurred at c.a. 20th s.

(that was measured by the tin dioxide sensor) is shown in Figure 1. It takes some time for the gas to diffuse inside the droplet and induce nematic-isotropic transition that is observed under the microscope through crossed polarizers after maximum vapor concentration has been reached (the area “T” between the arrows in Figure 1). The isotropisation transition is normally preceded by the formation of multiple bubbles on the top of the droplet (the area marked as “B” between arrows in Figure 1) where the phase separation and the mass transfer between the volumes of LC saturated with the gas and the rest of the sample takes place. The amount of VOC inducing the transition from the nematic to the isotropic state depends on the chemical composition of LC matrix and the nature of VOC. For ethyl alcohol and MBBA matrix the transition happens at concentrations of about 100μL/L, for ethyl alcohol and LC matrix based on cyanobiphenyl derivatives the isotropisation occurs at higher concentrations of about 250μL/L. The lower detection limits of VOCs can be significantly reduced if subtle changes in the interference pattern appearing at the edge of the droplet are analyzed, rather than bubbling (stage “B” in Figure 1) and transition to isotropic state (stage “I”). Both the order parameter and the orientation of LC matrix are more affected by the gas diffusion in the thinner part of the droplet, close to its edge (Figure 2). The intensity of light passing through the droplet (see Figure 2) depends on the average refractive index of the droplet experienced by passing light beam. The refractive index in turn depends on light polarization (arrow and star indicate the direction of electric field in Figure 2) and orientation of liquid crystal. The highest contrast of interference pattern is observed when polarizers are crossed. That means that intensity of light is mostly determined by the phase difference between ordinary and extraordinary light beams propagating in the droplet. Since the shape of the droplet before isotropisation transition does not change, the major contribution to the phase difference is due to the refractive index decrease (or diminishing order parameter) at the droplet’s top affected by VOCs. This should result in increasing distance between interference fringes. The exact relationship between the order parameter and light rays phase difference can be determined by a careful study of the droplet structure

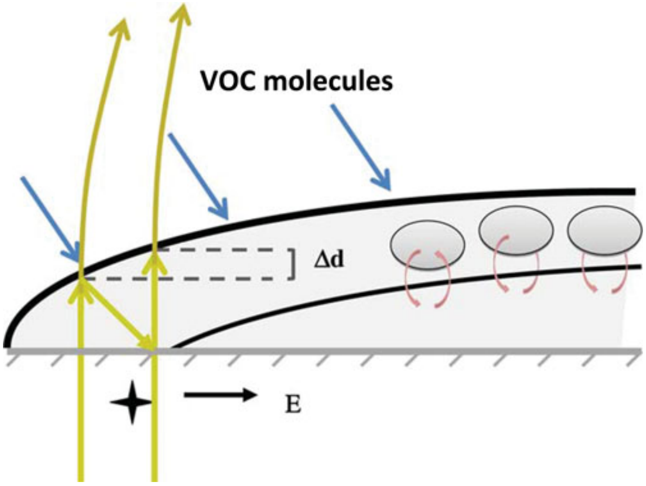

Figure 2. Schematic representation of the droplet, gas diffusion and interference between two light beams (explanations are in the text).

before it is affected by VOCs. This is a subject of future publications; here only the results related to pre-transitional changes in interference pattern are presented (Figure 3). It can be easily seen that the minima of light intensity shift away from the droplet's edge and this becomes visible before the bubbling or isotropisation occurs. The first detectable shift of interference minima happens in c.a. 10s after injection of VOCs (Figure 3) and, therefore, corresponds to a rising part of the curve shown in Figure 1 (this part of the graph is marked as "Int"). Careful analysis of data for the most sensitive nematic matrix (MBBA) and different VOCs shows that this shift is actually detectable at 3–6 times lower concentrations than

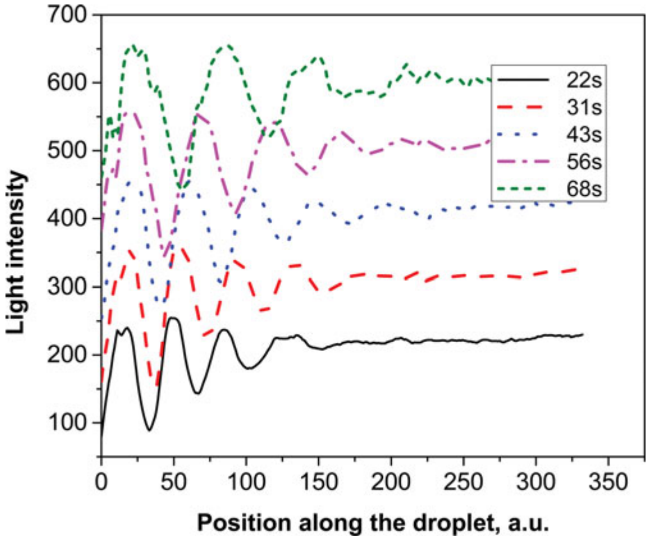

Figure 3. Changes in interference pattern corresponding to red light as time progresses after injection of VOC that occurred at c.a. 20th s.

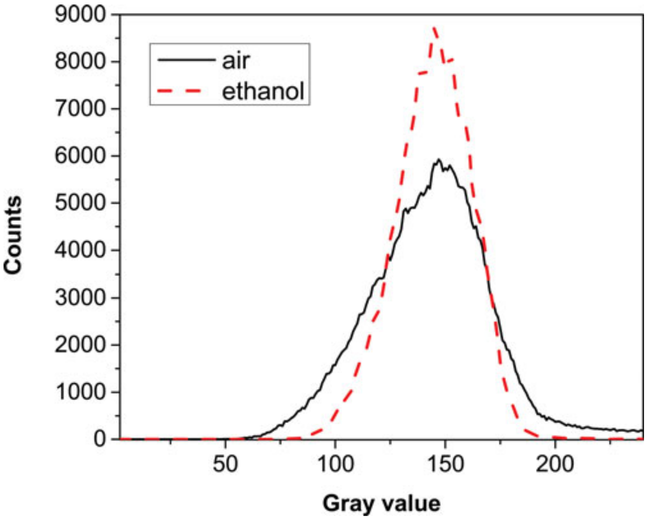

Figure 4. Changes in the brightness of chiral fingerprint structure before and after injection of ethanol.

those corresponding to saturation. The lowest detectable limits for acetone and toluene were determined to be less than 60μL/L that is well below corresponding exposure limits of 474μL/L and 420μL/L established by US government.

One of the objectives of this work was also to demonstrate that the use of chiral or twisted nematic LCs for gas detection is not limited to cholesteric materials with the selective reflection band lying in a visible range. The changes in helical pitch can also be easily observed if chiral nematic LCs are confined to specific geometries or display a fingerprint structure. Moreover, for some applications this may be more advantageous than using nematic droplets, the size and shape of which may be difficult to control. Chiral dopants with different chemical structures can also be used to enhance selectivity of LC response to specific gas molecules. In a present work the chiral liquid crystals with the helical pitch lying outside of visible range were used. Helical twist was induced in nematic LCs (MBBA, pentylcyanobiphenyl) by chiral dopants available commercially and synthesized in the lab. Here we present the results for chiral nematic mixture based on MBBA and ethylbenzylamine. Chiral droplets were spread over the surface in order to observe a distinct fingerprint structure through the microscope. All other details of the experiments were the same as in the case of nematic films. Almost immediately after injection of the VOC, the brightness and the contrast of the film changed, although the shape and the details of fingerprint structure remained the same. The diminishing contrast can be explained in terms of the CLC order parameter decrease in the areas that were affected by a diffusion of VOC molecules. These changes can be quantified by calculating the light intensity distribution (Figure 4) in the pictures taken at different VOC concentrations before isotropisation transition. Significant narrowing of dynamic range can be seen in Figure 4 when CLC film is exposed to ethanol vapor. The narrowing is an indicator of VOC presence in the air.

The drawback of using CLC droplets smeared over the surface is obvious: although they can be used in any laboratory to study the effects of VOC's diffusion, but they are too easily disturbed and unstable for any real life application. Thus, it is important to underscore the importance of the confinement of CLCs in certain geometries (for example, in micro grooves) in order to create reliable, highly sensitive VOC sensors. Our experiments show that such a confinement improves the stability of the structure and results in uniform optical changes over the larger area. Quantitative analysis of the observed changes and its application for determination of low VOC concentrations will be presented in future publications.

4. Conclusions

The concentration of VOCs (ethanol, toluene and acetone) in the air can be determined by the analysis of interference patterns inside the nematic droplets, rather than detection of isotropisation transition. The interference minima shifts correspond to certain concentrations of gas molecules and these concentrations can be determined by analyzing interference pattern. The detection limit of VOC molecules based on this principle is shown to be three to six times lower than that based on the detection of isotropisation transition. The analysis of contrast changes in CLC fingerprint structures, rather than shifts in spectral position of the selective reflection band, also results in detection of much smaller concentrations of VOCs.

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