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Nonlinear features of the transition of a liquid crystalline mixture into an isotropic state under the action of alcohol vapors

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The work of an optical sensor for determining the concentration of alcohols, in particular methanol, ethanol and isopropanol, based on a liquid crystal sensitive element, was studied. The sensitive element is a mixture of cholesteric liquid crystal CB15 and nematic impurity E7. The detection and reaction of the sensitive element to the presence of alcohol vapors is investigated.

Keywords: optical sensor, E7, alcohols vapor, CB15.

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Introduction

Optical gas sensors based on liquid crystal sensitive elements are a promising research direction in the field of electronics today [1-3]. Such sensors can detect substances in a gaseous state, in particular gases-markers of pathological conditions, as well as a whole range of organic substances, exceeding the concentration of which is unacceptable in production.

Alcohols, particularly methanol, ethanol, and isopropanol, which have been investigated, are flammable, colorless, and readily soluble in water. Their main application is in the medical and chemical industries, and also they can be used as fuel. All these substances are toxic to the human body to varying degrees [4, 5].

Thus, ethanol can be present in the mixture of human exhaled gases and serve as a biomarker of pathological conditions, the most obvious of which is alcohol intoxication. In addition, measurement of ethanol concentration may be necessary in other industries, for example, in chemical industries, distilleries, etc.

Methanol, in turn, is more toxic than ethanol, so it represents a greater danger for people [5]. Measuring its concentration in production is also important, in addition, due to the liquid crystal sensitive element, it is possible to distinguish between methanol and ethanol by the type of characteristic graphs. Such an opportunity can be useful for detecting low-quality alcohol, where more expensive ethanol can be replaced by methanol.

Chromatography and mass spectrometry methods are currently used to perform the above measurements [6, 7]. These methods require the presence of qualified personnel to perform measurements, are time-consuming, and also require specialized and expensive equipment. The introduction of new technologies for the analysis of the exalted gases mixture for the diagnosis of diseases is currently limited by a number of factors, in particular, the sensitivity to certain substances and the relative universality of the sensors.

I. Sensitive element

In the conducted research, the sensitive element of the optical sensor is a liquid crystalline cholesteric-nematic mixture consisting of a nematic liquid crystal E7 and an active impurity CB15 [8]. Quantitatively, the presence of an optically active impurity in the mixture is 37%. This amount of cholesteric impurity allows the mixture to be stable and respond well to changes in the concentration of the analyte substance in the environment.

The determination of the presence and concentration of alcohol vapors in the studied volume is based on the change in the optical properties of the liquid crystal mixture under the influence of the analyte.

Analysis of the interaction of alcohols, as large and structurally similar organic molecules with a liquid crystal mixture of a sensitive element, is close to the interaction of a similar sensor with acetone vapors [9].

Alcohols are derivatives of hydrocarbons in the molecules of which one or more hydrogen atoms are replaced by hydroxyl groups -OH. Alcohols can be classified according to the number of hydroxyl groups present - monoatomic, diatomic, and polyatomic [10, 11]. Thus, in this work, monoatomic alcohols are presented as the studied substances - methyl ($CH3OH$), ethyl ($C2H5OH$), and isopropyl ($CH3CH(OH)CH3$).

Alcohols exhibit weak acidic properties, such properties are due to the high polarity of the bond in the hydroxyl group. The polarity of alcohol molecules can be characterized by dipole moments, so ethyl alcohol has a dipole moment of 1.68 D, methyl alcohol - 1.69 D, and isopropyl alcohol - 1.66 D [12, 13].

Thus, considering the E7 liquid crystal mixture, which consists of four different, but structurally similar, liquid crystal substances - derivatives of cyanobiphenyls (4-alkyl-4-cyanobiphenyls), we can consider it homogeneous, since there is no specific interaction between different components. The general structure and percentage composition of the E7 mixture are shown in Fig. 1.

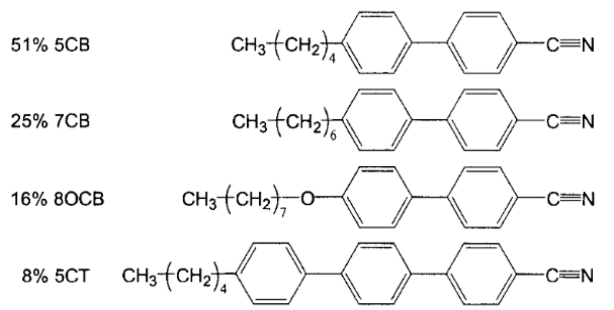

Fig. 1. Liquid crystalline substances contained in the E7 mixture and their percentage ratio.

The optically active admixture of cholesteric liquid crystal CB15 has a general structure similar to the components of the E7 mixture [14]. Namely, CB15 differs from 5CB by replacing the pentyl radical with a branched 2-methylbutyl with an asymmetric carbon atom, thanks to which it induces helical twisting in the system, but significant changes in orientational ordering are not observed. In general, the used liquid crystal mixture E7 and SV15 can be considered qualitatively homogeneous. That is, we get a cholesteric matrix that can interact with alcohol molecules.

The process of changing the optical characteristics of the liquid crystal mixture under the influence of alcohols is based on the change in the pitch of the cholesteric spiral during the interaction, which is described by expression (1). This expression reflects the change in the pitch of the cholesteric spiral in the first approximation.

$$p^{-1} = p_0^{-1}(1-w) + k_p w(1-w) + p_d^{-1} w \qquad (1)$$

The further principle of the interaction of alcohols with a liquid crystal mixture is similar to the interaction with acetone [15]. Thus, when the concentration of alcohol vapors increases and a certain critical concentration is reached, the orientational order parameter of the liquid crystal mixture decreases to a threshold value, after which the mixture transitions into an isotropic phase [16-18]. The reverse phase transition occurs similarly when the concentration of alcohol vapors decreases, in which case we observe the recovery of the initial color of the liquid crystal mixture. These processes reflect the basis of the operation of the presented liquid crystal optical sensor.

Also, based on previous experiments with similar sensors, it can be concluded that changes over time in the process of absorption of evaporated substances are qualitatively the same for all three color curves and to some extent reflect changes in the degree of optical transmittance [19-21]. We accept these changes as an analytical criterion for the action of alcohols.

II. Photodiode receiver for determining the transient characteristics of a sensitive liquid crystalline element

Determination of the intensities of the three spectral components and subsequent construction of graphs of the transition of the liquid crystal sensitive element to the isotropic state is carried out using the receiving photodiode module TCS3490 [22].

The basis of the receiver is a segmented circular photodiode module consisting of 16 separate photodiodes. 4 photodiodes for each spectral component - red, green, blue and infrared (Fig. 2).

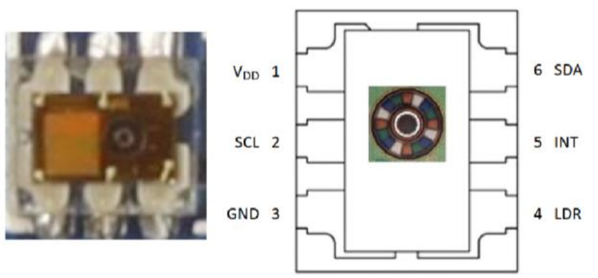

Fig. 2. Appearance and general structure of the TCS34903 photosensitive element

Each spectral component is served by a separate analog-to-digital converter. The high dynamic range of 1 to 1,000,000 and high speed allow the module to be used for measuring the level of ambient light, determining color temperature, controlling industrial processes, and medical diagnostics.

The spectral characteristics of the module are quite satisfactory for obtaining the transient characteristics of the liquid crystal sensitive element. The general spectral characteristics of the receiving module are shown in Fig. 3.

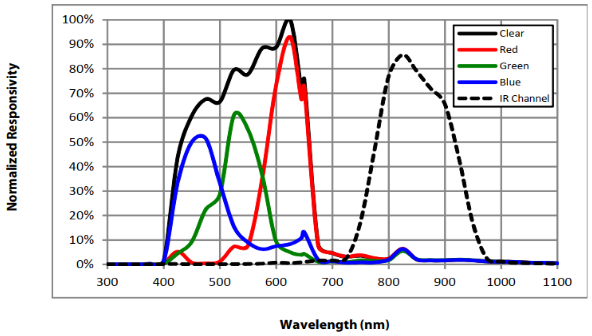

Fig. 3. Spectral characteristics of the receiving photodiode module TCS34903 [22].

In this case, we remove three spectral components for the study. The infrared spectrum is not used, due to the much smaller, about one hundred times, intensity obtained, but in general it repeats the typical appearance and characteristic points of the other three components. Other components and the general structure of the hardware part of the sensor are given in [9]

III. Experiment

The measurements of the change in transmission intensities of the optical liquid crystal sensor under the influence of various alcohols also showed similarities with similar studies of the interaction of the liquid crystal sensor with acetone.

Thus, the experiment with ethanol, the results of which are shown in Fig. 4, 5 clearly visualize the transient processes occurring in the sensitive element.

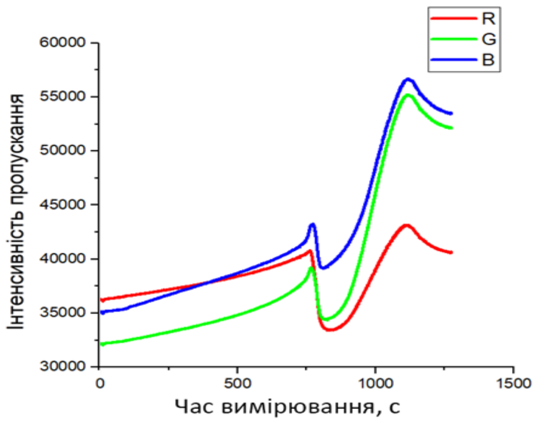

Fig. 4. The curve of change in the transmission intensity of a sensitive liquid crystal element under the influence of ethanol with a concentration of 0.5 ml.

In general, we can observe several typical areas during the transition of a sensitive element to an isotropic state. Thus, the first section represents a slow increase in the transmission intensities of all three components of the spectrum. The second section represents the trigger peak, which indicates the beginning of the intense transition of the mixture into the isotropic state, while the transmission intensities initially decrease slightly, especially for the red component. The next plot shows a sharp transition and increase in transmission intensities, especially for the green and blue components. The next peak reflects the moment of the beginning of the reverse process and, accordingly, the transition of the sensitive element to the initial state.

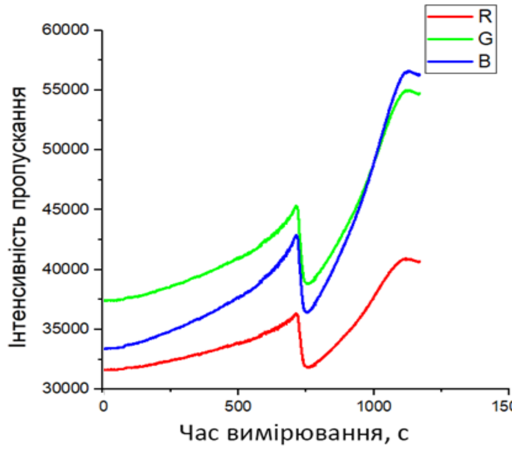

Fig. 5. The curve of changes in transmission intensities for a sensitive liquid crystal element under the influence of ethanol with a concentration of 1 ml.

For the one shown in fig. 5 of the experiment with an increased concentration of ethyl alcohol to 1 ml, a slight decrease in the transition time can be observed. In addition, there is a special characteristic point that appeared in experiments with acetone, namely the intersection of the intensities of the green and blue components of the spectrum.

The interaction with methyl alcohol, as can be seen in Fig. 6, is much weaker - despite the higher concentration (2 ml), the registered changes in transmission intensity are significantly smaller, and there are no signs of a change in the phase state.

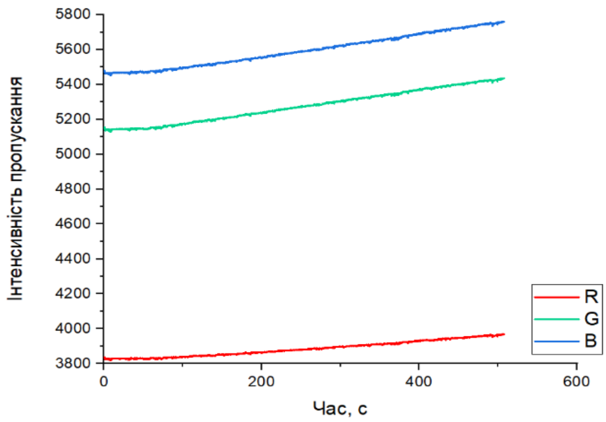

Fig. 6. Graph of changes in transmission intensities of a liquid crystal sensitive element when interacting with vapors of methyl alcohol, concentration 2 ml.

Next, a mixture of methyl and isopropyl alcohol in the proportions of 50 to 50 was placed in the volume of the sensor. The reaction of this mixture is close to the interaction of the sensitive element with ethyl alcohol. The concentration of the mixture in the studies was 0.5 (Fig. 7) and 1 ml (Fig. 8)

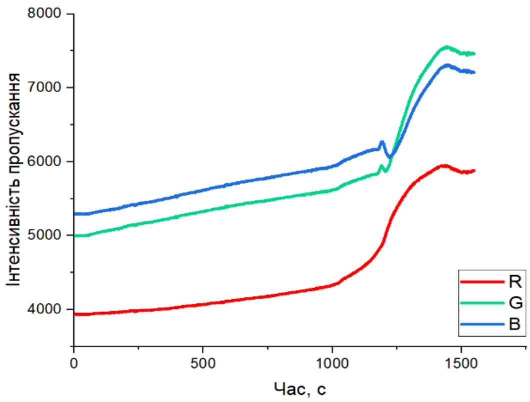

Fig. 7. Graph of the transition to the isotropic state of a sensitive liquid crystal element under the action of a mixture of methyl and isopropyl alcohol with a concentration of 0.5 ml.

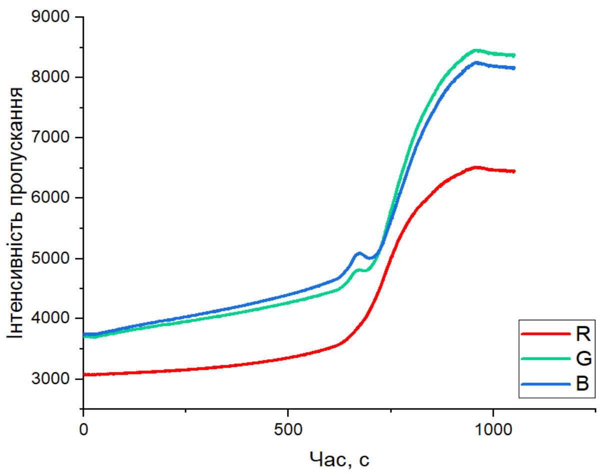

Fig. 8. Graph of the transition to the isotropic state of a sensitive liquid crystal element under the action of a mixture of methyl and isopropyl alcohol with a concentration of 1 ml.

The results of the measurements coincide with the expectations and correspond to similar results that were carried out with other organic solvents, in particular - acetone.

Conclusions

As a result of the study on the interaction of alcohol vapors with a liquid crystal sensitive element, we obtained results that correlate well with previous studies. The relatively low interaction of methyl alcohol with the sensitive element of the sensor can be compensated by heating the alcohol before placing it in the measuring volume of the sensor. In general, when interacting with alcohols, the liquid crystal mixture based on E7 nematic and CB15 cholesteric shows somewhat worse sensitivity than when interacting with acetone.

Another important result is the confirmation of the general typical form of graphs illustrating the transition of a liquid crystal mixture to an isotropic state. In contrast to the predicted linear transition, with a quick jump-like reaction of the sensitive element upon reaching the critical concentration of the analyte substance, already in the second series of experiments we obtained a clear reaction stretched over time, with characteristic points.

The obtained results are very similar to the manifestation of the so-called "blue phase" of the used liquid crystal mixture [23-25]. It was previously established that the "blue phase" for some liquid crystal mixtures is manifested in the vast majority under the influence of temperature, and not during interaction with surrounding substances, but research continues [26]. Further research will be aimed at establishing the correspondence between the known transition of this liquid crystal mixture into the "blue phase" under the influence of temperature, and the resulting transitions during interaction with substances and analytes.

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Нелінійні особливості переходу рідкокристалічної суміші в ізотропний стан під дією парів спиртів

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Проведено дослідження роботи оптичного датчика для визначення концентрації спиртів, зокрема, метанолу, етанолу та ізопропанолу, на основі рідкокристалічного чутливого елементу. Чутливий елемент представляє собою суміш холестеричного рідкого кристалу CB15 та нематичної домішки E7. Досліджується детектування та реакція чутливого елементу на присутність парів спиртів.

Ключові слова: оптичний сенсор, E7, пари спиртів, CB15.