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INVESTIGATION OF SPECTRAL CHARACTERISTICS OF CHOLESTERIC LIQUID CRYSTALS AT CARBOHYDRATES INFLUENCE

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Розглянута концепція взаємодії холестеричних рідких кристалів із вуглеводами з метою створення матеріалу активного середовища первинного перетворювача сенсора вуглеводів. Показано, що існує загальна тенденція зменшення кроку надмолекулярної спіральної структури з ростом концентрації водних розчинів для всіх досліджених вуглеводів. Досліджені їхні спектральні характеристики для різних концентрацій водних розчинів вуглеводів

Ключові слова: спектральні дослідження, холестеричні рідкі кристали, вуглеводи, вуглеводи, первинний перетворювач, оптичний сенсор

Рассмотрена концепция взаимодействия холестерических жидких кристаллов с углеводами с целью создания активной среды первичного преобразователя для датчика углеводов. Исследованы их спектральные характеристики для различных концентраций водных растворов углеводов. Показано существование общей тенденции уменьшения шага надмолекулярной спиральной структуры с ростом концентрации водных растворов для всех исследованных углеводов

Ключевые слова: спектральные исследования, холестерические жидкие кристаллы, углеводы, первичный преобразователь, оптический сенсор

1. Introduction

Determination of the concentration of the most common carbohydrates in the human body, food, pharmaceutical forms is a topical issue in medicine for diagnosing pathologies, and in the diet therapy for determining the carbohydrate concentration in food. Optical sensor systems in which detection of carbohydrates is based on the change in the spectral characteristics of the sensitive medium are the most promising. However, the vast majority of such optical systems have a number of unresolved problems caused by a difficulty of registration of the selected optical effect, or a complex multi-layered structure of the sensing element. This complicates their application mainly because of the high cost.

We suggest using a cholesteric liquid crystal with the reflection band, which lies in the visible spectrum as the sensing element of optical carbohydrate sensors.

2. Literature review and problem statement

Biosensors for determining the carbohydrate level are widely developed, most of which are electrochemical, namely amperometric. The operation of such biosensors is governed by enzymatic reactions. In [2–6], single-layer and multi-layer carbon nanotubes are used to increase the sensitivity of biosensors. Such glucose biosensors are highly selective and have a glucose determination range of 4–24 mM. Amperometric biosensors for lactose determination are in the range of 0.3–0.6 mM, and biosensors for fructose determination – in the range of 1–100 mM [7].

In addition to the electrochemical principle, research is carried out in the area of the development of optical systems, in which the detection of carbohydrates is based on the change in the spectral characteristics of the sensitive medium. In [8], films based on polystyrene-b-poly (2-vinylpyridine) (PS-b-P2VP), functionalized with 2-(bromomethyl) phenylboronic acid are used as a sensing material of the optical fructose sensor. A fragment of boric acid, introduced in the layered matrix can reversibly bind to fructose, providing photonic properties to the PS-b-P2VP film. The films have a fructose detection limit of up to 500 mM in water, causing a significant color change from blue to orange.

In [9], the development of optical carbohydrate sensors based on phenylboronic acid (PBA) and its derivatives as sensing materials is considered. Different chromophores and fluorophores in combination with the PBA film are used for developing sensing elements of PBA-based optical sensors.

In [10], the possibility of using surface plasmon resonance for developing the fructose sensor is shown. The film of 3-aminophenyl boric acid and L-glutamic acid (2,2,-2)-tryhloretyl ether is used as the sensing element. The interaction with fructose causes a shift to the red region of maximum absorption of surface plasmon resonance. A good correlation between the wavelength shift and fructose concentration is obtained, which indicates the possibility of developing a sensor for quantitative measurement of fructose.

In [11], the scheme of the glucose biosensor based on enzyme-modified inorganic/organic transparent films Prussian Blue is considered. The films change color under the influence of glucose, which can form the basis of developing optical sensors.

To resolve the problems caused by the difficulty of registration of the selected optical effect, a complex multi-layered structure of the sensing element, and the high cost of the active medium material, we propose to use a cholesteric liquid crystal as a material for the sensing element of optical carbohydrate sensors. The information signal in such sensors is formed by selective reflection (transmission) of light in the sensitive medium of primary converters of optical sensors [12, 13].

3. Research goal and objectives

The goal of the paper was to investigate the spectral characteristics of the cholesteric liquid crystal as an active medium of the primary converter of carbohydrate sensors.

To achieve this goal, the following objectives were formulated:

– to perform spectral studies of samples based on cholesteric liquid crystals doped with aqueous carbohydrate solutions;

– to carry out the analysis of the results;

– to draw conclusions based on the analysis of experimental results for the feasibility of using cholesteric liquid crystals as an active medium of primary converters of carbohydrate sensors.

4. Experimental study of spectral characteristics of carbohydrates

The most common carbohydrates are glucose, fructose and lactose. *Glucose* is a colorless crystalline substance, readily soluble in water. The chemical formula and the spatial structure of glucose are shown in Fig. 1. Like other monosaccharides, glucose exists in several forms. The crystalline glucose (α-form), when dissolved in water, first takes the chain, and then – β-form. The chain form exists only in solutions, moreover, in small quantities. Such forms of organic compounds, able to pass into another, are called isomeric.

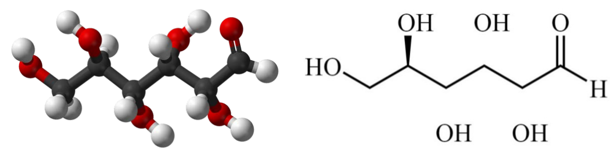

Fig. 1. The spatial structure and the chemical formula of the glucose molecule [14]

The chemical properties of glucose are similar to those of polyols. Glucose is widely used in medicine as a universal toxicide. Blood glucose determination is necessary to identify the presence and type of diabetes in humans. During diabetes treatment, diet is important, which lies in sharply limited intake of carbohydrates, especially glucose. Therefore, control of it in food is a topical issue.

Fructose is a carbohydrate from the monosaccharide group, colorless crystalline substance, readily soluble in water. The chemical formula and the spatial structure of fructose are shown in Fig. 2. The blood and urine fructose control is conducted to determine the nature of pathological changes in the human body. The fructose control in foods is also important since high fructose leads to the development of heart diseases and diabetes.

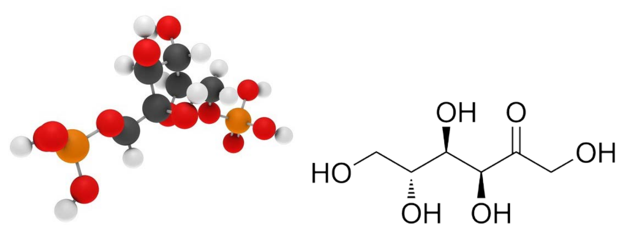

Fig. 2. The spatial structure and the chemical formula of the fructose molecule [14]

Lactose is a milk sugar. The chemical formula and the spatial structure are shown in Fig. 3. The lactose control in food is important, since 10–20 % of the population in Western Europe and up to 90 % in Asian countries cannot digest lactose. Such people can only eat specially manufactured dairy products, which contain a very small amount of lactose. In the dairy industry, the lactose control in milk is important for the fermentation process in the manufacture of dairy products.

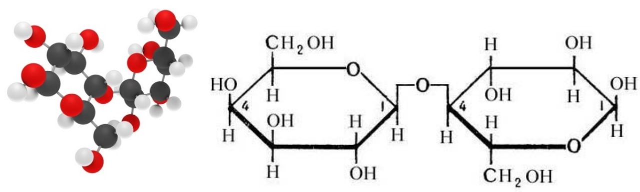

Fig. 3. The spatial structure and the chemical formula of the lactose molecule [14]

Based on the above, we can conclude that the carbohydrate control is extremely important in medical diagnostics, food, biotechnology and pharmaceutical industries [1].

The problem of detection of simple carbohydrates is not fully resolved, so intensive research is carried out in this area. Modern methods for carbohydrate determination require sophisticated equipment and, therefore, qualified personnel [1]. Therefore, the development of sensors for rapid analysis of carbohydrates is the urgent problem.

To obtain experimental samples, aqueous solutions of carbohydrates, namely, glucose, lactose and fructose in certain concentrations were added to the cholesteric mixture. The resulting mixtures were stirred for 5 minutes.

To measure the spectral characteristics and their changes under the influence of carbohydrates, the spectrophotometer USB-2000 in the range of 200–1100 nm was used.

Processing of experimental results was carried out using the OriginPro 8 software. The resulting spectral dependences were approximated by the Gaussian functions, making it possible to determine the wavelength of the position of the minimum light transmission of the samples.

The results of the studies of liquid crystal materials with the supramolecular helical structure and aqueous solutions of various concentrations of carbohydrates, which can be the basis for low-cost optical registration systems of simple carbohydrates are given below. The object of the study was the multicomponent cholesteric mixture BLO-61, EM Industries production, based on 5CB (4-cyano-4'-pentylbiphenyl). Its feature is the high temperature stability of optical properties. The concentration of simple carbohydrates in the aqueous solution ranged from 5 % to 40 %. The total content of the carbohydrate solution in the liquid crystal was 0–80 %.

Fig. 4 shows the dependence of the change of the minimum light transmission wavelength on the concentration of the 10 % aqueous solution of glucose, fructose and lactose in the liquid crystal material.

Two distinctive areas can be identified in all three curves, namely, the area of low concentration of the aqueous carbohydrate solution (25–45 %) and the area of high concentration (over 45 %). The area of low-concentration aqueous carbohydrate solutions is characterized by a monotonic decrease in the minimum transmission wavelength, and thus the helix pitch with increasing concentration of the aqueous solution. The spectral sensitivity coefficient of the cholesteric matrix is different for aqueous solutions of different carbohydrates. Fig. 5 shows the dependence of the spectral sensitivity coefficient on the aqueous carbohydrate solution concentration. The maximum spectral sensitivity coefficient is observed in aqueous glucose solutions.

Fig. 6–8 show the dependences of the minimum transmission wavelength of the LC-carbohydrate system in all investigated carbohydrate concentrations

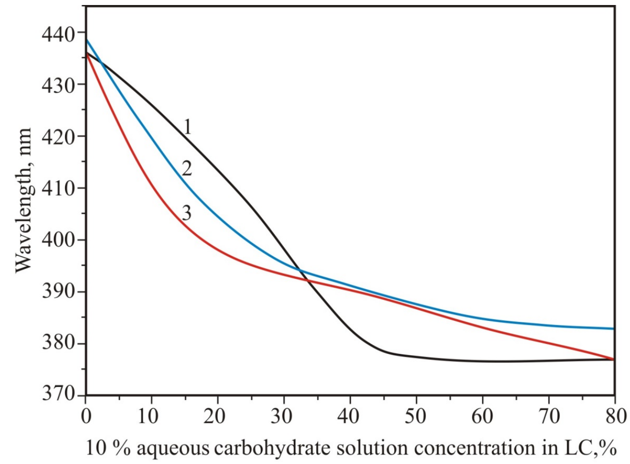

Fig. 4. The dependence of the change of the minimum light transmission wavelength on the 10 % aqueous carbohydrate solution concentration in LC: 1 – glucose; 2 – fructose; 3 – lactose

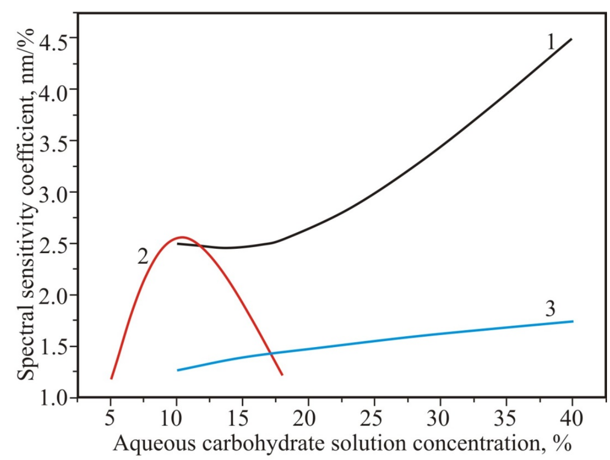

Fig. 5. The dependence of the spectral sensitivity coefficient on the aqueous carbohydrate solution concentration: 1 – fructose; 2 – lactose; 3 – glucose

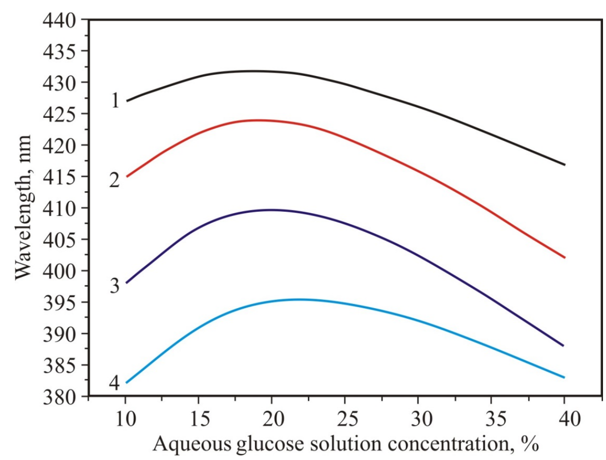

Fig. 6. The dependence of the minimum transmission wavelength of the LC-glucose solution on the aqueous glucose solution concentration: 1 – 10 % glucose solution concentration in LC; 2 – 20 % glucose solution concentration in LC; 3 – 30 % glucose solution concentration in LC; 4 – 40 % glucose solution concentration in LC

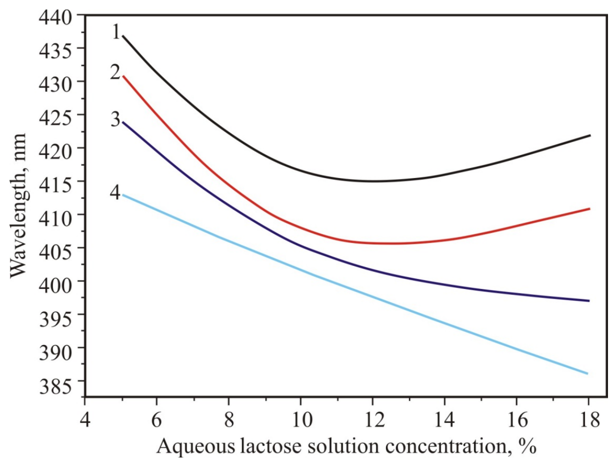

Fig. 7. The dependence of the minimum transmission wavelength of the LC-lactose solution on the aqueous lactose solution concentration: 1 — 10 % lactose solution concentration in LC; 2 — 20 % lactose solution concentration in LC; 3 — 30 % lactose solution concentration in LC; 4 — 40 % lactose solution concentration in LC

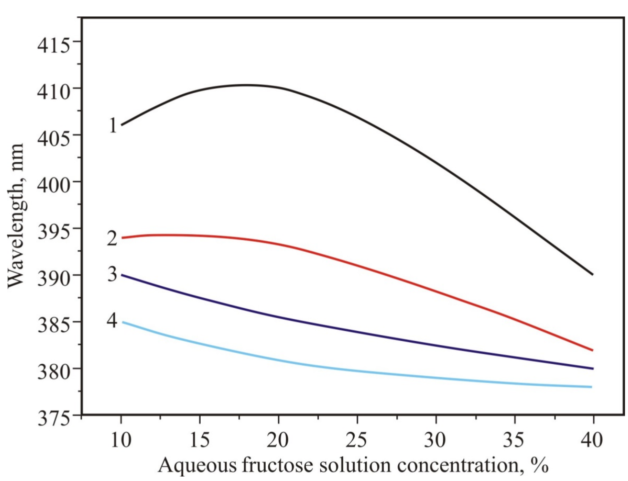

Fig. 8. The dependence of the minimum transmission wavelength of the LC-fructose solution on the aqueous fructose solution concentration: 1 — 10 % fructose solution concentration in LC; 2 — 20 % fructose solution concentration in LC; 3 — 30 % fructose solution concentration in LC; 4 — 40 % fructose solution concentration in LC

Similar dependences are observed in all investigated carbohydrates. The maximum shift towards an increase (glucose, fructose) and decrease (lactose) in the transmission wavelength is observed in all carbohydrates at a certain concentration of aqueous solutions.

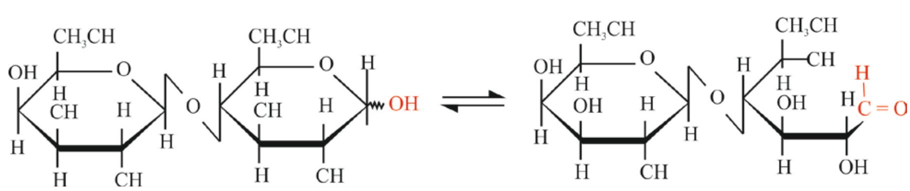

Fig. 10. Isomeric forms of lactose in aqueous solution

5. Analysis of the mechanisms of interaction of cholesteric liquid crystals with aqueous carbohydrate solutions

Based on the analysis of the results, the mechanism of interaction of the aqueous solution of simple carbohydrates and multi-component liquid crystal chiral mixture is proposed. First, let us consider the features of aqueous solutions of simple carbohydrates. The equilibrium mixture of cyclic and open forms is formed in aqueous glucose solutions since tautomerism occurs only in aqueous solutions, i. e. monosaccharides react both in the cyclic, and in the chain form. According to the Le Chatelier's principle, once the chain form begins to react with some reagent, the tautomeric equilibrium shifts towards the restoration of the concentration of the chain-form compounds.

Fructose is a monosaccharide, like glucose. It also exists in solution as an equilibrium mixture (70 % of fructopyranose, about 22 % of fructofuranose and small amounts of three other forms).

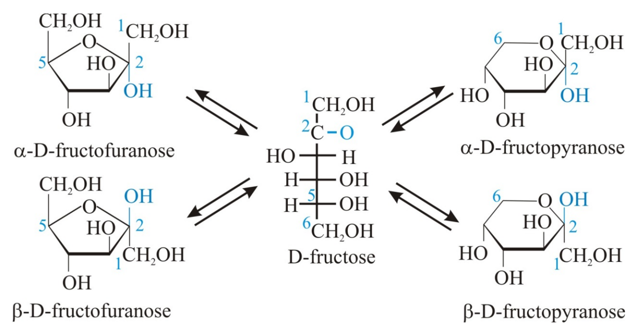

Fig. 9. Isomeric forms of fructose in aqueous solution

Lactose is a disaccharide, that is composed of two monosaccharide residues, bound by glycosylic linkage, namely, β-D-galactopyranose and α-D-glucopyranose. Glycoside hydroxyl of one monosaccharide only is used for the occurrence of the oxygen linkage in the lactose molecule. Therefore, lactose is a reducing disaccharide, since there is a glycoside OH group of the second monosaccharide which is capable of ring-chain tautomerism to form the aldehyde group:

All carbohydrates contain the carbonyl group (=C=O). Due to the polarity of linkages of C=O, the carbon atom acquires an effective positive charge (electrophilic center), and oxygen – negative charge (nucleophilic center). Therefore, carbon can be attacked by nucleophiles (e. g., negative cyanide ions) or negative parts of another molecule.

Since the individual liquid crystal components contain the cyano group (nitrile group), the interaction between it and the oxo group of simple carbohydrates to form hydrogen cyanide is likely to occur.

Hydrogen cyanide is a weak nucleophile, and the reaction is extremely slow in the acidic medium. However, the above suggests that the formation of stable associates of simple carbohydrate molecules and strongly polar components of the liquid crystal mixture resulting from the interaction between the carbohydrate carbonyl groups and the cyano group in LC is possible in the systems of simple carbohydrate aqueous solution – liquid crystal. The presence of a certain asymmetry of the associate formed (the presence of chiral center) can also be assumed. Therefore, an increase in the concentration of such associates leads to the reduction of the pitch of the supramolecular helical structure of the system and, consequently, the minimum light transmission wavelength.

6. Conclusions

1. The possibility of using cholesteric liquid crystals of the supramolecular helical structure as a material sensitive to the presence of aqueous carbohydrate solutions due to changes in the minimum transmission on spectral characteristics of cholesteric liquid crystals is shown.

2. Based on the study of the spectral characteristics, it can be argued that there is a general tendency to reduce the pitch of supramolecular helical structure with increasing concentration of aqueous solutions in all investigated carbohydrates. Furthermore, the maximum sensitivity of the cholesteric matrix is observed at low solution concentrations, which can be used for their detection. The highest spectral sensitivity coefficient is observed in aqueous fructose solutions.

3. Analysis of the data shows that the reason for the areas of abnormal behavior of the pitch at high concentrations of the aqueous carbohydrate solution is the interface when the aqueous carbohydrate solution concentration in the liquid crystal matrix exceeds 80 %. In fact, separation of the liquid crystal into separate bridges located in the aqueous carbohydrate solution is observed in this concentration range. Therefore, using the cholesteric liquid crystal as an active medium of the primary converter of carbohydrate sensors becomes impossible when the aqueous solution concentration exceeds 80 %.

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