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Interaction of amino acids with cholesteric liquid crystals: spectrophotometric evidence

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Effects of amino acids on selective reflection and optical transmission of steroid and non-steroid cholesteric liquid crystal systems have been studied. At temperatures close to the isotropic transition, optical transmission in the vicinity of selective reflection band has been shown to be highly sensitive to the presence of amino acids despite very low solubility of these substances. The response of different types of cholesterics was qualitatively similar. For nematic-cholesteric mixture BLO61, an anomalous decrease in optical transmission was observed in a narrow temperature range close to the isotropic transition, with subsequent substantial shift of the selective reflection maximum towards longer wavelengths. Possibilities are discussed of using the proposed approach in development of liquid crystal sensor materials for detection of biological substances.
Keywords: liquid crystals, composites, amino acids, optical transmission.

Исследовано влияние аминокислот на селективное отражение и оптическое пропускание стероидных и нестероидных холестерических жидких кристаллов (ХЖК). Показано, что при температурах, близких к температуре изотропного перехода, оптическое пропускание вблизи полосы селективного отражения весьма чувствительно к присутствию аминокислот, несмотря на их очень низкую растворимость. Отклик ХЖК разных типов был качественно подобным. Для нематико-холестерической смеси BL061 отмечено аномальное снижение оптического пропускания в узком температурном интервале вблизи изотропного перехода с одновременным значительным смещением максимума селективного отражения в длинноволновую область. Обсуждаются возможности применения предложенного подхода при разработке жидкокристаллических сенсорных материалов для детектирования веществ биологического происхождения.

Взаємодія амінокислот з холестеричними рідкими кристалами: спектроскопічні прояви. *О.М.Самойлов, С.С.Міненко, З.М.Микитюк, Л.М.Лисецький.*

Досліджено вплив амінокислот на селективне відбивання та оптичне пропускання стероїдних та нестероїдних холестеричних рідких кристалів (ХРК). Показано, що при температурах, близьких до температури ізотропного переходу, оптичне пропускання поблизу смуги селективного відбивання вельми чутливе до присутності амінокислот, незважаючи на їх дуже низьку розчинність. Відгук ХРК різних типів був якісно подібним. Для нематико-холестеричної суміші BL061 відзначено аномальне зниження оптичного пропускання у вузькому температурному інтервалі поблизу ізотропного переходу з одночасним значним зсувом максимуму селективного відбивання у довгохвильову область. Обговорюються можливості застосування запропонованого підходу при розробці рідкокристалічних сенсорних матеріалів для детектування речовин біологічного походження.

1. Introduction

One of the earliest practical applications that were proposed for cholesteric liquid crystals (CLC) was detection of chemical substances (in particular, vapors) by changes in selective reflection properties caused by absorption of substance molecules by a thin layer of sensor material in the cholesteric phase. The first stage of these works was summarized in [1]. Later, there was not much interest in this topic, and only a few works could be mentioned [2–4].

In recent years, development of the instrumental base and the use of functionalized LC materials allowed selective detection of a number of organic substances and gases by LC sensors [5–8]. The state of art of the present stage of research and appli cation has been reviewed in [9].

A challenging task is detection of biological substances that have low solubility in hydrophobic media using CLC sensors. An indirect way was proposed in [10], where CLC polymer films were used for detection of amino acids. A sufficient sensitivity was obtained using structural changes related to rupture of hydrogen bonds between the components of CLC polymer upon immersion into amino acid water solution. However, the question persisted on possibilities to directly detect the effects of amino acids on conventional thermotropic CLC systems.

The literature analysis did not show any studies on the effects of amino acides on optical properties of cholesterics. In fact, cholesteric matrices were generally considered as inert with respect to amino acids. A somewhat similar situation was established with so-called inert matrices like solid argon, in which conformations of distributed organic molecules (e.g., amino acids) would be the same as conformations of these molecules in vapor phase, with no intermolecular in teractions. However, a recent set of studies [11–14] shows that interaction of amino acids with argon atoms in solid state, though extremely weak, can still be detected by appropriate spectroscopic methods. In a similar way, we aimed at detection of the effects of amino acids upon spectral characteristics of CLC, with an attempt to find compositions of CLC systems and measurement conditions that could lead to observable changes in selective reflection spectra and other measurable characteristics caused by amino acids.

2. Materials and methods

The cholesteric mixture M5 consisted of 30 cholesteryl formate ($C_{28}H_{46}O_2$), 5 % cholesteryl butyrate ($C_{31}H_{52}O_2$) and 65 % cholesteryl nonanoate $C_{36}H_{62}O_2$. These cholesterol esters were obtained from Chemical Reagents Plant, Ukraine and used without further purification. The nematic 5CB (4-*n*-pentyl-4′-cyanobiphenyl) of 99.5 % purity was obtained from Chemical Reagents Plant, Ukraine. The chiral nematic mixture BLO61 was obtained from Merck, Germany. Amino acids serine and proline of biological origin had melt ing tempertures of 228°C and 210°C, respectively. The amino acids were added to the liquid crystal mixture in the isotropic state; the presence of unsolved particles (observed under optical microscope) was neglected, assuming that actual concentration of the dopant was equal to its solubility limit.

Optical transmission and selective reflection spectra were measured in sandwich-type LC cells (20 μm thickness) using a Shimadzu UV-2450 spectrophotometer (Japan) within 300–900 nm spectral range. The cell walls were treated with polyvinyl alcohol water solution and, after drying, rubbed in one direction to obtain the planar texture. The sample was introduced between the cell walls using the capillary forces at the temperatures above the transition to the isotropic phase. The measurements were done within the temperature range of 20–80°C in the heating and cooling modes, and the temperature was stabilized using a flowing-water thermostat (±0.1 K).

3. Results and discussion

From the measured transmission spectra of CLC systems doped with amino acids, we obtained the wavelength of maximum selective reflection λ_{max} as function of temperature. The results for M5 (mixture of cholesterol esters) and mixture of M5 and nematic 5CB are shown in Fig. 1.

With M5, λ_{max} slightly (but clearly and reproducibly) decreases with temperature, and addition of amino acids shifts λ_{max} towards increased helical twisting ($\lambda_{max} = np$, where n is the refraction index, and p is the helical pitch). This reflects the interaction of dopant molecules with steroidal moieties of cholesterol esters ([15]). Another possible factor could be related to chirality (optical activity) of the amino acid dopants, but,

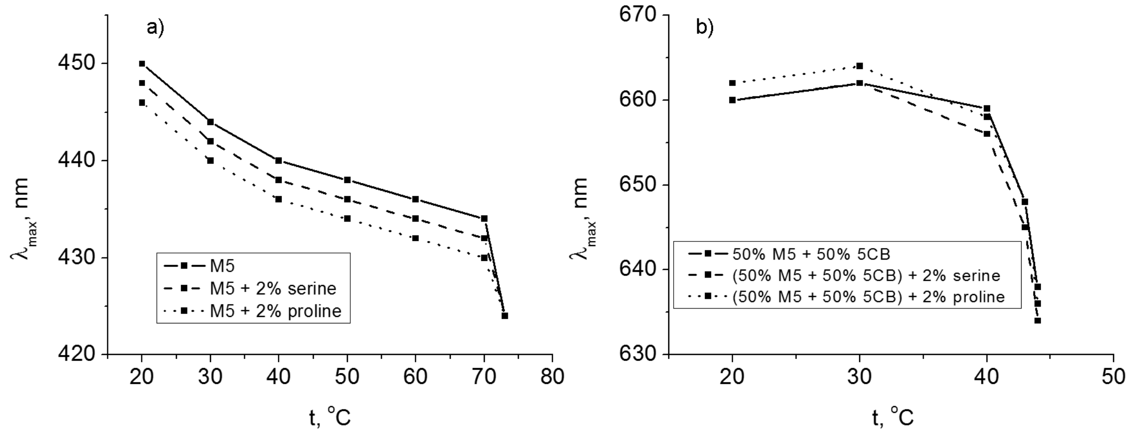

Fig. 1. Wavelength of maximum selective reflection λ_{max} as function of temperature for cholesteric systems M5 (a) and 45 % M5 + 55 % 5CB (b): ■ — undoped CLC; ♦ — CLC + serine; ▲ CLC + proline. The introduced dopant concentration was 2 %; the actual concentration corresponds to maximum solubility.

since this effect is absent with M5 + 5CB, we prefer the first explanation.

With M5 + 5CB, λ_{max} is practically unchanged with temperature. In both cases, λ_{max} decreases drastically when the isotropic transition temperature T_i is approached. The latter fact suggests testing the effects of amino acids on selective reflection at temperatures close to T_i (Fig. 2).

Thus, setting the temperature at ~ 1 K below T_i and the photoreceiver at ~ 420 nm, one could record significant changes in light transmission intensity upon addition of amino acids in minor quantities, which formally allows considering thermotropic CLC systems as sensor materials for detection of amino acids, with a technical problem of increasing the sensitivity.

For the same systems, optical transmission T was measured as function of temperature (Fig. 3). The measurement conditions were the same as for $\lambda_{max}(t)$ plots in Fig. 1 (in fact, the data were taken from the same optical transmission spectra at 600 nm for M5 and 800 nm for M5 + 5CB, i.e., sufficiently far from absorption and selective reflection bands).

In both cases, lower transmission in the presence of dopants was presumably due to scattering from unsolved particles of amino acids, which is typical for dispersions of nano- and microparticles in liquid crystals [16, 17]. The solubility of amino a cids was slightly better with M5 + 5CB and, as it could be expected, increased with temperature.

At the next stage of our studies, we used another cholesteric LC matrix, namely, chiral nematic mixture BLO61, and carried out

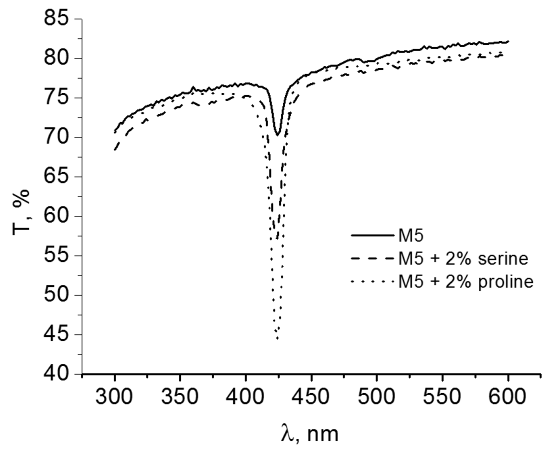

Fig. 2. Selective reflection bands of M5 at 73°C: undoped (solid line), doped with serine (dashed line), doped with proline (dotted line). T_i = 74°C.

similar experiments in the same conditions as with M5 and M5 + 5CB. This matrix was previously used as possible sensor material for detection of quercetin (it is also a substance of biological origin with very low solubility in thermotropic LC media) [18]. Fig. 4 shows the transmission spectra of BLO61 doped with amino acids. As distinct from Fig. 2, in this case the introduced quantity of dopants was much lower (0.2 %); however, in this case the maximum solubility was still below this value. We see a noticeable variation of transmission T at 390 nm, which could be recorded even at room temperature.

Since due to high birefringence of the matrix it was not possible to directly specify the location of selective reflection maximum, the values of λ_{max} were taken as the

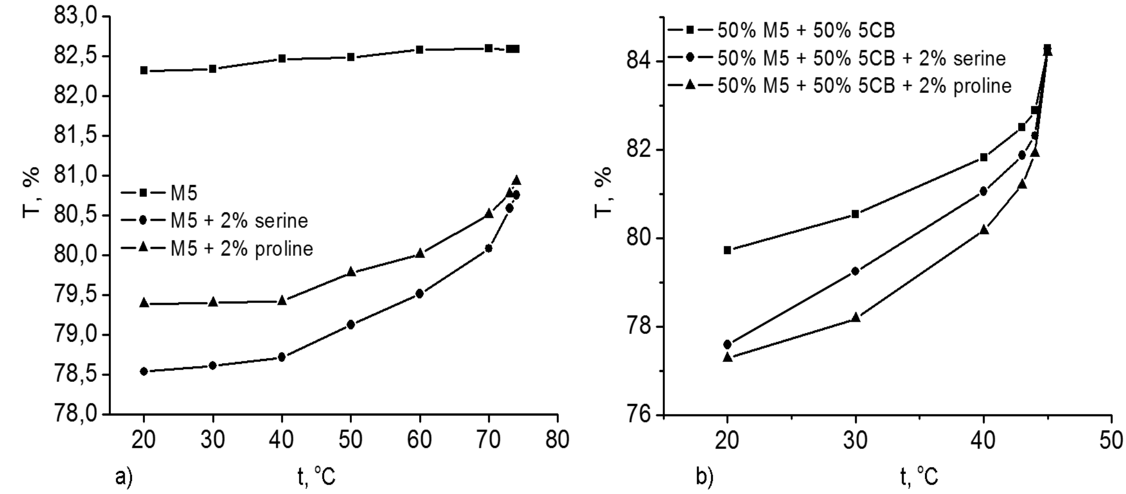

Fig. 3. Optical transmission outside the absorption and selective reflection bands as function of temperature for cholesteric systems M5 (a) at 600 nm and 45 % M5 + 55 % 5CB (b) at 800 nm: ■ — undoped CLC; ♦ — CLC + serine; ▲ — CLC + proline.

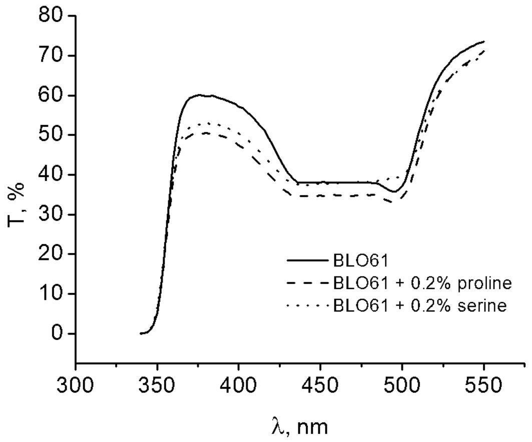

Fig. 4. Selective reflection bands of BLO61 at 25°C: undoped (solid line), doped with 0.2 % serine (dotted line), doped with 0.2 % proline (dashed line).

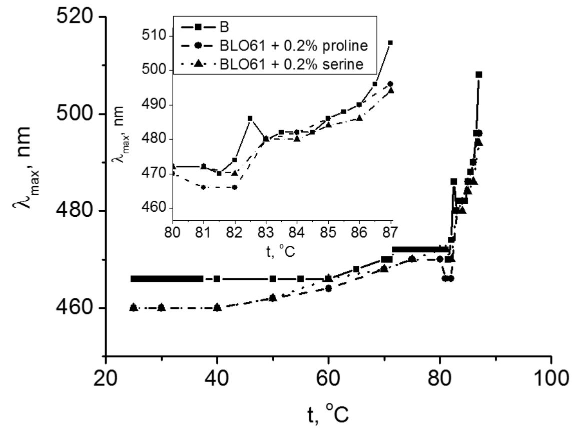

Fig. 5. Location of selective reflection band as function of temperature for chiral nematic CLC systems The region close to isotropic transition is shown in Inset.

middle of selective reflection band. The resulting λ_{max} vs. temperature plots are shown in Fig. 5.

It should be noted that with BLO61 we could observe an unusual feature in temperature dependences of optical transmission (Fig. 6). Below the isotropic transition, there was a narrow interval with a drastic decrease in optical transmission. This is not typical for most CLC systems (however, this could have been unnoticed because this temperature range is not relevant for most applications of liquid crystals). Still, similar behavior was noted for nematic LC [19]. This could be explained by deterioration of the local orientational ordering accompanied by re-arrangement of liquid crystal structure in the pre-transitional region with en-

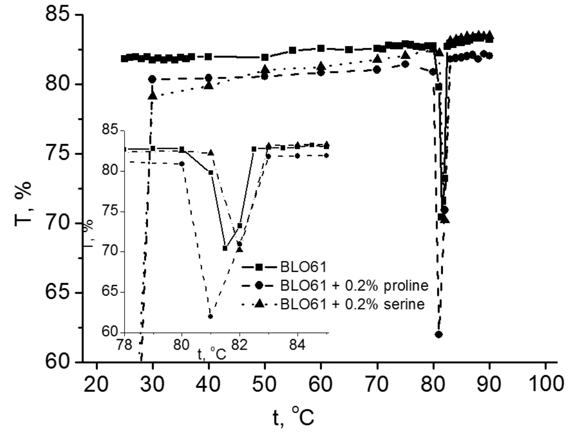

Fig. 6. Optical transmission as function of temperature (at 800 nm) for chiral nematic LC systems.

hanced light scattering on local director fluctuations. Multi-component composition of BLO61 could contribute to this phenomenon (which is accompanied by a sharp increase in λ_{max}, i.e., untwisting of the cholesteric helix). It can be noted that similar behavior was reported for a mixture of two nematics with different signs of dielectric anisotropy close to the compensation point [20].

4. Conclusion

Thus, we have shown that cholesteric liquid crystals can be used as sensor media of organic compounds of biological origin, giving a clear response even in cases of extremely poor solubility. The obtained data for amino acids serine and proline show possibilities for increase in detection sensitivity using appropriate cholesteric mixtures and measurement conditions.

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