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Effects of vitamin D group steroids on mesomorphic phase states of cholesteric sensor materials

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Effects of non-mesogenic provitamin D and vitamin D upon thermal stability of cholesteric and smectic-A phases formed by mixtures of cholesterol esters have been studied. Widening of DSC and selective reflection peaks were noted for higher (>5 %) concentrations of provitamin D, which were accompanied by deviations from linearity of concentration dependences of cholesteric — isotropic and cholesteric — smectic transition temperatures. The respective limiting concentrations for provitamins D_2 and D_3 in different matrices correlate with eutectic concentration values calculated using Schroeder-van Laar equations. The results obtained present a physico-chemical basis for development of optimized sensor materials for bioequivalent UV detectors that would meet contradictory requirements of high sensitivity and high thermodynamic stability.

Исследовано влияние немезогенных провитамина D и витамина D на термостабильность холестерической и смектической-А фаз, образованных смесями эфиров холестерина. Отмечено размытие пиков дифференциальной сканирующей калориметрии и селективного отражения для повышенных (>5 %) концентраций провитамина D, сопровождающееся отклонениями от линейности концентрационных зависимостей температур переходов холестерик — изотропная жидкость и холестерик — смектик. Соответствующие граничные концентрации для провитаминов D_2 и D_3 в различных матрицах коррелируют со значениями эвтектических концентраций, рассчитанных по уравнениям Шредера-ван Лаара. Полученные результаты могут быть физико-химической основой для разработки сенсорных материалов для биоэквивалентных детекторов УФ излучения, которые сочетали бы высокую чувствительность и термодинамическую стабильность.

In our previous papers [1, 2], we have shown a possibility to create a sensor material for dosimetry of biologically active UV radiation on the basis of cholecteric liquid crystals (CLC) doped by provitamin D (ProD). The response mechanism of such systems is based on ProD photoisomerization reaction (Fig. 1) under UV irradiation, which is monitored by recording shifts of selective reflection maximum (λ_{max}) of the cholesteric planar texture.

Effects of the reaction medium (including its liquid crystalline phase state) upon ProD photoisomerization process, as well as effects of intensity and spectral composition of UV radiation, have been a subject of numerous studies [3–8]. Advantages of the use of CLC as matrix materials for ProD have been discussed, and requirements to CLC compositions to be used as UV sensor materials have been formulated [9–11].

According to generally accepted notions [12–14], the CLC + ProD system is a liquid crystalline solution of a non-mesogenic substance, which, at low concentrations, is conventionally called a non-mesogenic dopant

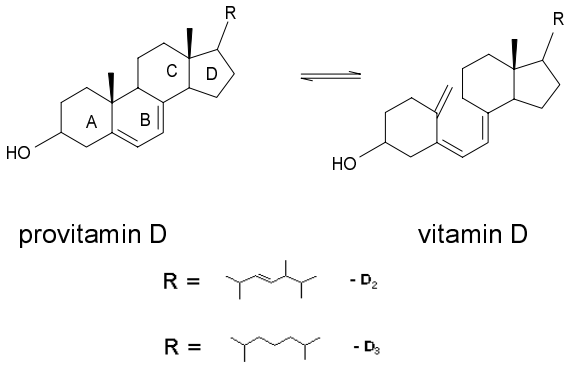

Fig. 1. General photoisomerization scheme of provitamin D group steroids.

(NMD). This system can exist as a true solution in a specified range of temperatures and concentrations. In the case of limited NMD solubility, a homogeneous solution can become (via a possible stage of metastability) a heterogeneous system (which can be characterized by the degree of its (micro)heterogeneity or described in terms of lyophilic colloids [15]); ultimately, as the most obvious manifestation, the surplus dopant can be precipitated in the form of solid particles. In developing a CLC-based sensor material, a contradiction arises — the concentration of a photoactive dopant should be as high as possible to ensure high sensitivity, and at the same time it should not exceed the solubility limit to ensure stable operational characteristics of the sensor.

The objective of the present work was to study the behavior of vitamin *D* group substances as NMD in cholesteric solvents with the aim of laying down physico-chemical foundations for optimizing the CLC sensor material composition.

In our experiments, we used the following CLC matrices:

CN (cholesteryl nonanoate);

CM (cholesteryl myristate);

CNM (60 % CN + 40 % CM; here and below the concentrations are given in mass per cent);

CNCC (60 % CN, 20 % cholesteryl caprinate, 20 % cholesteryl caprylate);

CNCCe (59.6 % CN, 32.1 % cholesteryl caprinate, 8.3 % cholesteryl caprilate).

As non-mesogenic dopants, we used ergosterol ($ProD_2$), 7-dehydrocholesterol ($ProD_3$), and ergocalciferol (vitamin D_2).

Temperatures and enthalpies of phase transitions were determined by differential scanning calorimetry (a Mettler TA 3000 thermoanalytical system, Switzerland),

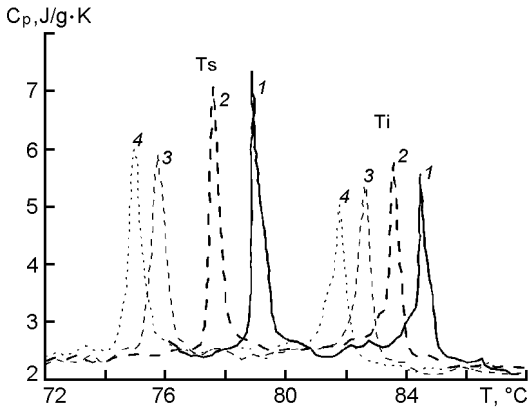

Fig. 2. DSC thermograms for the CM + $ProD_2$ system (heating): *1* — 0 % $ProD_2$, *2* — 1 % $ProD_2$, *3* — 2 % $ProD_2$, *4* — 4 % $ProD_2$.

which was also used to check the purity of the substances.

For some of the matrices (CNCC, CNCCe), DSC could not provide data on the cholesteric to smectic-A phase transition, since the corresponding peaks were smeared (in fact, hardly discernible) as it could be expected for a multi-component mixture. In these cases, the cholesteric-smectic transition temperatures (T_s) were evaluated indirectly from the color-temperature characteristics (i.e., λ_{max} (T) dependences) in the region of pre-transitional phenomena [16, 17] and checked by polarization microscopy.

Measurements of λ_{max} were carried out using a Hitachi 330 spectrophotometer equipped with a specially designed temperature-controlled cell; the sample thickness was 10 μm. The procedure of sample preparation, filling the cell and formation of the planar texture of the cholesteric phase was the same as in our previous works [1, 2, 9], with the most detailed description given in [18].

Typical DSC thermograms for CLC matrices doped with provitamin D and vitamin D are shown in Figs. 2, 3. $ProD_2$ and D_2, as typical NMD, lower the temperatures of cholesteric-isotropic (T_i) and cholesteric-smectic A (T_s) phase transitions, with the peaks getting smeared as the dopant concentration is increased. The effect of vitamin D is more pronounced as compared with the provitamin. This is in agreement with the molecular structure of these dopants (Fig. 1): the D molecule is less rigid due to breaking of the bond in ring B, which leads to lower molecular anisotropy.

Introduction of $ProD_2$ decreases T_i of CM by ~0.7 K/% in the linear region both on heating and cooling (Fig. 4, insert). In all

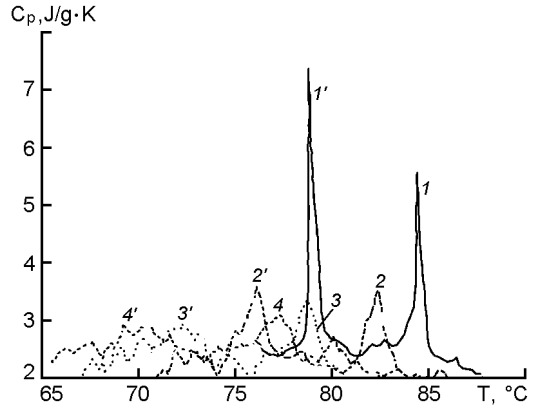

Fig. 3. DSC thermograms for the CM + D_2 system (heating): *1* — 0 % D_2, *2* — 1 % D_2, *3* — 2 % D_2, *4* — 3 % D_2. Numbers marked and not marked with primes refer to T_s and T_i peaks, respectively.

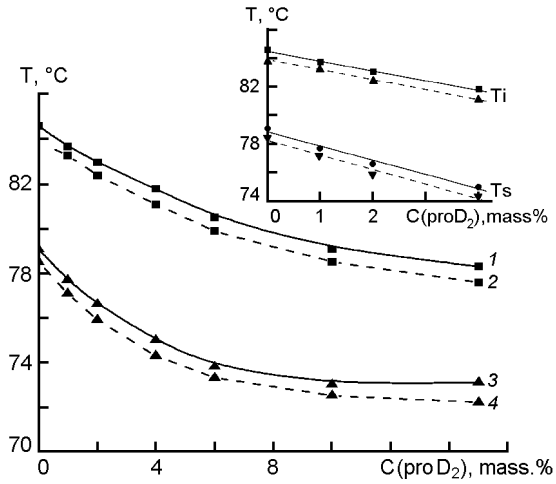

Fig. 4. Lowering of phase transition temperatures T_i (*1*– heating, *2* – cooling) and T_s (*3*– heating, *4* – cooling) in the CM matrix doped with $ProD_2$. Insert: linear decrease of T_i and T_s with dopant concentration.

the $ProD_2$ concentration range studied (up to c = 15 %), both cholesteric-isotropic and cholesteric-smectic transition peaks remained clearly discernible. At $ProD_2$ concentrations above ~5 %, the $T_i(c)$ plot became non-linear, which could be naturally related to limited solubility of $ProD_2$ (i.e., not all $ProD_2$ formally introduced into the system actually entered the thermodynamically stable homogeneous solution during the time period and in conditions of the experiment).

Effect of D_2 upon T_i is stronger (~2.5 K/%); $T_i(c)$ linearity persists up to ~5 % (Fig. 5). Its effect upon widening of the DSC peaks is also more marked as compared to $ProD_2$. The same applies to T_s — in CM, the relative T_s decrease was ~2.5 K/% with D_2 and ~1 K/% with $ProD_2$. In CN, CNM and CNCC, the effect of D_2 upon T_s was noticeably stronger than in CM (~4.2 K/%). This can be related to lower enthalpy of the cholesteric-smectic transition (~1 J/g for CN and CNM, ~3 J/g for CM). Phase transition parameters obtained for the studied matrix-dopant systems are presented in Table.

As noted above, in CNCC matrix determination of cholesteric-smectic phase transition parameters by DSC is hardly possible because of strong smearing of the corresponding peaks. Therefore, we used the helix unwinding in the vicinity of the cholesteric-smectic A transition, which is observed as a steep rise of λ_{max} (T) when T_s is approached on cooling [16, 17]. As an estimate of T_s, we assumed the temperature at which λ_{max} reached 700 nm, i.e., the temperature at which visible colors of the planar texture were disappearing [19].

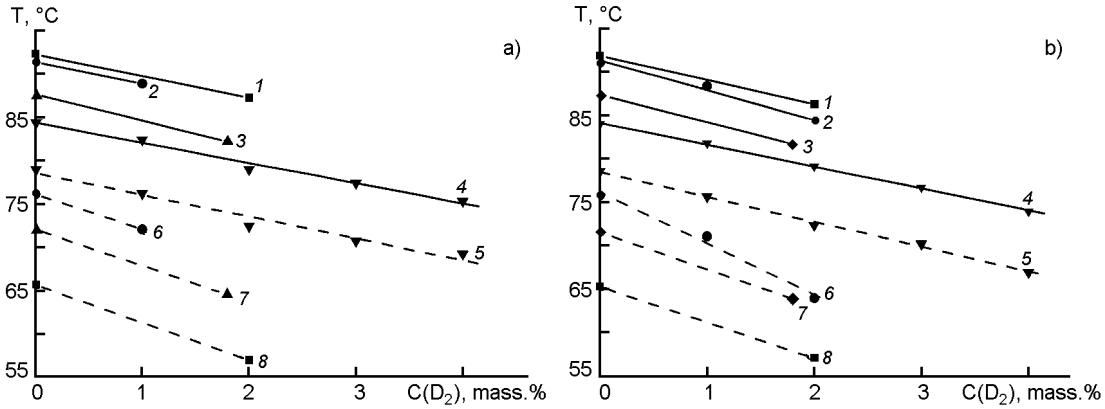

Fig. 5. Lowering of phase transition temperatures T_i (*1-4*) and T_s (*5-8*) in different matrices doped with D_2 (a — heating; b — cooling). *1,8* –CNCC; *2,6* –CN; *3,7* – CNM; *4,5* – CM

Table. Phase transition parameters of cholesteric matrices doped with $ProD_3$, $ProD_2$ and D_2

Matrix and dopant		Heating				Cooling			
		T_i, °C	ΔH_i, J/g	T_s, °C	ΔH_s, J/g	T_i, °C	ΔH_i, J/g	T_s, °C	ΔH_s, J/g
CN	0 %	91.5	1.5	76.2	1.2	91.0	1.4	75.7	1.0
	1 % D_2	89.0	1.1	72.1	0.7	88.3	1.7	74.1	0.8
	2 % D_2	–	–	–	–	84.1	1.4	73.9	0.9
CM	0 %	84.6	2.7	79.1	2.3	83.9	2.6	78.5	2.8
	1 % D_2	82.5	1.7	76.3	1.2	81.7	1.8	75.6	2.8
	2 % D_2	79.1	1.8	72.5	2.0	79.1	1.8	72.3	2.0
	3 % D_2	77.5	2	70.8	1.9	76.6	1.8	70.2	1.4
	4 % D_2	75.6	0.7	69.3	1.4	73.9	0.9	66.9	1.7
CNM	0 %	87.8	1.8	72.1	0.7	87.3	2.2	71.5	1.0
	1.8 % D_2	82.3	1.8	64.6	0.6	81.6	1.2	63.8	0.5
CNCC	0 %	92.4	1.3	65.7	0.3	91.8	1.6	65.2	0.4
	2 % D_2	87.4	1.2	57.0	–	86.2	1.3	78.5	–
CM	0 %	84.6	2.7	79.1	2.3	83.9	2.6	57.0	2.8
	1 % $ProD_2$	83.7	1.9	77.7	2.2	83.3	2.1	77.1	2.4
	2 % $ProD_2$	83.0	2.0	76.6	2.3	82.4	2.1	75.9	2.3
	4 % $ProD_2$	81.8	2.2	75.0	2.4	81.1	2.1	74.3	2.4
	6 % $ProD_2$	80.5	2.1	73.8	2.3	79.9	2.5	73.3	4.0
	10 % $ProD_2$	79.1	1.8	73	2.4	78.5	2.7	72.5	3.6
	15 % $ProD_2$	78.3	2.1	73.1	2.7	77.6	2.2	72.2	3.4
CM	0 %	84.6	2.7	79.1	2.3	83.9	2.6	78.5	2.8
	5 % $ProD_3$	80.3	2.3	–	–	79.3	2.6	70.6	2.2
	10 % $ProD_3$	79.2	2.1	–	–	77.9	2.0	69.0	2.4
	15 % $ProD_3$	78.9	2.3	70.8	1.2	77.4	2.0	69.3	4.0

It has been found that introduction of $ProD_2$ and $ProD_3$ into CNCC causes similar decreases in T_s (about 2.2 K/% at low dopant concentrations). However, with $ProD_2$ $T_s(c)$ remained linear only up to ~6 %, while with $ProD_3$ this linearity persisted also at concentrations up to ~9 % (Fig. 6). This can be presumably related to higher solubility of $ProD_3$ in cholesteric matrices (which was also assumed in [11]). These deviations of $T_s(c)$ from linearity are accompanied with worsening of the measured selective reflection spectra: starting from the same concentrations (i.e., ~6 % and ~9 %, respectively), the peak halfwidth increases, and the reflection bands become asymmetric with formation of "shoulders".

It can be concluded that linear regions of $T_s(c)$ and $T_i(c)$ plots correspond to the concentration range where the dopant is completely dissolved. Saturation of these dependences, accompanied by worsening of selective reflection peaks, indicates that dissolution is not complete, i.e., the liquid crystal system is not in the state of true thermodynamically stable solution.

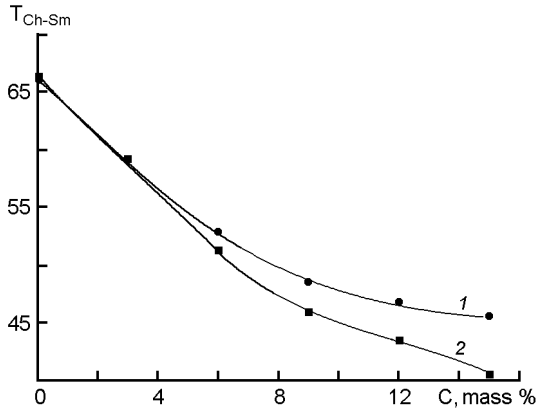

Fig. 6. Cholesteric to smectic-A transition temperature T_s for CNCC doped with $ProD_2$ (*1*) and $ProD_3$ (*2*). T_s values obtained from the selective reflection data.

As a natural next step for understanding the behavior of vitamin D steroids in CLC systems as components of limited solubility,

we studied the effects of these NMD on melting temperatures (T_m) of cholesteric matrices. (In our studies, we did not pay any specific attention to crystallization temperatures, since all the systems studied showed a marked tendency to supercooling).

Our studies were based on the Schroeder-van Laar equation [20]:

$$-\ln x_k = \frac{\Delta H_k}{R}\left(\frac{1}{T} - \frac{1}{T_k}\right), \quad (1)$$

where x_k is the mole fraction of the k-th component, ΔH_k is the melting enthalpy of the k-th component (J/mol), T_k is the melting temperature of the k-th component (K), and R (8.31 J/mol·K) is the universal gas constant. Applicability of the Schroeder-van Laar equation to liquid crystalline systems was discussed in [21, 22].

In our experiments, the DSC thermogram of CNCC showed several subsequent melting peaks, which could be expected since the composition of this matrix did not correspond to the eutectic composition of the components involved. We endeavored to modify the quantitative composition of CNCC with the aim of approaching the theoretical eutectic composition. Having all the required data for all three components of CNCC, we solved the equation system (1), finding the required quantitative composition (this matrix is designated as CNCCe). In fact, CNCCe showed just one melting peak at 331.9 K, which was in good agreement with the calculated value of 331.6 K.

The introduction of $ProD_2$ decreased the melting temperatures of the CLC matrices studied, but this decrease was less significant than that observed for T_i and T_s. The results for CNCCe are shown in Fig. 7. No clear eutectic point could be seen on the phase diagram. This can be attributed to a certain miscibility of the components in the solid state, with the picture similar to that observed for mixtures of cholesterol esters (see, e.g., [23]). Estimates of the eutectic dopant concentrations in the CLC matrices studied gave values of about 6–9 % for $ProD_2$ and 10–13 % for $ProD_3$ (higher percentage values apply to matrices melting at higher temperatures, i.e., CM and CN). Thus, our theoretical calculations using the Schroeder-van Laar equation have fully supported our assumption of higher solubility of $ProD_3$ in cholesteric matrices made from our measurements in the mesophase.

Thus, the results obtained show a clear physico-chemical picture of the effects of

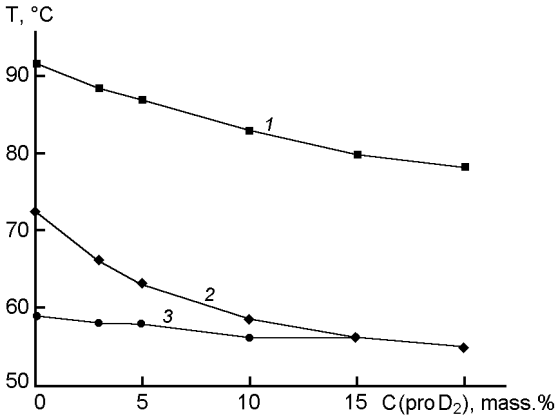

Fig. 7. Lowering of phase transition temperatures (*1* – T_i, *2* – T_s, *3* – T_m in CNCCe matrix doped with $ProD_2$.

vitamin D group steroids on mesomorphic phase states of cholesteric liquid crystalline systems, which can be used in further development of optimized sensor materials for bioequivalent UV dosimetry that would meet contradictory requirements of high sensitivity and high thermodynamic stability.

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Вплив стероїдів групи вітаміну D на мезоморфні фазові стани холестеричних сенсорних матеріалів

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Досліджено вплив немезогенних провітаміну D та вітаміну D на термостабільність холестеричної та смектичної-А фаз, утворених сумішами естерів холестерину. Відзначено розмиття піків диференціальної скануючої калориметрії та селективного відбивання для підвищених (>5 %) концентрацій провітаміну D, яке супроводжується відхиленнями від лінійності концентраційних залежностей температур переходів холестерик — ізотропна рідина та холестерик — смектик. Відповідні граничні концентрації для провітамінів D_2 та D_3 у різних матрицях корелюють зі значеннями евтектичних концентрацій, розрахованих за рівняннями Шредера-ван Лаара. Отримані результати можуть бути фізико-хімічним підгрунтям для розробки сенсорних матеріалів для біоеквівалентних детекторів УФ-випромінювання, які б поєднували високу чутливість та термодинамічну стабільність.