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Dissolution of steroid crystals in a nematic droplet: effect of rotation

I. A. Gvozdovskyy[a*], I. P. Terenetskaya[a†], V. Yu. Reshetnyak[b‡]

[a]Institute of Physics, National Academy of Sciences of Ukraine
46 Prospekt Nauki, 03039 Kyiv-39, Ukraine

[b]Physics Faculty, Kyiv Taras Shevchenko University
6 Prospekt Glushkova, 03022 Kyiv-22, Ukraine

ABSTRACT

The nematic liquid crystals (LCs) can be converted into cholesteric LCs by different chiral dopants. For the first time the dynamics of a cholesteric phase induction was investigated on dissolution of the single steroid crystal (vitamin D isomers and relative compounds) at the nematic droplet and the new effect of the crystal rotation has been discovered. In all cases the correlation between the rotation direction and screw sense of the cholesteric helix was found. A theoretical model and interpretation of the rotation effect has been proposed.

Key words: nematic droplet, steroid crystals, vitamin D isomers, chiral dopants, Lehmann effect.

1. INTRODUCTION

In a cholesteric liquid crystal the rod-like molecules are typically arranged in a helical fashion and are in a position to free movement as in liquid. The cholesteric phase can be induced in a nematic LC by a chiral dopant that is accompanied by the director **n** twist, creating cholesteric macrohelix with a pitch P[1, 2].

It is known that many optically active compounds (like molecules with steroid ring system) are capable to form own cholesteric LC and to induce cholesteric phase in nematic LC[1]. The screw sense and value of a cholesteric pitch is dependent on the molecular conformation of the steroid moiety and the cholesteric screw sense is right- or left-handed [1-3].

One of the first experiments reported in the liquid crystal physics was the Lehmann effect[4]. In 1900 he observed uniform rotation of a droplet liquid crystalline structure[4] when a temperature gradient was parallel to the cholesteric helix axis. Only in 1968 Leslie did the theoretical interpretation of the Lehmann's observations[5].

In this paper we describe the effect of rotation which was first experimentally observed during dissolution of the single steroid crystal at surface of a nematic droplet[6]. We also present the phenomenon theoretical model.

2. MATERIALS AND METHODS

As chiral dopants we used vitamin D isomers and a number of relative compounds (cholesterol, 7-dehydrocholesterol and their benzoate, ergosterol, lumisterol$_3$ and ergocalciferol). All steroid chiral dopants are powder-like substances that represent different shapes, depending on the crystallization conditions, namely the needle-shaped (7-dehydrocholesterol, lumisterol$_3$), prismoidal (ergocalcalciferol, cholesterol, 7-dehydrocholesterol benzoate and cholesterol benzoate) or disk-shaped (ergosterol) shown in Fig.1. The needle-shaped and prismoidal steroid crystals were of 0.1÷1mm length and the disk-shaped crystals were of 2×3mm^2 area. (The disk-shaped crystals of ergosterol were transformed into the needle-shaped ones by recrystallization from hexane).

Steroid substances were dissolved in two nematic liquid crystals, namely ZhK-805 (1:1 mixture of 4-n-butyl- and 4-n-hexyl-trans-cyclohexancarbon acids, NIOPIK, Russia) and ZLI-1695 (the mixture of cyclohexylcyclohexanes, Merck,

* Correspondence: E-mail: igvozd1@yahoo.com; Telephone: (380 44) 265 0813; Fax: (380 44) 265 1589.
† Correspondence: E-mail: teren@iop.kiev.ua; Telephone: (380 44) 265 0813; Fax: (380 44) 265 1589.
‡ Correspondence: E-mail: reshet@iop.kiev.ua; Telephone: (380 44) 266 4477; Fax: (380 44) 265 0830.

Germany). Both nematic LCs have different temperatures of the mesophase-isotropic phase transition (T = 72^0C – for ZLI-1695 and T = 95^0C – for ZhK-805). Besides, ZhK-805 is more viscose than ZLI-1695.

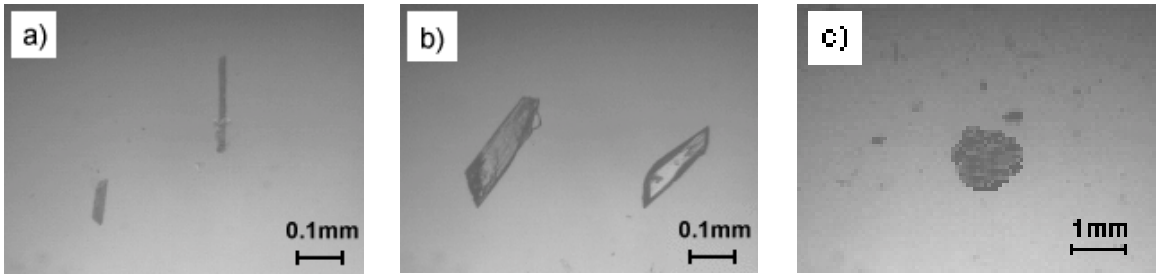

Fig.1. Different shapes of the steroid crystals: a) needle-shaped; b) prismoidal and c) disk-shaped.

To determine of the cholesteric screw sense induced by steroid substances we used the Grandjean-Cano method[7] with wedge-like cell of 20×30mm^2 area and of 60μm thickness. The glass substrates ensured planar alignment of the LCs with chiral dopants.

`The sense of rotation of the cholesteric helix was determined according to the known rule[7]. The cell was positioned between crossed polarizers and the shift direction of the interference pattern was investigeted upon turning the polarizer located under the cell (top view). The shift to the region of smaller wedge-thickness on the polarizer rotation in the clockwise direction corresponds to the right-handed (or plus) cholesteric helix, and the shift in opposite direction corresponds to the left-handed (or minus) cholesteric helix.

The dissolution process of a single steroid crystal in a nematic droplet was studied by experimental scheme (Fig.2). The nematic droplet was deposited on the glass substrate without any orientation conditions by a capillary with diameter 1.5mm. After deposition the droplet spread over the glass plate forming a segment with ~6mm diameter and ~1mm height.

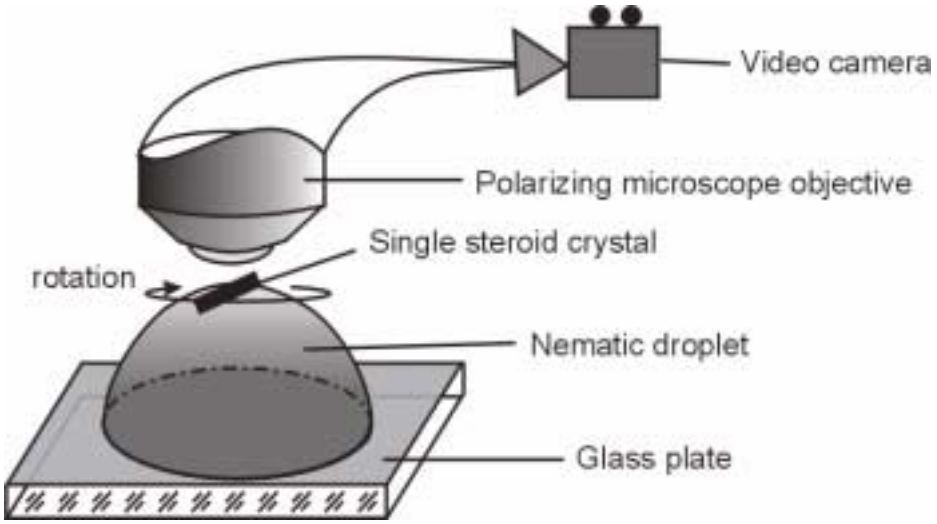

Fig.2. Experimental scheme for the observation of the single steroid crystal dissolution.

3. RESULTS AND DISCUSSION

3.1 Experimental studies

Recently we observed that on dilution in concentration ~5÷10wt.-% vitamin D isomers and relative compounds (cholesterol, 7-dehydrocholesterol and their benzoate, ergosterol, lumisterol$_3$ and ergocalciferol) induce the cholesteric phase in the nematic liquid crystals (ZhK-805 and ZLI-1695) [8]. Transformation of the nematic LCs into cholesteric phase using steroid chiral dopants was detected by observation the Cano-Grandjean texture[9] in the wedge-like cell (Fig.3a) or “fingerprint” texture in a droplet (Fig.3b) using polarizing microscope.

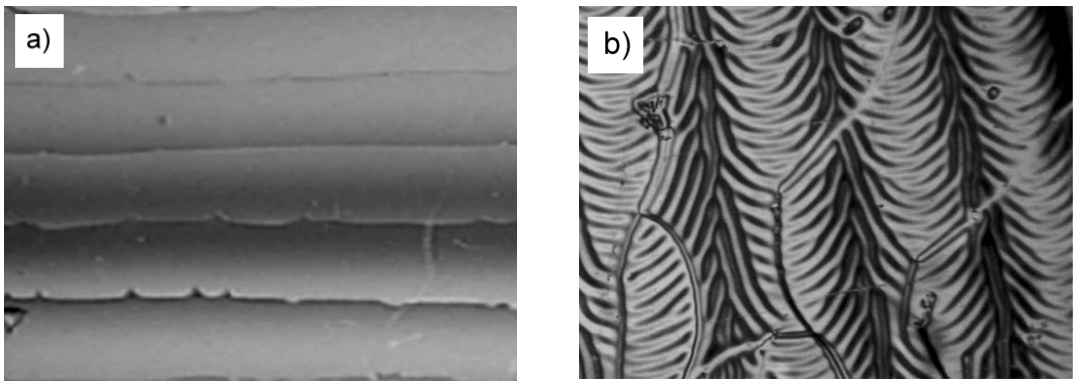

Fig.3. Typical textures of the cholesteric liquid crystals induced by vitamin D isomers and relative compounds: a) Cano-Grandjean texture; b) "fingerprint" texture.

In all cases the left-handed cholesteric helixes were observed except provitamins D_3 and D_2 (7-dehydrocholesterol and ergosterol respectively), which induced right-handed helix (see Table1).

What is the most interesting, we have first observed at room temperature the effect of rotation of a single steroid crystal of 0,1÷1mm length during its dissolution in a nematic droplet (ZLI-1695)[6].

We experimentally observed the following phenomena using a polarizing microscope:

1. Dissolution of a single steroid crystal placed at the nematic droplet was accompanied by the crystal rotation. However, when a number of steroid crystals were placed at the nematic droplet and coagulated with each other[10] no rotation was observed.
2. For all the steroids the correlation between the rotation direction and the screw sense of induced cholesteric helix was found. For example, the clockwise rotation of the steroid crystals of provitamins D_2 and D_3 was observed (Fig.4). As above mentioned these steroids induced right-handed cholesteric helix being added into nematic LCs (ZLI-1695 and ZhK-805). For the other steroids that induced left-handed helix, the rotation of individual crystals in the counterclockwise direction was observed (see Fig.5 and Table 1).

Table 1. Screw sense of the induced cholesteric helix and the direction of rotation of a single steroid crystal.

Steroids	**Screw sense of the cholesteric helix**	**Rotation of a single steroid crystal**
Cholesterol	Left-handed (-)	Counterclockwise
7-dehydrocholesterol (provitamin D_3)	Right-handed (+)	Clockwise
Ergosterol (provitamin D_2)	Right-handed (+)	Clockwise
Lumisterol$_3$	Left-handed (-)	Counterclockwise
Cholesterol benzoate	Left-handed (-)	Counterclockwise
7-dehydrocholesterol benzoate	Left-handed (-)	Counterclockwise
Ergocalciferol (vitamin D_2)	Left-handed (-)	Counterclockwise

3. It is found that the angular velocity of a single crystal is dependent on its dissolution rate and the crystal size. So, more massive crystals rotated slower. The uniform rotation with an angular velocity ~6degrees/sec has been recorded on dissolution of a needle-shaped 7-dehydrocholesterol crystal of 0.1mm length (Fig.4). The dissolution of prismoidal vitamin D_2 crystal in ZLI-1695 was more efficient as compared with all other compounds and the vitamin D_2 crystal of 0.5mm length exhibited the least speed of rotation ~1degree/sec (Fig.5).

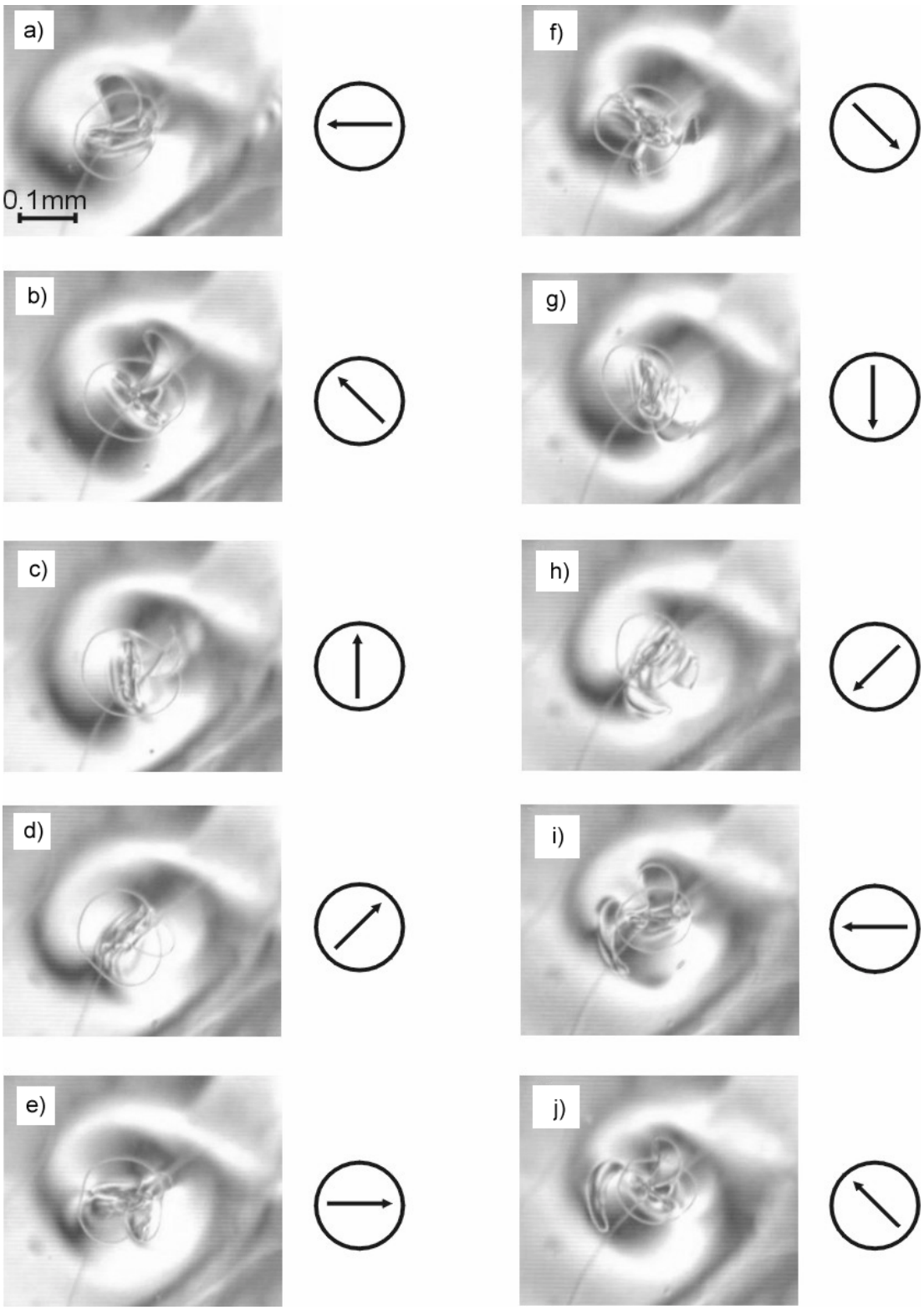

Fig.4. Microimages (a-j) present the dissolution of a single steroid crystal (7-dehydrocholesterol) in a nematic droplet (ZLI-1695) with time interval 7.5 seconds. Arrows show the direction of rotation. The movie is available at ftp://ftp.iop.kiev.ua/pub/effects/movie2.zip

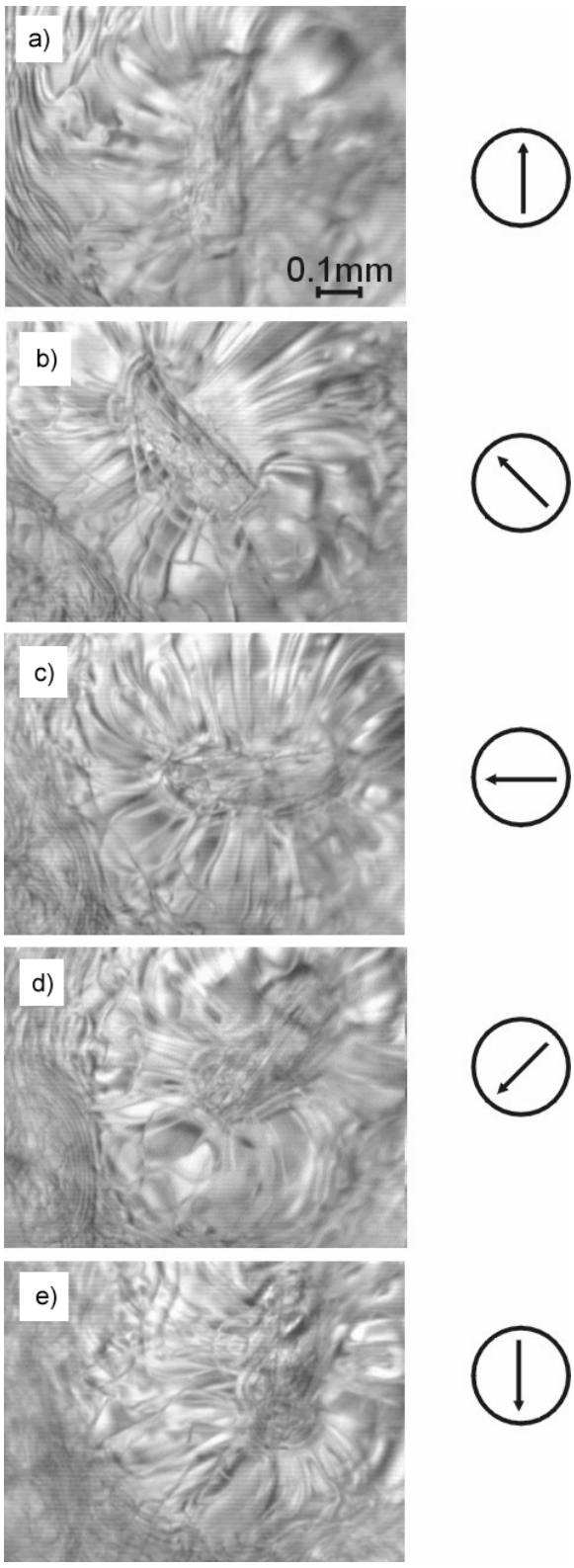

Fig.5. Images (a-e) present the dissolution of the vitamin D_2 crystal (ergocalciferol) in a nematic droplet (ZLI-1695) with time interval 45 seconds. Arrows show the rotation direction. The movie is available at ftp://ftp.iop.kiev.ua/pub/effects/movie3.zip

4. At room temperature the rotation was observed only for the ZLI-1695 droplet. In case of the ZhK-805 the effect of rotation was found after heating the glass plate up to 60^0C.
5. It should be emphasized that the rotation was observed neither in a viscous solvent (glycerol) nor in the isotropic phase upon heating both nematics to isotropic phase transition temperatures. It appears from this that a long range ordering in nematic liquid crystals is responsible for the effect revealed.

3.2 Theoretical model of the rotation effect

The theoretical model of rotation effect of the steroid crystals (particles) upon dissolving in the nematic LCs has been developed. It is suggested that the particles are of large size in comparison with liquid crystalline molecules and the diffusion of the chiral molecules is fast. Due to large size of particles we shall solve one-dimensional problem without consideration of the diffusion of steroid molecules in quasinematic layers.

One-dimension diffusion equation for concentration of chiral molecules in the nematic matrix can be written in the form:

$$\frac{\partial c}{\partial t} = D\frac{\partial^2 c}{\partial z^2},$$

with the following initial and boundary conditions

$$\begin{aligned} &c(z, t=0) = 0, \\ &\frac{\partial c(t, z=L)}{\partial z} = \frac{a}{D} = const, \\ &\frac{\partial c(t, z=0)}{\partial z} = 0 \end{aligned}$$

The last equation means that there is no flux of particles at $z = 0$.

It is regarded that the diffusion of the chiral molecules is fast and the director **n** is adiabatically changing during the dissolution of crystalline particle.

Solution to this problem has the form

$$c(z,t) = \frac{a}{D}\left(\frac{Dt}{L} + \frac{3z^2 - L^2}{6L} + \frac{2L}{\pi^2}\sum_k (-1)^{k+1} \frac{\exp\left(-\frac{k^2\pi^2 D}{L^2} t \right)}{k^2} \cos\frac{k\pi z}{L} \right)$$

It is seen that $\tau_1 >> \tau >> \tau_k$, therefore

$$c(z,t) \approx \frac{a}{D}\left(\frac{Dt}{L} + \frac{3z^2 - L^2}{6L} \right)$$

In addition we consider that the director anchoring condition is strong at the substrate (the director easy axis is along *OX* axis) whereas director freely rotates at the nematic droplet surface (z = *L*). It is supposed that the director anchoring condition is also strong when putting a particle at the droplet surface.

In such a case for the cholesteric LC the thermodynamic functional to be minimized has the following form:

$$F = \frac{1}{2}K_{11}\int(\mathrm{div}\mathbf{n})^2\,dV + \frac{1}{2}K_{22}\int(\mathbf{n}\cdot\mathrm{curl}\mathbf{n} + q(\mathbf{r},t))^2\,dV + \frac{1}{2}K_{33}\int(\mathbf{n}\times\mathrm{curl}\mathbf{n})^2\,dV\ ,$$

here K_{11}, K_{22}, K_{33} are the *splay*, *twist* and *bend* elastic constants respectively, $q = \frac{2\pi}{P}$ is the helix wave vector (inverse pitch) of unbounded cholesteric, its sign distinguishes between right- and left-handed helices liquid crystal. For induced cholesteric phase $q = 4\pi\beta \cdot c$, where *c* is the concentration of chiral dopant and β is its twisting ability.

The director field, because of symmetry, is given by

$$\mathbf{n}(z,t) = (\cos\phi(z,t), \sin\phi(z,t), 0),$$

where *Z*-axis is perpendicular to the substrates.

The Euler-Lagrange equation and the boundary conditions for director take the form:

$$\frac{d}{dz}\left(\frac{d\phi}{dz} + q(z,t)\right) = 0$$

$$\phi(0) = 0,$$
$$\phi'(L) + q(L,t) = 0$$

Solution to the Euler-Lagrange equation has the following form:

$$\phi(z) = bz - \int q(z,t)dz \approx bz + 4\pi\beta \cdot a\left(\frac{t}{L} + \frac{z^2 - L^2}{6DL}\right)z + d$$

here *b* and *d* should be found from the boundary conditions. Finally time-dependant part of the director angle at $z = L$ we can write in the form:

$$\phi(L,t) \approx 4\pi\beta \cdot at$$

In the presented theoretical model the particle is rotated with constant angular velocity and the direction rotation depends on the sign of twisting ability of the chiral dopant β. In addition the angular velocity is determined by the dissolution speed *a* of a particle.

4. CONCLUSIONS

In this paper we described the experimental results which for the first time demonstrated direct conversion of the chirality of steroid molecules into mechanical rotation of a single crystal. In our opinion this phenomenon is similar to the Lehmann effect but in this case the concentration gradient due to the dissolution of a steroid crystal plays the role of the temperature gradient and results in the crystal rotation as the cholesteric phase is induced. The theoretical model describing the phenomenon revealed is presented. The further investigations of the rotation effect are in progress.

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