Interaction of dyes CD–1 and SD–1 with the surface of oligodimethysiloxane

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Abstract. We carried out the modeling orientation of the dyes CD–1 and SD–1 relative to the surface of oligodimethysiloxane using the atom–atom potentials method. We have discovered the dependence of the interaction energy in dyes molecules on the angles which characterizes their orientation relative to the surface of the oligodimethysiloxane crystal. It was found out that the obtained energy value of interaction with the surface can explain weak adhesive qualities of the dyes and the orientation type relative to the surface. We identified the break–loose force for the dyes on the oligodimethysiloxane crystal surface.

1. Introduction
Nowadays the most prospective materials for LC displays are so–called photo-anisotropic materials oriented on the surface of different materials which have organic and non–organic origin. They are used or potentially useful for polarization-optical structures as thin–film anisotropic-optical protective and identification equipment for various industrial products.

The orientation of aliphatic hydrocarbons absorbed on the crystal surfaces is well studied. [1–6]. At the same time, there are few studies on dyes orientation on the crystal surface.

The goal of the study is to study intermolecular interactions of the dyes CD–1 and SD–1 with the oligodimethysiloxane surface. Many derivates from oligodimethysiloxane or silicones are known as the materials that orientate liquid crystals [7–13].

2. Simulation Method
Structural formulae of photochemically stable materials SD–1 and CD–1 are shown in Fig. 1, the molecules lined up according to the coordinates of their atoms. In the B dyes molecules the surface of phenyl rings of carboxyl groups and –N=N– groups make up an angle of 16° between two phenyl groups in biphenyl. Atoms coordinate optimization at lining up dyes was carried out using the special software for physics and chemistry modeling GROMACS.
Within the structure of oligodimethoxysiloxane silicon and oxygen atoms form a zigzag–like chain. The distance between atoms Si–O in the chain is 63Å, the distance Si–C – 1.88Å. Valence angle value Si–O–Si is 168°, the angle O–Si–O – 109.5° fig. 2.

Orientation of the molecule to the crystal surface is defined by angles θ, φ, ψ (fig. 3) which changed from 0° to 180° at a pitch of 10°. Here X,Y,Z – is the system of axes connected with the crystal surface; 1,2,3 – is the system of axes connected with the macromolecule; θ – the polar angle of axis 1 in rigid axes system; φ – azimuth of axis 1 (the angle of XZ with 1Z surfaces); ψ – azimuth of the moving coordinates system (the angle of 1Z surface with 12 surface).

The initial distance value a from a molecule centre of attraction to the surface going through the centers of attraction of oligodimethoxysiloxane atoms, which form the surface, was taken as 3 Å and minimizing the energy was performed according to altitude a.
The calculations were carried out using atom–atom potentials method [14–17]. The interaction energy $E$ is shown as a sum of energy of interaction values between the atoms of the molecule and the atoms of the crystal surface, which is determined by the correlation (Lennard–Jones potential) [17]:

$$E = \sum_{ij} E_{ij},$$

$$E_{ij} = 4\varepsilon \left[ \left( \frac{\sigma}{r_{ij}} \right)^{12} - \left( \frac{\sigma}{r_{ij}} \right)^{6} \right]$$

(1)

in which $\varepsilon > 0$ – depth parameter, $\sigma$ – distance between certain atoms, at which $E_{ij}=0$; $r_{ij}$ – the distance between the atom surface $i$ and the atom of the molecule $j$.

The interaction energy was found by the correlation (1), where the interaction parameters values for groups С’…С’, Si…Si, O…O were taken from the works [24–26]. Interaction potentials С’…О, and С’…Si were calculated using the well–proven additivity concept of van der Waals radiuses and the rule of geometric mean which were found in [27]. We can mention that using these values of atom–atom potentials we obtained the values for molecules orientation for liquid crystal octylcyandiphenyl on the surface of graphite and polyethylene crystals [20–21] which are in the accordance with the test data [22–23].

3. Results of numerical simulation

As the result we proved the dependence of the interaction energy of the oligodimethysiloxane crystal and dyes molecules SD–1 и CD–1 on the orientation angles $\theta$, $\varphi$, $\psi$.

Figure 4. Dependence of the interaction energy in the oligodimethysiloxane system – CD–1 on orientation angles $\theta$, $\varphi$, at $\psi=30^\circ$ (a) and orientation angles $\theta$, $\psi$, at $\varphi =10^\circ$ (b)

Figure 5. Dependence of the interaction energy in the oligodimethysiloxane system – SD–1 on orientation angles $\theta$, $\varphi$, at $\psi=30^\circ$ (a) and orientation angles $\theta$, $\psi$, at $\varphi =10^\circ$ (b)
We can see in figures 4 – 5, that the intermolecular interaction energy of the dyes on the oligodimethysiloxane crystal surface essentially depends on three orientation angles $\theta$, $\varphi$, $\psi$, herewith, there is an area of orientation state for the dyes molecules, whose interaction energy of the oligodimethysiloxane surface is massively more than the energy in other state, (Table 1).

| Dyes | $\theta$,° | $\varphi$,° | $\psi$,° | $E_{\text{max}}$, kJ/mol | $\theta$,° | $\varphi$,° | $\psi$,° | $E_{\text{min}}$, kJ/mol |
|------|------------|------------|----------|--------------------------|------------|------------|----------|--------------------------|
| CD–1 | 90         | 40         | 40       | -27.75                   | 10         | 10         | 30       | -191.31                  |
| SD–1 | 80         | 80         | 30       | -23.24                   | 10         | 10         | 30       | -167.25                  |

**Figure 6.** Energy a) and force b) of the interaction between CD–1 at the main line symmetry OX direction shift 1) and OY direction 2) of oligodimethysiloxane, dye orientation angles are $\theta=10^\circ$, $\varphi =10^\circ$, $\psi=30^\circ$

In figure 6 a) curve 1 shows that the anisotropy of interaction energy for molecule CD–1 at the direction shift along silicon–oxygen atomic bridge Si–O–Si in oligodimethysiloxane is not more than 5%, herewith the force $F = \partial E / \partial x$, (fig. 6 b curve 1) is near zero. At the same time, curve 2 (fig. 6 a) shows that anisotropy of the interaction energy for molecule CD–1 at a perpendicular shift to chain Si–O is ~50%. Due to it we can evaluate the orientation degree of the dye in different directions in oligodimethysiloxane.

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