

УДК 539.2.535.37.541.18.

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Thermodynamic properties of epitropic liquid crystals

In this paper we used developed theoretical model earlier (called "two-component") for numerical calculation of temperature dependencies of equilibrium ELC layer thickness $h_s(T)$, its specific heat $C_p(T)$ and latent molar heat of phase transition ELC-bulk liquid $q(T)$ with further comparison with experiment. This model postulates the existence of both monomers and dimers in the wall-adjacent layer, and the appearance of ELC layer is caused by the orientational interaction between these liquid particles and the solid substrate. The calculations were compared with results of experimental investigation of thin nitrobenzene interlayer symmetrically bounded by quartz substrates.

Introduction. Earlier [1-4] we conditionally classified organic liquids into three classes, according to their degree of mesogeneity:

- 1) thermotropic liquid crystals with high degree of molecular mesogeneity (molecular shape – anisometric sphere-cylinders or flat discs);
- 2) common isotropic liquids; which don't form mesophase under any conditions due to low degree of molecular homogeneity;
- 3) liquids, which don't form mesophase in the bulk, but are able to form orientationally ordered wall adjacent layer under the action of solid substrate surface forces.

This layer is similar to thermotropic liquid crystal and usually called epitropic liquid crystal (ELC).

Results and discussion. In the framework of earlier developed theoretical model we numerically calculated the temperature dependencies of equilibrium ELC layer thickness $h_s(T)$, its specific heat $C_p(T)$ and latent molar heat of phase transition ELC-bulk liquid $q(T)$ with further comparison with experiment.

1. Temperature dependence of elc layer thickness. Numerical calculation was based on the so called **two-componential model** [1-3]. In the framework of this model we assumed the coexistence of monomers (M) and dimers (D) – liquid particles – in the wall-adjacent layer, which are in dynamical equilibrium. The formation of ELC orientational structure is conditioned by interaction between liquid particles and solid substrate.

Developed model takes into account following types of molecular interactions [6–9]: dipole-dipole between M–M; dispersive interactions between pairs "M–M", "M–D" and "D–D"; orientational interaction between M and D with solid substrate.

General physical considerations determine the decreasing of equilibrium thickness with heating because of lowering of interaction forces [6-7].

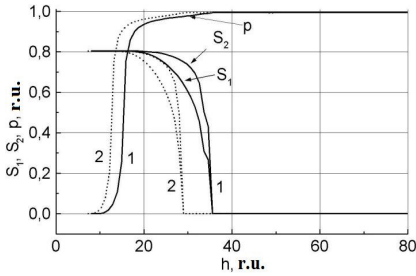


Fig. 1. Thickness dependencies of order parameters $S_{1,2}$ and relative M-concentration for 2 values of $|C_2|$ coefficient – 0.7 (1) and 0.4 (2)

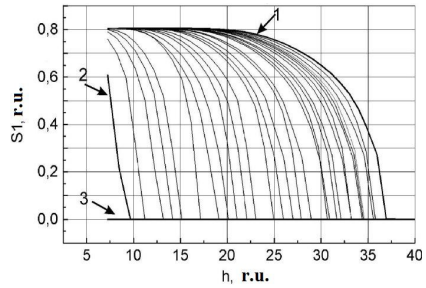


Fig. 2 Series of thickness dependencies $S_1(h)$ near interface ELC – bulk liquid plotted for different values of C_2 parameter ($C_2 \in [-0.8, 0]$)

The self-consistent systems of equations for determination of M and D order parameters $S_{1,2}$ (index 1 – corresponds to M and 2 – to D) as well as relative concentration of monomers p (its value is near to unit in isotropic liquid) was written

$$\left\{ \begin{aligned} S_k &= \frac{1}{I_k^a} \int_{-1}^{+1} P_2(x) \exp \left\{ \left[p A_2^k S_1 + \frac{1-p}{2} A_2^k S_2 + W_k(h, T) B_2^k S_k \right] P_2(x) \right\} dx \\ p &= \frac{P_0}{p_0 + (1-p_0) \cdot I_2 / I_1 \cdot \exp(E_d / kT)} \quad (k=1,2) \end{aligned} \right. \quad (1)$$

here p_0 – is M-concentration in bulk liquid ($p_0 \approx 0$), is the bond energy E_d of dimer.

To obtain the system of equations (1) the effective dispersion interaction potentials between liquid particles ($A_{ij}(x)$) and between liquid particles and solid substrate $C_i(h, x, T)$ were written in the form in Legendre polynomials:

$$\begin{aligned} A_{ij}(x) &= A_0^{ij} + A_2^{ij} S_i P_2(x); \\ B_i(h, x, T) &= [C_0 + C_2 S_i P_2(x) + \dots] W_i(h). \end{aligned} \quad (2)$$

Only anisotropic part of potential (C_2 – coefficient) of orientational interaction between liquid particle and substrate determines the effect of formation of ELC layer. Note that the C_2 value decreases with temperature $C_2 = G_2 / kT$, that in turn causes decreasing of ELC layer thickness.

Fig.1 illustrates thickness dependencies of order parameters $S_{1,2}$ and relative M-concentration. One can see that temperature lowering $|C_2|$ (increasing) leads to increasing of equilibrium ELC thickness (it corresponds to the condition $S_1 = 0$).

Fig.2 illustrates series of thickness dependencies $S_1(h)$ near interface ELC – bulk liquid plotted for different values of C_2 parameter. In case $|C_2| = 0.02$ the ELC

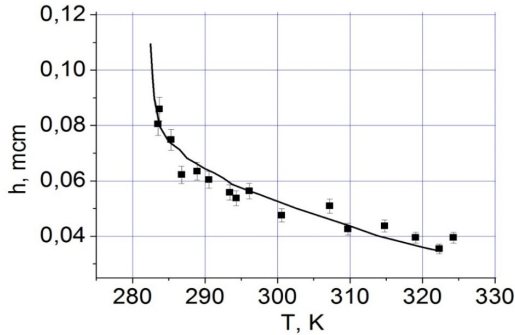


Fig.3 Temperature dependence $h(T)$

layer is practically destroyed (curve 2) and the value $C_2 = 0$ corresponds to the condition of complete melting (curve 3).

This set of curves allowed us to determine the dependence $h(C_2)$ and after recalculation in reverse scale $h(1/C_2)$ to determine the temperature dependence $h(T)$, and further compare it with experimental results for nitrobenzene ELC phase near lyophilic quartz substrate [8]. Fig. 3 illustrates relatively good agreement of experimental results and theoretically calculated dependence.

2. Temperature dependence of elc molar heat capacity. Using DSC method for disperse systems with developed surface (quartz powder – nitrobenzene) the thickness and temperature dependencies of heat capacity in confined systems were measured [8]. Experimental data are presented in fig.5. The lowering of C_p value near the solid surface may be explained because of the existence of orientational nematic-like ordering in wall-adjacent layers. Such ordering is equivalent to the effect of freezing out of some degrees of freedom. The curve jump of $C_p(T)$ dependence is connected with latent heat of the first order phase transition (orientational melting and dimers destruction) in ELC layer. Finally for large distances the C_p value coincides with the bulk one.

After the solution of equations (1) we may write the expression for system free energy $F(S_1, S_2, T)$ in dimensionless form [4]:

$$F_0(S_1, S_2, p) = \frac{F}{NkT} = \frac{p^2}{2} (A_0^{11} + A_2^{11} S_1^2) + \frac{1}{2} \left(\frac{1-p}{2} \right)^2 (A_0^{22} + A_2^{22} S_2^2) + \frac{p(1-p)}{2} (A_0^{12} + A_2^{12} S_1 S_2) - \frac{1+p}{2} + C; \quad C = \text{const.} \quad (3)$$

Finally the free energy of infinitely thin layer disposed at the distance h to the solid surface is determined as:

$$F = mTF_0 \quad (4)$$

here m is dimension factor.

Taking into account the relation between free and internal energy:

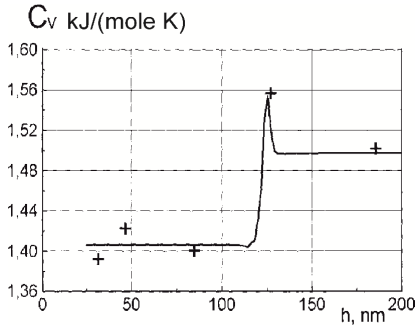


Fig. 4 Dependence $C_v(h)$

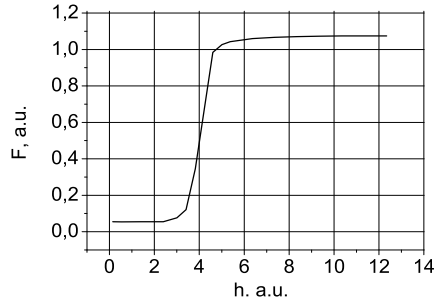


Fig. 5 Dependence $F_0(h)$

$$U = F - T(\partial F / \partial T) \tag{5}$$

we obtained:

$$U = -mT^2 \frac{\partial F}{\partial T} = -mT^2 \frac{\partial}{\partial h} \left(\frac{\partial F_0}{\partial T} \right) \frac{\partial h}{\partial T}. \tag{6}$$

For the whole liquid layer we may rewrite this equation as:

$$\begin{aligned} U &= -mT^2 \int_0^h \frac{\partial}{\partial h} \left(\frac{\partial F_0}{\partial T} \right) \frac{\partial h}{\partial T} dh = \\ &= -mT^2 \frac{\partial h}{\partial T} \cdot F_0(h(T)) = mT^2 \left| \frac{\partial h}{\partial T} \right| \cdot F_0(h(T)) \end{aligned} \tag{7}$$

Then taking into account $C_v = \left(\frac{\partial U}{\partial T} \right)$ we then obtain:

$$C_v = \alpha F_0(h(T)) + \beta \frac{\partial F_0(h(T))}{\partial h} + \gamma, \tag{8}$$

here α, β, γ – are thickness independent fitting constants. Their values were chosen in order to achieve the best agreement with experimental results. For example, in case of nitrobenzene near quartz substrate, it was found $\alpha=0.01, \beta=2.91, \gamma=1.4$. Fig. 4 illustrates the relatively good agreement of theoretical calculation with experimental results [8].

3. Temperature dependence of latent molar heat of phase transition. The calculated in accordance with (3) dependence $F_0(h(T))$ is illustrated in fig. 5. One can see that for the thickness ranges of ELC phase ($h < 2$ arb.units) and of bulk liquid ($h > 6$ arb.units) its value is almost constant. Contrary the transitional layer is described by monotonous function with the inflexion point in the centre of the layer.

So there exist 2 principally different types of solutions: one of them describes isotropic bulk liquid ($S_1=0, S_2=0, p=1$) and the second one – orientationally or-

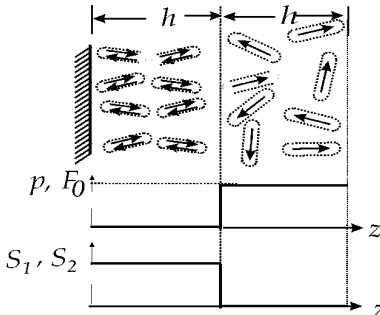


Fig. 6 Structure of studied system is described by step-like Heaviside functions

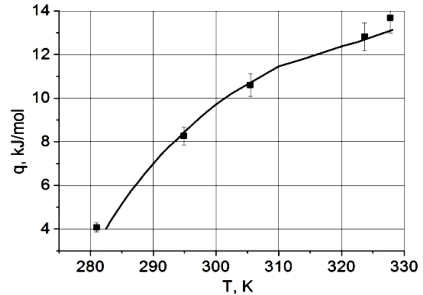


Fig. 7 Dependence $q(T)$ for nitrobenzene near quartz substrate

dered *ELC* phase ($S_1=0, S_2 \neq 0, p=0$). These states are characterized by following values of dimensionless free energy F_0 :

$$F_0(S_1, S_2, p) = \begin{cases} F_0(0, 0, 1) = \frac{1}{2} A_0^{11} - 1 + C, & \text{in case of bulk liquid} \\ F_0(S_1, S_2, 0) = \frac{1}{8} (A_0^{22} + A_2^{22} S_2^2) - \frac{1}{2} + C, & \text{in case of ELC} \end{cases},$$

here C is some constant. Phase transition takes place if $F_0(S_1, S_2, 0) < F_0(0, 0, 1)$.

Schematically, assuming the absence of transition layer, the structure of studied system is described by step-like Heaviside functions as it is presented in fig. 6. It allows us to use the following expression for internal energy of liquid layer:

$$U = U(S_1, S_2, 0) + U(0, 0, 1) \tag{9}$$

here:

$$\begin{cases} U(S_1, S_2, 0) = mT \int_0^{2h} F_0(S_1, S_2, 0) dz - mT \int_0^{2h} \frac{\partial}{\partial h} (TF_0(S_1, S_2, 0)) \frac{\partial h}{\partial T} dz \\ U(0, 0, 1) = mT \int_0^{2h} F_0(0, 0, 1) dz - mT \int_0^{2h} \frac{\partial}{\partial h} (TF_0(S_1, S_2, 0)) \frac{\partial h}{\partial T} dz \end{cases} \Rightarrow$$

$$\Rightarrow \begin{cases} U(S_1, S_2, 0) = 2mThF_0(S_1, S_2, 0) \\ U(0, 0, 1) = 2mThF_0(0, 0, 1) \end{cases}$$

Kirchhoff equation was used to calculate heat transition value q :

$$\frac{dq}{dT} = C_0 - C_s \tag{10}$$

here C_0 and C_s are molar heat capacities of the bulk isotropic liquid and ELC phase.

It's obvious that:

$$\begin{cases} C_0 = C(0,0,1) = \frac{\partial U(0,0,1)}{\partial T} \\ C_s = C(S_1, S_2, 0) = \frac{\partial U(S_1, S_2, 0)}{\partial T} \end{cases}$$

Consequently Kirchoff equation may be rewritten in form:

$$\frac{dq}{dT} = \frac{\partial U(0,0,1)}{\partial T} - \frac{\partial U(S_1, S_2, 0)}{\partial T}$$

After integration we obtain:

$$q(T) = U(0,0,1) - U(S_1, S_2, 0) + C, \quad (11)$$

here C is integration constant which is determined by the condition $C = q(T_0) = q_0$ (T_0 is crystallization point). Then:

$$q = \Delta F \cdot (T - T_0)h + q_0, \quad (12)$$

here $\Delta F = m[F_0(0,0,1) - F_0(S_1, S_2, 0)]$ is fitting factor.

Fig. 7 illustrates coincidence of experimental results and theoretical calculation of $q(T)$ dependence for nitrobenzene near quartz substrate.

Monotonic increase of this dependence may be explained by the fact that wall adjacent liquid layer is in inhomogeneous van der Waals field and interaction energy of dimers with the substrate increases near solid surface. That is why their destruction and further disordering need more energy.

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Термодинамические свойства эпитропных жидких кристаллов

АННОТАЦИЯ

Проведен расчёт температурной зависимости толщины и теплоты фазового перехода из ЭЖК в изотропную жидкость, а также зависимости молярной теплоёмкости от толщины пристенного слоя на примере тонкой прослойки нитробензола вблизи поверхности кварцевой подложки. Для расчёта использовалась так называемая «двухкомпонентная модель», в которой постулируется существование в пристенном слое как мономеров, так и димеров, а возникновение ЭЖК-слоя обусловлено ориентационным взаимодействием между частицами жидкости между собой и твёрдой подложкой

Михайленко В. І., Поповський О. Ю.

Термодинамічні властивості епітропних рідких кристалів

АННОТАЦІЯ

Проведено розрахунки температурної залежності товщини й теплоти фазового переходу з ЕРК в ізотропну рідину, а також залежності молярної теплоємності від товщини пристінного шару на прикладі тонкого прошарку нітробензолу поблизу поверхні кварцової підкладки. Для розрахунків використовувалася так звана «двокомпонентна модель», у якій постулюється існування в пристінному шарі як мономерів, так і димеров, а виникнення ЕРК-шару обумовлено орієнтаційною взаємодією між частками рідини між собою і твердою підкладкою.