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THE RESEARCH OF TRIBOLOGICAL CHARACTERISTICS OF SMECTIC LAYER OF BOUNDARY FILM

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There were developed the technique and calculation results of bearing capacity of boundary film, cohesion force and friction in the smectic layer of boundary film. As a basis in calculations was taken Van-der-Waal's interaction between molecules in layer and methyl groups of smectic crystal adjacent layers. The attractive forces and repulsive forces between the molecules in crystal and methyl groups, and additive superposition of these forces were taken into account. Depending on temperature was established the regularity of changes of bearing capacity, cohesion force and friction in the smectic crystal of stearic acid.

Key words: boundary film, surfactants, smectic crystal, methyl group, Van-der-Waal's interaction, bearing capacity, cohesion force, friction force.

Introduction

The main requirements to surfactants that are added to the hydrocarbonic basic oils are maximum adhesion to the solid friction surface and minimum cohesion between its molecular films [1, 2]. In this case the minimum friction forces are achieved in wide load range. The limit load for layers of surfactants is determined by its bearing capacity that is force sufficient for destruction. There is a huge amount of experimental material concerning tribological properties of various surfactants. However, there is no strict theory that would satisfy all experimental data. For example, Bowden basing himself upon his own researches [3] and study of Hardy [4] proposes to subdivide existing lubricants into those which do not change the friction coefficient with external load and those for which the friction coefficient decreases at the initial stage with increasing load. The last group of lubricants includes alcohols and fatty acids [5]. These substances especially fatty acids allow to obtain the lowest value of friction coefficient at certain concentration [6]. The mechanism of its lubricating action is connected with the property to form on friction surface multimolecular film of crystal structure [5]; however it doesn't explain the obtained dependence of friction coefficient on external load. Most likely such friction behaviour is caused by layered structure of the boundary film; each layer has its own tribological characteristics. Then the results obtained by Bowden, Hardy and others, are explained by low bearing capability and high friction coefficient of the top layer, and the bottom layers (close to friction surface) have inverse properties. If we take as a basis this idea about boundary film, we can assume that the lower layer is close in structure to the smectic liquid crystal, and the top one - to nematic liquid crystal [7, 8].

When studying such properties of crystal layers of boundary film, one of the major tasks is theoretical determination of bearing capability and bonding force in layers, as in normal direction – the force of cohesion, and in tangential one – friction force. It enables to make expected calculations of tribological characteristics of friction assemblies, surfaces of which under certain loads and temperatures are divided by boundary film with various degree of molecule order. In work was solved the problem of defining molecule forces in smectic crystal layers, as the main component of boundary film.

Purpose and problem definition

The purpose of this work is to determine bearing capability of smectic layer, cohesion force arising between the smectic crystal layers of fatty acids molecules, and friction forces between these layers depending on temperature. Partly this problem was solved in A. Cameron's [9] work, namely, cohesion force and friction force for fatty acids layers were determined considering Van-der-Waals attraction of methyl groups. However, basic assumptions made in his work caused a number of doubts. For example, when calculating friction force the author neglects the minimum value of system potential energy, calculating the interaction between CH_3 – groups of molecules in crystal he possesses the value of bonding energy for CH_2 – groups, he makes calculation of forces for an arbitrary distance (3,09 Å) between methyl planes of crystal. Except these observations made by B.V. Deryagin, A.S. Akhmatov and other scientists [5] it should be pointed out one more significant observation: when calculating interaction force, thermal vibrations of molecules in crystal should be taken into account; these vibrations determine the average distance between molecules at different temperatures.

Despite a large number of observations, A. Cameron's approach is reasonable because molecular friction forces are significant; however there is no unified theory to describe them. If we apply this approach we have to determine the influence of temperature on energy and bonding force in crystal of fatty acid, and also we have to take into account structure and properties of a particular selected substance.

Statement of research material

The application of general interaction law to determine interaction energy in crystal

Imagine smectic crystal of stearic acid as a set of layers of molecule dimers with distance between layers and distance between molecules, Fig. 1.

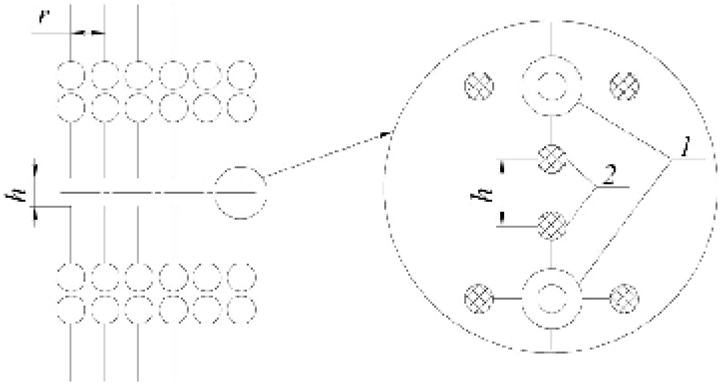

Fig.1 – Molecular arrangement of fatty acid in smectic boundary layer:
1 – carbon;
2 – hydrogen atom

As distance between molecules in layer is very small and compared with molecule size, then in calculations we should take into consideration both Van-der-Waal's attraction and repulsion. To calculate total energy we use Lennard-Jones law, «6 - 12» [10]:

$$U(r) = 4\cdot\varepsilon\left(\left(\frac{\sigma}{r}\right)^{12} - \left(\frac{\sigma}{r}\right)^{6}\right), \tag{1}$$

where ε – depth of potential well, J;

σ – distance at which energy is equal to zero, m.

The right term in brackets signed «–» corresponds to Van-der-Waal's attraction of molecules in layer, the left one to repulsion. The values ε and σ for stearic acid are calculated under procedure [10], namely:

$$\varepsilon = 1{,}92\,K\,T_{П}, \tag{2}$$

$$\sigma = \sqrt[3]{1{,}261 b_0}, \tag{3}$$

where K – Boltzmann's constant, J/K;

$T_{П}$ – melting temperature, K.

$$b_0 = 2{,}0\,V_{КИП}, \tag{4}$$

where $V_{КИП}$ – molar volume at boiling temperature, cm^3/mole. It is determined by Kopp's method.

$$V_{КИП} = 11{,}0\,Ч(C) + 7{,}8\,Ч(O') + 12{,}2\,Ч(O'') + 5{,}5\,Ч(H), \tag{5}$$

where (C) – number of carbon atoms in molecule;

(O') – number of oxygen atoms in molecule connected with two carbon atoms;

(O'') – number of oxygen atoms in molecule connected with one carbon atom: $O=C$;

(H) – number of hydrogen atoms in molecule.

After performing calculations from the formula (1) we obtain the curve of total interaction energy of stearic acid molecules in crystal, Fig. 2. In this case $U_{\max} = \varepsilon$ is dissociation energy i.e. maximum bonding energy at temperature 0 Kelvin.

Using curve 3 Fig. 2 we can determine the distance change between molecules dr depending on temperature. We should take into account the energy of molecule thermal vibrations in crystal, which is determined as:

$$U_T = K\,T. \tag{6}$$

The determination of distance dr is graphically shown in Fig. 2, where curve 4 reflects the distance change depending on energy growth of thermal vibrations from $U_{\max}$ to *KT3*. At any temperature distance is equal to:

$$dr = r_0 + r_{cp} = r_0 + \frac{r_{\min} + r_{\max}}{2}\,. \tag{7}$$

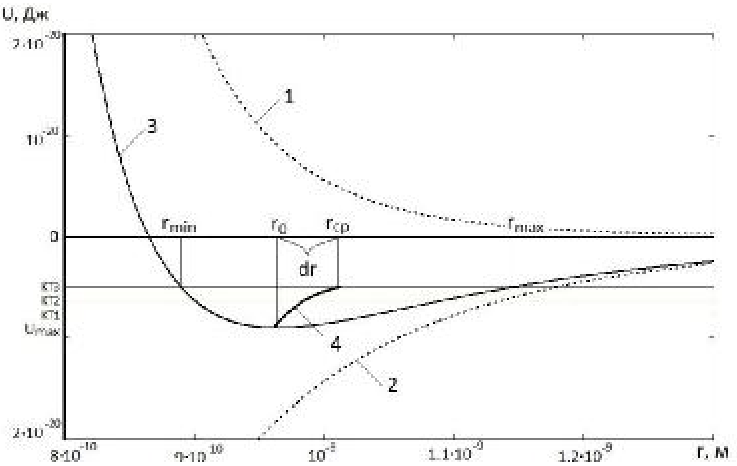

Fig.2 – energy change in molecules interaction of stearic acid depending on distance.
1 – repulsion energy;
2 – attractive energy;
3 – total energy

The calculations using dependence (7) are displayed in table 1, they show that crystal temperature essentially influences on distance between molecules in it.

Table 1

Distance change between molecules
in crystal depending on temperature

T, °C	0	20	40	60	80	100
dr, Å	1,061	1,172	1,289	1,415	1,55	1,696

The obtained data on energy and temperature influence on intermolecular distance enable, at a later stage, to perform force analysis of molecule interaction.

Determination of smectic layer bearing capacity of boundary film

If we understand by bearing capacity force required to destruct crystal, then such force can be determined through bonding energy. For this purpose we use dependence (1) and obtain a function of bonding force at distance:

$$F(r) = \frac{d}{dr}U(r) = 48\varepsilon\frac{\sigma^{12}}{r^{13}} - 24\varepsilon\frac{\sigma^{6}}{r^{7}}\,. \tag{8}$$

We bring in concept of specific force, or force per unit area, then:

$$P(r) = \frac{F(r)}{S}, \tag{9}$$

where S – area of cell cross-section which is occupied by one molecule of layer, m^2:

$$S = (r_0 + dr)^2 \tag{10}$$

Force change P at distance is shown in Fig. 3. The curve in Fig. 2 reflects total force by analogy with curve 3 Fig. 1, i.e. the sum of repulsion and attraction forces between molecules in crystal layer. Force P_H corresponds to external force required to destruct crystal layer that is its bearing capacity at certain temperature, to which corresponds own value of distance dr.

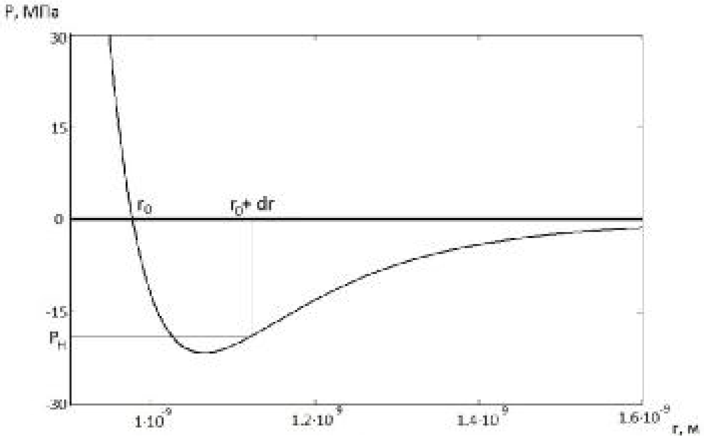

Fig. 3 – Change in specific interaction force of molecules in layer depending on temperature

If we take into account the obtained earlier distance change dr depending on temperature, so we can build a diagram of temperature dependence of crystal layer bearing capability which is shown in Fig. 4.

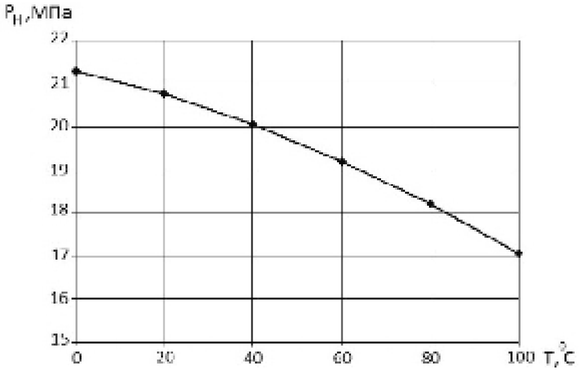

Fig.4 – Change in layer bearing capacity depending on temperature

As shown in Fig. 4 bearing capacity of crystal stearic acid nonlinearly decreases with temperature growth. It should be noted that melting temperature of stearic acid in normal conditions (under atmospheric pressure without any external influence) is 69.6 °C that is why physical content has only a part of table in Fig.4 limited by melting temperature.

Determination of cohesion force for smectic layer of boundary film

Out of all general ideas about the structure of smectic liquid crystals [7], it can be claimed that minimum cohesion or attraction force between adjacent layers for fatty acid crystals is defined by Van-der-Waal's interaction of its methyl CH_3 groups as shown in Fig. 1. When calculating cohesion force additivity of these forces should be taken into account then total cohesion force is defined not as sum of forces of pair interaction of methyl groups, but as sum of forces which act between methyl group of one layer and all neighbours of another layer. Design diagram is shown in Fig. 5.

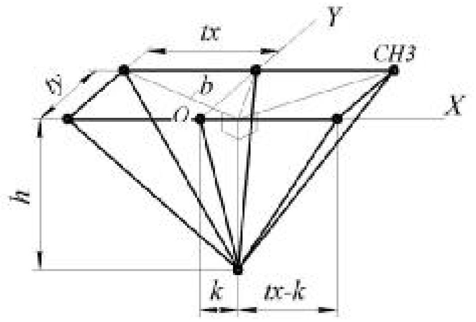

Fig. 5 – Design diagram for determination of cohesion force

In accordance with diagram (Fig. 5) methyl group of smectic lower layer is in area XOh and interacts with six adjacent groups of upper layer which form a rectangular lattice with parameters tx and ty. When calculating we consider that lower methyl group is displaced along an axis X by value k. Displacement along an axis Y is missing. In this case the expression of total interaction force for lower methyl group with upper ones is

$$F_K(k) = 2\left(\sum_{y=0}^{n}\sum_{x=0}^{n} F\left(\sqrt{(t_x+k)^2+t_y^2+h^2}\right)+\sum_{y=0}^{n}\sum_{x=0}^{n} F\left(\sqrt{(t_x-k)^2+t_y^2+h^2}\right)-F\left(\sqrt{(k^2+h^2)}\right)\right), \quad (11)$$

where $tx = ty = h = r_0 + dr$.

Multiplication by «2» in dependence (11) is brought in to account the interaction with methyl groups of upper layer, which are in negative part of axis Y. The last member of dependence (11) with the sign «-» is brought in to account double summation.

Force F is calculated using dependence (8), however values for parameters ε and σ are selected for group CH_3. By analogy with the previous calculation we determine specific cohesion force, i.e.

$$P_K(k) = \frac{F_K(k)}{S}. \quad (12)$$

The obtained results of calculations using dependence (11) and (12) are shown in Fig. 6. The distance value dr corresponds to temperature 100 °C.

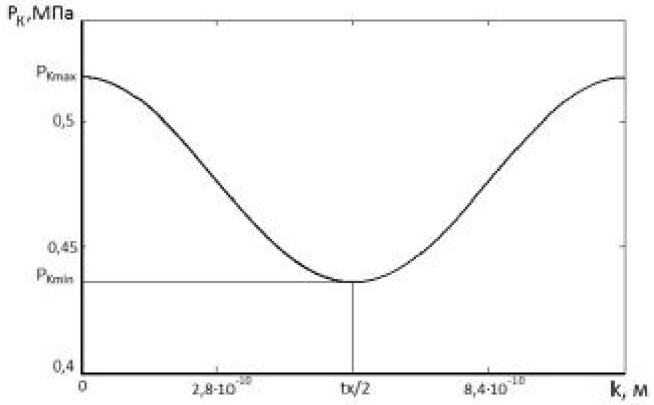

Fig. 6 – Change in specific cohesion force in relative shift of smectic layers

According to Fig. 6 cohesion force in smectic layers is changing at half-cycle of crystal lattice from maximum value $P_{K\max}$ to minimum one $P_{K\min}$. To take into account the influence of temperature on cohesion force, we will make a similar calculation using distance values dr shown in Table 1. The calculation results are shown in Fig. 7. The values $P_{K\max}$ are specified at certain temperatures.

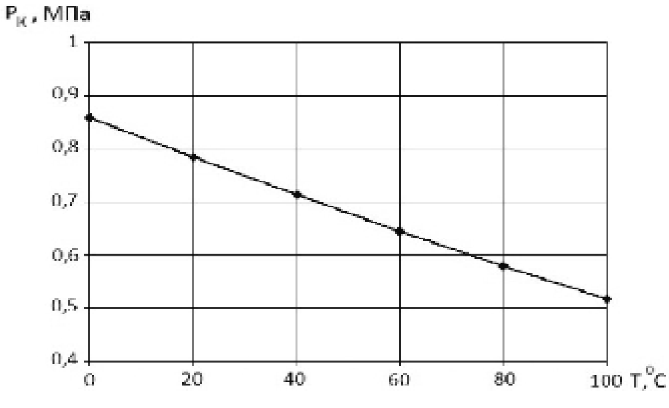

Fig. 7 – Change in specific cohesion force depending on temperature

As shown in Fig. 7, cohesion force decreases linearly as crystal temperature increases and equals from 0,86 MPa to 0,52 MPa in the range under study. The obtained values and rate of curve for cohesion force enable to calculate friction force between layers of smectic crystal in their relative shift.

Determination of specific friction force between layers of smectic crystal

As in relative shift of smectic layers by value $tx/2$ cohesion force changes from maximum value to minimum one then such a shift is accompanied by consumption of a certain work, which is specific work of friction force. It equals:

$$A_T = \int_0^{tx/2} P_K(k)\frac{d}{d_k} - \frac{P_{K\min}\, tx}{2}. \qquad (13)$$

Then specific friction force between layers of smectic is:

$$P_{TP} = \frac{A_T}{(tx/2)}. \qquad (14)$$

After we have made calculations using dependences (12), (13) and (14), it is possible to determine a regularity of change in specific friction force for smectic crystal of stearic acid, Fig. 8.

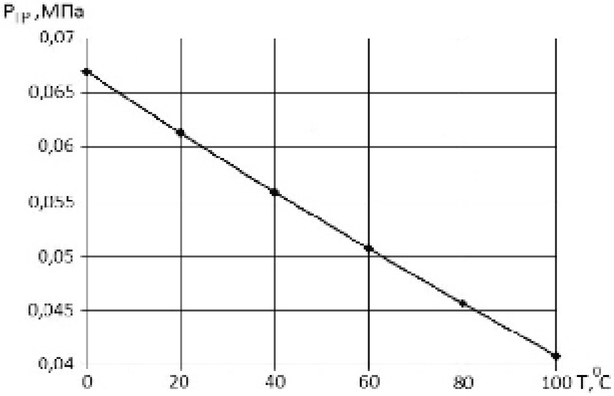

Fig. 8 – Changes in specific friction force in layers of smectic liquid crystal

According to Fig. 8 specific friction force like cohesion force decreases linearly as temperature of smectic crystal increases. In comparison with nematic crystal of stearic acid [12], it is possible to claim that friction forces in smectic have lower values, while its bearing capacity significantly exceeds bearing capacity of nematic. The obtained value of nematic bearing capacity is 0,45 MPa [12], and according to carried-out calculations depending on temperature, smectic values are from 17 ... 21 MPa, Fig. 4. These data confirm the results of previous studies, in which was established the reduction of friction coefficient with growth of external load. It should also be noted that specific friction force, its values are shown in Fig. 8, is not the total friction force for tribonode, but is its molecular component.

Conclusions

There were developed mathematical models to determine bearing capacity, adhesion force and friction force of smectic crystal of stearic acid. According to developed models, smectic crystal has a high bearing capacity and lower friction force in comparison with nematic crystal. These models can be used to define specified characteristics of other fatty acids and similar substances when adding them as additives to lubricants.

There were determined dependences of bearing capacity, adhesion force and friction force of smectic crystal of stearic acid depending on temperature. Bearing capacity decreases nonlinearly with temperature growth, the forces of cohesion and friction decreases linearly; to each of these characteristics temperature has a significant contribution. Thus, when the temperature increases from 0 to 100 °C, bearing capacity decreases by 20 % and specific friction force by 38 %. These dependences should be considered when developing friction knots and in requirements to their loads and temperature modes.

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Воронін С.В., Стефанов В.О. **Дослідження трибологічних характеристик смектичного шару граничної плівки.**

Наведена методика та результати розрахунку несучої здатності смектичного шару, сил когезії та тертя в смектичному шарі граничної плівки. При виконані розрахунку за основу прийнята Ван-дер-Ваальсова взаємодія між молекулами в шарі та метильними групами сусідніх шарів смектичного кристалу. Враховані як сили притягування, так й сили відштовхування між молекулами в кристалі та метильними групами, а також адитивне накладення цих сил. Встановлена закономірність зміни несучої здатності, сили когезії і тертя в смектичному кристалі стеаринової кислоти в залежності від температури.

Ключові слова: гранична плівка, поверхнево-активні речовини, смектичний кристал, метильна група, Ван-дер-Ваальсова взаємодія, несуча здатність, сила когезії, сила тертя.