

Результаты статьи относительно предложенного синергетического метода оценки предпринимательских рисков в рамках методологии VaR могут найти применение в современной практике риск-менеджмента предприятий различного профиля финансово-хозяйственной деятельности.

Прогнозные предположения о развитии объекта исследования – проведение оценок предпринимательских рисков с использованием соответствующих финансово-экономических сведений о состоянии рынка и деятельности предприятий различного профиля с целью совершенствования предложенного метода.

КЛЮЧЕВЫЕ СЛОВА: ПРЕДПРИНИМАТЕЛЬСКИЙ РИСК, МЕТОДОЛОГИЯ VALUE-at-RISK, КРИВАЯ РИСКА, СИНЕРГЕТИЧЕСКИЙ МЕТОД, СИСТЕМА ЛОРЕНЦА.

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NATURE STUDY OF TEMPERATURE PHASE TRANSITIONS IN ASPHALT LAYERS WITH HYDROCARBONS PLASTICIZERS

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Problem. Development of technology for building durable asphalt layers of warm asphalt manufactured using solid hydrocarbons (waxes sosobit, rediset, etc.) is an important step in solving these practical problems [1-5]:

- expansion construction season (concluding asphalt mixtures at low temperatures);
- reducing energy costs for cooking warm asphalt mixtures;
- improvement of environmental characteristics of environment when using warm asphalt compared with conventional hot asphalt concrete.

The nature of temperature reduction stacking mixture affects the quality of the finished road surface, so changing thermophysical properties of the mixture by adding carbohydrate polymer plasticizers is significant as a scientific and practical interest. However, the current understanding of the nature, character and mechanisms of bitumen in such materials and the impact of such plasticizers on the rheological properties of these materials are in qualitative at best phenomenological level [6].

The main part. It is known [6] that the bitumen is spatially polydispersed system which dispersed phase - asphaltenes (multimolecular compounds), with lyophobic-lyophilic mosaic surface swell in hydrocarbon dispersion medium, in turn, to varying degrees structured resins. In the presence of solid paraffin in bitumen it is possible the formation of additional crystallization spatial grids. This gives grounds for certain approximations considered bitumen materials as organic polymeric compounds are structured in a reactive environment, and therefore used to study of their micro characteristic relevant experimental and theoretical methods.

Along with this, various methods found that the physicochemical properties of these materials, probably due to multipoint (local) interactions are shown at actual molecular fragments bitumen composite components and can be transferred under certain reservations on objects higher degree complexity. Therefore, the first step is probably advisable to conduct a comprehensive investigation of the properties of relatively simple (model), but at the same time representative of hydrocarbon molecular systems to identify the main features of the processes that occur in bitumen materials, and the impact of these processes on their rheological properties.

These convenient model objects for studying the structure, dynamics and corresponding temperature phase transitions in bitumen, in our opinion, may be normal (n-) paraffins C_nH_{2n+2} , as low hydrocarbon compounds. In addition, these compounds exhibit a variety of polymorphs, which are considered depending on the length of zigzag molecular chain (number n), its symmetry (parity number n) and temperature. This situation with the need actualizes basic research of structural and dynamic properties of paraffin, mechanisms of intermolecular interactions (ИМ) in them for a fundamentally new information for the development of general ideas about the physics of condensed matter, and determine the optimal development of scientific bases of technological processes can get those road-building materials with a complex set of properties.

Promising in terms of this goal can be considered the use of spectral methods, including methods of vibrational spectroscopy (Raman scattering, infrared (IR) absorption, etc.). In particular, the study by IR spectroscopy ИМ effects and dynamics of molecules in crystals of homologous series of aliphatic

compounds (n-paraffins, δ -olefin etc.) found the temperature dependence of the maxima frequency spectral bands Davydov splitting components resonant intra-molecular vibrations which leads to the coincidence of these components in the transition region of I kind "order - orientational disorder" that occurs at temperatures of 5 - 10 °C lower than the melting point of these compounds [7, 8]. At this time there is no single point of view on the nature of the detected temperature dependence [8].

In this paper, on the example of n-paraffins the mechanism that adequately describes the effect was found. This mechanism is associated with attenuation of intra-molecular vibrational excitons in a crystal in their interaction with the lattice orientation defects arising from excitation libration - rotational degrees of freedom of organic molecules in the transition of the crystal to a specified rotational phase.

Consider a low-temperature phase of crystalline paraffins which have orthorhombic and monoclinic modification with two molecules per unit cell [11]. In general case, the eigen frequencies for transversal vibrations which correspond to the components of Davydov multiplets can be found with the use of the standard procedure (see for example [9]) which involves diagonalization of the matrix

$$\left\{ \bar{\omega}_0^2 - \bar{D} \right\} \quad (1)$$

when passing to the coordinates of symmetry, which are transformed according to irreducible presentations of corresponding factor-group of the crystal. Here $\bar{\omega}_0^2$ is a diagonal (in the coordinates of symmetry) matrix of squares of frequencies of intramolecular vibrations in the crystal in the absence of the resonance dynamic intermolecular interaction, and \bar{D} is the corresponding matrix of resonance dynamic intermolecular interaction.

For crystal with two molecules per unit cell, one can present the frequencies of the components of the Davydov multiplets of j-th normal fundamental vibrational mode $\omega^{(j)}$ (wave vector $\vec{k} = 0$) in the convenient form [10]

$$\begin{aligned} \omega_1^{(j)} &\approx \omega_0^{(j)} + \Delta\omega^{(j)} \quad , \\ \omega_2^{(j)} &\approx \omega_0^{(j)} - \Delta\omega^{(j)} \quad . \end{aligned} \quad (2)$$

Here $\omega_0^{(j)}$ is the frequency of j-th intramolecular vibrations not perturbed by resonance dynamic intermolecular interaction, and $\Delta\omega^{(j)} \approx \frac{D^{(j)}}{2\omega^{(j)}}$ is the frequency shift caused by the resonance dynamic intermolecular interaction. The expression (2) is written when neglecting the quantities of second order of smallness.

It is known [7, 8] that, for crystalline the odd-numbered normal paraffins, a phase transition to hexagonal or rotary-crystalline modification occurs when increasing the temperature and approaching to melting. This phase transition is accompanied, in particular, by sharp expansion and coming together of the infrared absorption spectral bands, which correspond to the components of Davydov multiplets of normal vibrations of corresponding compounds. In this case, in our opinion, random irregularities in the lattice, first of all connected with orientation disorder of the molecules positioned in the lattice points, rapidly grow and greatly influence the nature of the spectral changes. In such a state, there exists a possibility of librational-rotational movements of the molecules around their long axes. These processes are characterized by corresponding potential barriers and by the changes of the entropy of the system.

Here we describe the contribution of the intermolecular interaction effects and molecular dynamics in paraffins in the orientationally disordered phase to the formation of the spectral bands of intramolecular vibrations in the framework of stochastic equations according to [11-13].

For this purpose, we consider (N+1) reactively coupled identical oscillators which form an actual system (cluster) with (N+1) states of the selected optical (IR) active mode in the bath which includes also the molecules which undergo Brownian reorientation. At some approximations, the time correlation function of this selected mode is described by the equation [13]

$$\frac{d}{dt} \hat{G}(t) = \hat{G}(t) [i\hat{\Omega} + \hat{\Gamma} + \gamma \hat{1}] \quad , \quad \hat{G}(0) = 1. \quad (3)$$

The time correlation function $\widehat{G}(t)$ includes oscillations ($\widehat{\Omega}$ is the matrix of oscillations), γ is pure relaxation due to anharmonic interaction of the selected vibrational mode with vibrations of bath and due to Brownian reorientation of the molecules ($\gamma \widehat{1}$, $\widehat{1}$ is the unity diagonal matrix), and reactive relaxation due to interaction between the oscillators of the actual system ($\widehat{\Gamma}$ is a matrix of reactive relaxation). The corresponding normalized spectral function $\widehat{J}(\omega)$ can be determined from $\widehat{G}(t)$ with the use of Fourier transformation [13]:

$$\widehat{J}(\omega) = \frac{1}{\pi} \int_0^{\infty} \widehat{G}(t) e^{-i\omega t} dt \quad (4)$$

To determine the matrix of frequency oscillations $\widehat{\Omega}$ which is a part of the expression (3), we write the stochastic Hamiltonian of the system in the form

$$\widehat{H}(t) = \widehat{H}^{(0)}(t) + V^{(1)}(t) \quad (5)$$

Here $\widehat{H}^{(0)}(t) = \widehat{P}(t) + V^{(0)}(t)$ is the Hamiltonian of the system, which describes weak influence of the thermostat, $V^{(0)}(t)$ is the stochastic potential energy of interaction between the molecules of the actual system and the bath, $V^{(1)}(t)$ is the stochastic potential energy of interaction between the molecules of the actual system. For convenience we assume that it is precisely the resonance dynamic intermolecular interaction that gives the main contribution to the perturbation of frequencies which are the elements of the matrix of oscillations $\widehat{\Omega}$ and determines the magnitudes and the structure (symmetry) of the actual system. All possible intermolecular interaction effects of other nature (for instance, resonance static intermolecular interaction) are sufficiently small here and are described by the potential $V^{(0)}(t)$.

Then, taking into account the processes of discrete frequency modulation, according to [13], we write the elements of the matrix of oscillations $\widehat{\Omega}$ in (3) for i -th component of the Davydov multiplet of j -th normal vibration in the form

$$(\widehat{\Omega}_i^{(j)}) = \delta_{l,n} (\omega_0^{(j)} + n \Delta \omega_i^{(j)}), \quad l, n = 0, 1, 2, \dots, N \quad (6)$$

We also assume that turning in (when the molecules of the actual system are in fixed state) and turning out (during librational-rotational movements of the molecules) of the processes of modulation of frequency occur independently. Then the elements of the matrix of reactive relaxation $\widehat{\Gamma}$ which are determined by the rate of transition of the molecules to their excited (librational-rotational) state can be written in the following form [13]:

$$(\Gamma)_{l,n} = R \left[(N - n) \delta_{l+1,n} + k n \delta_{l-1,n} - (N - n + k n) \delta_{l,n} \right]. \quad (7)$$

Here the modulation of the frequency of the intramolecular vibrational mode due to resonance dynamic intermolecular interaction is switched on with the rate R and switched off with the rate kR . These rates can be presented in the form of adapted Arrhenius law [14]:

$$R = A \exp\left(-\frac{E_A}{k_B T}\right), \quad k = \exp\left(\frac{\Delta S T - \Delta E_A}{k_B T}\right), \quad (8)$$

where E_A is the activation energy; k_B is the Boltzmann constant; T is absolute temperature; ΔS , ΔE_A are, respectively, variations of entropy and energy of activation required for turning out the discrete modulation processes in the excited state.

Having taken into account the binomial distribution of the states of the actual system and having performed averaging over the ensemble according to (8), we obtain the corresponding spectral function

$$\tilde{J}(\omega) = \frac{1}{\pi} \left\langle \left[i \left(\omega - \langle \Omega_i^{(j)} \rangle \right) - \gamma - \Gamma \right]^{-1} \right\rangle, \quad (9)$$

where $\langle \dots \rangle$ denotes averaging. Then the average value of the frequency of vibrations of the i -th component of the Davydov multiplet of j -th normal vibration has the form

$$\langle \Omega_i^{(j)} \rangle = \omega_o^{(j)} + \Delta \omega_i^{(j)} \frac{N}{1+k}. \quad (10)$$

The analysis of the expressions (8) and (10) shows that, with the increase of temperature, the values of the frequencies of the Davydov components $\langle \Omega_i^{(j)} \rangle$ tend to reach the value of the frequency of the vibrational mode nonperturbed by the intermolecular resonance ω_o due to the growth of the parameter k (Eq. (8)). In this case (see Eq. (8)), the role of entropy ΔS as the measure of disordering of the system becomes dominant in the comparison with the intermolecular interaction energy. In addition to the growth of the processes of discrete modulation of the frequency of the vibrational mode, this leads also to spatial damping of the intramolecular vibrational excitons (see Eq. (7)) on the orientational defects of the crystal, whose amount increases with temperature. As a result, some modification of the exciton branches and the loss of the condition for the wave vector $\vec{k} \approx 0$ occur, the Brillouin zone opens, and, consequently, in addition to coming together of the frequencies of the maximum (see Eq. (10)), broadening of the spectral bands of the components of the Davydov multiplets takes place.

In [7] experimentally found to be most sensitive to the phase transition in the infrared absorption spectra of paraffin n-C23 is the bands corresponding to deformation vibrations of methylene chains of molecules with a frequency of 1465 cm^{-1} . In Fig. 1 (dots) shows the results of experimental studies of changes Davydov splitting value $\Delta v_{1,2}$ of these oscillations by heating the samples from $299 \text{ }^\circ\text{C}$ temperature to the melting point.

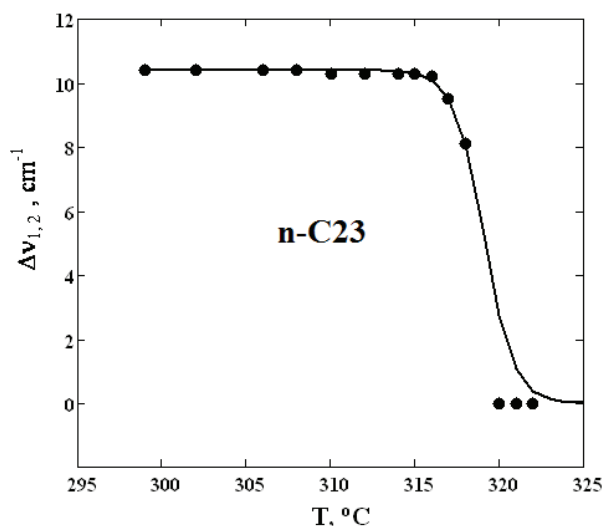


Fig. 1. The temperature dependence of Davydov splitting for deformation vibrations of methylene chains of molecules odd normal paraffin n-C23. Points - experiment [7], line - theory.

Theoretical dependence of the corresponding splitting of the temperature we obtain from equations (2), (8), (10), which has the form

$$\Delta\Omega_{1,2}^{(j)}(T) = \frac{\Delta\omega_{1,2}^{(j)}}{1 + \exp\left\{\frac{\Delta S T - \Delta E_A}{k_B T}\right\}} \quad (11)$$

It $\Delta\omega_{1,2}^{(j)} = N(\Delta\omega_2^{(j)} - \Delta\omega_1^{(j)})$ corresponds to the Davydov splitting intra-molecular vibrations of crystals ordered low-temperature (orthorhombic) phase.

In Fig. 1 shows the results of combining the method of least squares theoretical dependence (11) with the corresponding experimental data. This yielded the following values: $\Delta E_A = (230.68 \pm 0.14)$ kcal / mol, $\Delta S = (0.72294 \pm 0.00017)$ kcal / mol·K. As shown in Fig. 1 there is good agreement between theoretical and experimental temperature dependences. All this clearly indicates the correctness of the proposed in this paper the mechanism of resonance dynamic intra-molecular vibrations, which adequately describes the features of Davydov splitting of vibrational modes in the transition region "order - disorder orientation" of crystalline n-paraffins. Some differences between the experimental and theoretical dependences $\Delta\nu_{1,2}$ (see Fig. 1) possibly associated with neglect here changes the distance between the molecules at increased temperature, which in some way affect the value of Davydov splitting. Obviously, presented in this paper, the theoretical understanding of resonance dynamic intra-molecular vibrations in the study of phase transition of crystalline n-paraffins are generic and can be applied to the analysis of the vibrational spectra of rotational crystals.

Conclusions. From the experimental results [7] and theoretical spectral studies of temperature phase transition of I kind in n-paraffins follows a practical conclusion. In this transition there is a sharp change in the nature of the molecules in the crystal lattice sites: the molecule is due to thermal excitation is carried out libration and rotational movements. This leads to dramatic (nonlinear) changes in structural and mechanical properties of hydrocarbon components of bitumen - particularly sharp on some orders reducing their viscosity even at temperatures below the melting point. Introduction polymeric hydrocarbon plasticizers in bitumen, due to the formation of certain chemical bonds between nanoparticles and molecules bitumen increases the temperature range of existence of the orientation phase, and thus to increase the temperature range of plasticity and deformability bitumen up to temperatures below zero. Thus, there is reason to believe that one of the factors that determine the appropriate rheological properties of bitumen is the existence in certain temperature ranges rotational phase of hydrocarbon components.

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РЕФЕРАТ

Данчук В.Д., Кравчук А.П. Дослідження природи температурних фазових переходів в асфальтобетонних шарах із вуглеводними пластифікаторами. / Віктор Дмитрович Данчук, Анатолій Пилипович Кравчук//Вісник НТУ.- К.: НТУ. – 2012. – Вип. 26.

У статті в термінах стохастичних рівнянь теоретично проаналізовано вплив резонансної динамічної міжмолекулярної взаємодії на формування спектральних коливальних смуг молекулярного кристалу в області переходу в ротаційну (пластичну) фазу. Запропоновано механізм, який адекватно описує температурну поведінку величини давидовського розщеплення внутрішньо - молекулярних коливань кристалу в дослідженій фазі, що спостерігається, зокрема, в нормальних парафінах. Цей механізм пов'язаний із затуханням коливальних екситонів при їх взаємодії з орієнтаційними дефектами ґратки, які виникають внаслідок теплового збудження лібраційно обертальних ступенів свободи молекул. Визначено, що одним з чинників, які визначають відповідні реологічні властивості бітумів є існування в певних діапазонах температур ротаційної фази їх вуглеводневих компонентів.

КЛЮЧОВІ СЛОВА: АСФАЛЬТ, БІТУМ, ВУГЛЕВОДНІ ПЛАСТИФІКАТОРИ, ПАРАФІНИ, ЕКСІТОНИ, ДАВИДОВСЬКЕ РОЗЩЕПЛЕННЯ, РОТАЦІЙНА ФАЗА

ABSTRACT

Danchuk V.D., Kravchuk A.P. Nature study of temperature phase transitions in asphalt layers with hydrocarbons plasticizers./Viktor Danchuk, Anatoliy Kravchuk//Bulletin NTU.- K.: NTU. – 2012. – Vol. 26.

In the paper in the concepts of stochastic equations the theoretical analysis of the influence of resonant dynamic intermolecular interaction on formation of spectral vibrational bands of molecular crystal in the region of the transition in the rotary (plastic) phase is performed. An adequacy mechanism of temperature behaviour of davydov splitting of intramolecular vibrations value for paraffins crystals at the rotary phase transition is proposed. This mechanism is related with vibrational excitation damping at their interaction with orientated defects in the crystal lattice. Such defects arise due to thermal activation of molecular libration and rotation freedom degrees. It is determined that one of the factors that determine the appropriate rheological properties of bitumen is the existence in certain temperature ranges rotational phase of hydrocarbon components.

KEYWORDS: ASPHALT, BITUMEN, HYDROCARBON PLASTICIZERS, WAXES, EKSITONY, DAVYDOV SPLITTING, ROTATIONAL PHASE

РЕФЕРАТ

Данчук В.Д., Кравчук А.П. Исследование природы температурных фазовых переходов в асфальтобетонных слоях с углеводными пластификаторами. / Виктор Дмитриевич Данчук, Анатолий Филиппович Кравчук//Вестник НТУ.- К.: НТУ. – 2012. – Вып. 26.

В статье в терминах стохастических уравнений теоретически проанализировано влияние резонансного динамического межмолекулярного взаимодействия на формирование спектральных колебательных полос молекулярного кристалла в области перехода в ротационную (пластическую) фазу. Предложен механизм, который адекватно описывает температурное поведение величины Давыдовского расщепления внутренне - молекулярных колебаний кристалла в исследованной фазе, которая наблюдается, в частности, в нормальных парафинах. Этот механизм связан с затуханием колебательных экситонов при их взаимодействии с ориентационными дефектами решетки, которые возникают вследствие теплового возбуждения либрационных вращательных степеней свободы молекул. Установлено, что одним из факторов, которые определяют соответствующие реологические свойства битумов, есть существование в определенных диапазонах температур ротационной фазы их углеводных компонентов.

КЛЮЧЕВЫЕ СЛОВА: АСФАЛЬТ, БИТУМ, УГЛЕВОДНЫЕ ПЛАСТИФИКАТОРЫ, ПАРАФІНИ, ЕКСІТОНИ, ДАВИДОВСКОЕ РАСЩЕПЛЕНИЕ, РОТАЦИОННАЯ ФАЗА