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NONLINEARITIES CORRELATION OF N-ALKANES AND N-ALCOHOLS PHYSICOCHEMICAL PROPERTIES

Correspondences between the changes nonlinearity in substance physico-chemical parameters and the influence mechanisms on them by the substance supramolecular structure in the calculated dependencies form for n-alkanes and n-alcohols was established. Similarity, change features and correlation between such parameters as melting point, boiling point, flash point, self-ignition, density, solubility in water, viscosity, vaporization heat, surface tension were investigated. The paper obtained 14 calculated dependencies that calculate these parameters on the established similarity basis between them and the lengths of the molecule or cluster with sufficient correlation coefficients. For viscosity, vaporization heat and surface tension, change general dependences are established, but without taking into account oscillatory deviations. Calculated dependences between substance characteristic temperatures were obtained: melting temperatures of alkanes and alcohols, boiling and flash temperatures in homologous series, autoignition and melting temperatures (flash, boiling). This correlation is explained by the fact that supramolecular structures are formed according to a similar principle in matter different states and during the combustion initiation. Such structures modeling for the solid, liquid state, and solubility in water was carried out, taking into account different coordination numbers, globulation, and changes in the clustering place according to the molecule length. On the such modeling basis and the "melting ease" indicator, dependencies have been developed for calculation with the dependencies nonlinearities reflection of alkanes and alcohols density and melting temperature. For the boiling and flash point, vaporization heat of alcohols, the deviation from linearity is taken into account by the cluster length reduction parameter. It is shown that the considered dependencies modulation by the cluster length allows to describe their anomalies and increases the calculation convergence.

Keywords: n-alcohols, n-alkanes, physicochemical properties, cluster, model, nonlinearity, calculation convergence

1. Introduction

Ensuring the fire safety in production and in the civil sphere is realized through forecasting and control of substances certain indicators. It can be said that this knowledge branch is material science about critical states. The combustible substances and building materials properties are formed on the basis of physicochemical properties combinations. Accordingly, there is a correlation relationship between them. Usually, in practical calculations of fire hazard parameters, pairwise correlations between them and certain "fundamental" properties are used. But, as the previous analysis showed, none of the physicochemical and fire hazard properties behaves identically to another parameter [1]. This leads to inadequate prediction of some substances fire hazard in the hydrocarbons homologous series in a "random" way. There are calculation equations based on clear physico-chemical models that claim to be universal and allow calculations for various homologous classes; but these equations, in addition to the calculation complexity and the certain data lack for their wide application, have a drawback in the form of the model incompleteness, which incorrectly takes into account the certain factors ratio or omits a certain factor. Nevertheless, the existing improvement and the new universal methods development with high forecasting accuracy is of great interest.

The problem arises of a more detailed study of correlations between substance various properties with the possibility of predicting fire hazard parameters of hydrocarbons several homologous classes at the same time. A significant drawback of the existing calculation methods in this direction is the ignoring and lack of mechanisms for taking into account contributions of intermolecular interaction and the supramolecular structures presence on nonlinearity in changes of homologues certain properties. Nevertheless, recent studies indicate the such structures presence and their corresponding influence on substance certain parameters, in particular, the cluster equivalent length is adopted as the basic modulating parameter [2].

Thus, at present, the problem of taking into account the substance supramolecular structure, which can exist in the form of stable clusters or temporary structures, in the formation processes of fire hazard parameters and their forecasting methods remains unsolved. The determined state of the substance physico-chemical properties forecasting issue indicates the relevance and perspective of conducting additional research on the new methods or calculation basis creation.

2. Analysis of literature data and problem statement

Solving the systematic errors presence problem in calculation methods for predicting fire hazard parameters involves conducting a comparative analysis of substance various physicochemical properties within one homologous series and in relation to hydrocarbons another class. It is possible to single out the substences and environment properties levels, which consistently determine the formation of the properties next level, starting with the atomic one. For example, the flash point (t_{fp}) value will be affected by the following chain of factors: atomic composition – molar mass – type and number of chemical bonds – molecular structure – content of clusters and individual molecules – substance formation heat – vaporization heat – initial conditions – saturated vapor pressure – vapor concentration – ignition source parameters – lower flammable limit (LFL) – air mixture thermophysical parameters – flash point [1]. Such a sequence means that any of the previous parameters can be used to predict t_{fp} individually or in combination with another parameter. Then, for a homologous series, one of these levels can become modulating to describe the change in the actual dependence of another parameter, and therefore will reflect oscillatory, stepped, pulsating nonlinear features within the calculation method limits.

Many models are known for the mathematical description of the hydrocarbons vaporization heat (H_{vap}) [1, 3, 4], which are narrowly specialized for n-alkanes or n-alcohols, and also do not describe some anomalies. For example, for n-alkanes with n_C=5–40, a formula was developed: $H_{vap}=5684,27+5295,41n_C-17,2732T_{bp}$, J/mol [3], that indirectly and does not fully take into account the nonlinearities of H_{vap}, does not work for first representatives of homologous series, and does not rely on supramolecular structure peculiarities. We previously developed an equation for n-alcohols $H_{vap}=37,3+4,75(n_C-1)$, kJ/mol [1], but this equation does not take into account deviations from the dependence linearity for alcohols with n_C >13 [1]. It was noted that H_{vap} correlates with t_{bp}: for n-alkanes with R=0,979, for n-alcohols with R=0,997. The better correlation for alcohols is explained by the fact that for them both H_{vap} and t_{bp} have a character close to linear with synchronous oscillations. For n-alkanes, H_{vap} and t_{bp} do not have significant fluctuations, but if for H_{vap} the dependence is almost linear, then for t_{bp} it is close to exponential.

Nevertheless, the relationship between H_{vap} and t_{bp} is widely used in computation-

al methods, but requires separate approaches for polar and nonpolar liquids. The best alternative is considered to be the method based on the Laidler bond extended additivity, which takes into account the solvent polarity, 165 input parameters using the software environment, divides the molecule into constituent conditional functional groups, applies certain descriptors for them, which ensures an error of up to 1 %, but the method does not consider the supramolecular structure [4]. We improved the existing calculation methods and developed a universal, more complex formula using additional coefficients for predicting the H_{vap} of different homologous classes [1]. Due to the reliance on t_{bp}, this calculation method partially approximates some fluctuations of H_{vap}, but does not take into account their cause in the form of supramolecular structure features.

The statistical associative theory based on the molecules coarse-grained model is used to model liquids and predict their parameters wide range [5–10]. The corresponding model describes the molecule as a hard balls set that replace a functional group [5, 8, 9] or several framework hydrocarbon atoms of 2–4 pieces each [5, 6]. A certain matrix is filled with formed sets of balls. The model allows predicting such substance parameters as a density, vaporization heat, surface tension, solvation energy, internal diffusion coefficient: for alcohols [5], alkanes [6] and even polymer compounds [10]. But this method has a number of disadvantages: the atoms grouping into balls occurs in the "manual" mode, and results obtained do not reflect the certain parameters actual fluctuation, each compound is modeled individually, for example, octacosane with $n_C=28$ [7]. Due to the description discreteness, this technique does not work for short molecules: models have been developed for alcohols, starting with ethanol, for alkanes – with pentane. Due to the atoms grouping into "balls", this technique indirectly takes into account effects of electron density redistribution in the molecule and partially – intermolecular interaction, but this does not modulate the features associated with the cluster structure alternation in homologous series. For example, this method does not allow to describe the decrease in the «long» alcohols density.

For the substances solid state, an amorphous or crystalline structure is noted. Studies have shown that melting temperatures (t_{mp}) values are not correlated with the molecular structure, but mainly with a dimeric or other supramolecular structure with a clear coordination number. For example, a gold cluster has a t_{mp} that coincides with the t_{mp} of lump gold starting from the atoms number in the cluster – 1000 [11]. Moreover, the change in the substance crystalline structure often occurs at a slightly higher temperature than t_{mp} [12]. The liquid state is a mixture of clusters and individual molecules [13], as the liquid temperature increases, the ratio between them changes. Evaporation in the stable dimers form is known for some substances (formic acid) [14]. These works do not shed light on the connection between the supramolecular structure and the substance properties. It is the detection and analysis of the substance properties oscillation dependence that shows changes in the cluster structure [15], and the monomolecular state does not describe this phenomenon.

In most cases, gas systems are characterized by a monomolecular state. But for combustion processes, it was established that the autoignition temperature (t_{ai}) of mixed organic solvents behaves like the azeotropic solutions characteristic temperatures, that is, it can be higher or lower than components [16]. This is explained by clustering, and according to the ratio of components mole fractions, the coordination number for different solvents varies within 20–50. That is, the azeotrope behaves according to certain properties as a new chemical compound, which is determined by the formation of an atypical cluster. The clusters presence for the gaseous state can be explained by analo-

gy: one of flaming combustion stages, as well as coal spontaneous combustion, is the unstable organic peroxides formation [17, 18]. But these works do not consider the supramolecular structure influence on the combustion occurrence. Therefore, taking into account the substance cluster structure makes it possible to predict both t_{mp} [15] and combustion processes [19]. But these works did not use the analytical comparison possibility of various physico-chemical quantities parameters to establish the supramolecular structure features.

We have previously determined the smallest supramolecular structure that determines the solubility maximum proportion [1]. The model assumes the solute coordination number from 1 to 17 and the associated water molecules number according to the principle: 4 lateral water molecules near each carbon atom of the hydrocarbon molecule and additionally 2 more molecules on the end groups, as well as between the hydrocarbon molecules in the cluster. Moreover, it turned out that molecules of methanol, ethanol, and propanol do not combine into a cluster, but are associated with water molecules each separately. But according to the "alcohol solution in a water" model, there is still a maximum solubility for these compounds. Then, at alcohol higher concentrations, the solution should have alcohol clusters centers in addition to the micelle-like structure. But this model is not suitable for describing the individual liquids supramolecular structure.

The research current state on modeling the substances liquid state in order to predict their properties demonstrates either an approximation approach or an attempt to describe the supramolecular structure «force fields». Both approaches have a lack of accuracy [5, 18] due to the fact that they do not track the causes, and therefore do not use the mechanisms for taking into account deviations from the smooth dependence for the substance physico-chemical parameters in homologous series. Currently, a modeling method the cluster structure of the substance using the cluster equivalent length as a modulating parameter is being developed. But this technique does not yet have clear mechanisms for predicting parameters for which there are no experimental data, although it has mechanisms for describing the corresponding dependencies profile, taking into account anomalies.

Thus, the scientific problem of developing effective modeling mechanisms and mathematical description of smallest supramolecular structures of hydrocarbon liquids for predicting the substance parameters, including those describing the fire and explosion hazard, needs to be solved. Solving this problem involves establishing deviations from the smooth change of physicochemical properties parameters in hydrocarbons homologous series and establishing correspondences to them in the form of molecule conformal changes and changes in the supramolecular structure organization scheme with the parameter determination that reflects such changes. As a parallel path, it is necessary to note the finding properties possibility that have the deviations same type from the main tendency of dependence, which will allow establishing proportionality between them with a high correlation degree.

3. The purpose and tasks of the research

This work purpose is to establish correspondences between the changes nature in the substance same physicochemical parameters and the influence mechanisms on these parameters of the substance supramolecular structure in the calculated dependencies form using the example of n-alkanes and n-alcohols homologous series.

To achieve the purpose, the following tasks solution is provided:
– to analyze the relationship between the same physicochemical parameters

change nature in n-alkanes and n-alcohols homologous series and to propose calculation models;

– to invent the taking into account possibility supramolecular structures in methods of predicting certain physicochemical parameters of n-alkanes and n-alcohols.

4. Research materials and methods

The research object is the hydrocarbons physicochemical properties.

The research subject is the correlation dependence between the hydrocarbons physicochemical properties parameters.

The research hypothesis is the possibility of detecting synchronous anomalies in the substance physicochemical properties some parameters change as a supramolecular structure peculiarities consequence, which will allow establishing improved correlation dependencies, as well as taking into account these anomalies in the calculation by introducing the «cluster length» parameter.

The research method is to conduct the substance properties changes comparative analysis by the modulating parameter – the hydrocarbons carbon atoms number and the improved modulating parameter development – the cluster length.

The organic substances basic class is alkanes; alcohols are widely studied substances with the oxygen content. Therefore, normal structure alkanes and alcohols physical, chemical, and fire hazard properties with the carbon atoms number up to 20 were investigated in this paper, that is, 40 compounds are investigated. The simplest way to compare dependencies is graphically. A comparison of n-alkanes and n-alcohols physicochemical properties, the profile (linear or exponential), the amplitude and fluctuation of these dependencies, as well as the search for mechanisms for predicting corresponding parameters according to the general calculation principle.

The substance supramolecular structure description according to the parameter that demonstrates the largest fluctuation is adopted as the modeling basic principle. Previously, we described the change in the t_{mp} of hydrocarbons several homologous series according to this principle [1, 2, 15]. Connection in a cluster other than the hydrocarbon molecule terminal carbon shortens the cluster longest carbon chain, so t_{mp} decreases. That is, side links relative to the cluster longest chain are not taken into account. If the cluster coordination number increases, the cluster length and t_{mp} increase. For modeling the n-alkanes shortened chain, a restriction is adopted: the clustering point cannot move more than chain half. Then the need for chain greater shortening to describe a certain dependence can be achieved by taking into account bending, globulization or other molecule conformational changes that can affect its equivalent length. Thus, a cluster consists of two or more monomers. Under the clustering condition by last groups of normal structure molecules – the cluster length (n_{Ceq}) is determined by multiplying the number of molecule framework atoms (the molecule length n_C) by the coordination number K; in the clustering case not by the final carbon atom, for a linear structure cluster (not cyclic), the shortened monomer length is determined, multiplied by «K–1», then one molecule full length is added.

In order to analyze and take into account the cluster structure, we previously developed [15] the "melting ease" indicator $n_M = n_{Ceq} M^{0.2}$, on the which basis, taking into account the cluster molar mass M, a universal formula for the hydrocarbons t_{mp} predicting was created: $t_{mp} = 101,85 \ln(n_M) - 452,37$, $^{\circ}C$. This formula, in the analysis reverse order, helps in modeling the hydrocarbon particular cluster structure. At the same time,

such a supramolecular structure is chosen that, for a cluster with a certain coordination number and M, forms such the cluster length that corresponds to t_{mp}.

Changes in physical properties following parameters of n-alkanes and n-alcohols were studied (according to PubChem and NIST data [20, 21]): melting t_{mp}, boiling t_{bp}, flash t_{fp}, autoignition temperatures t_{ai}, density ρ, solubility in a water γ, viscosity ν, surface tension σ, vaporization heat H_{vap}. These parameters comparison was carried out according to the absolute value, then the simplest scaling of one of parameters was carried out as an amendment to the general formula. Then, possible molecular and supramolecular effects were considered to describe the dependence anomalies. The only indicator for which it is difficult to conduct the graphical dependence visual analysis and comparison between homologues is solubility, since it varies by 7 orders of a magnitude (even without taking into account the unlimited solubility of first three n-alcohols); therefore, γ was analyzed as a function: $f(\gamma)=6\gamma^{0.1}$.

5. Analysis results of the relationship between hydrocarbons physicochemical parameters

We investigate the hypothesis that for substance properties adequate prediction, it is necessary to model the supramolecular structure. Differences in it and conformational changes of molecules can be reflected by calculating the equivalent cluster length n_{Ceq}. But first, it is necessary to consider the corresponding dependences on the carbon atoms number for normal structure compounds.

If we consider the process of solubility in a water, the ratio of 1 mol of an alcohol (alkane) to 1 mol of a water, when each hydrocarbon molecule is associated with one water molecule (or options: 2 to 1 mol and 1 to 2 mol) seems ideal. But then the solubility maximum mass concentrations would be to some extent proportional to the carbon atoms number in the molecule. However, solubility decreases much faster. According to the analysis, the ratio of the water molar mass to the alcohol molar mass from n-butanol to n-eicosanol decreases by less than a magnitude order, while the solubility decreases by 7 magnitude orders (similarly for alkanes, but starting with methane), Fig. 1. This may indicate the longer molecules clustering at some point along the carbon chain length in addition to the final group association with hydroxyl groups or instead of this clustering type. It is also possible that the indicated effect reduces the alcohols hydrogen bond intensity, and, accordingly, the solubility.

But the decrease in the solubility is most likely related to slightly different processes. For example, it is known that some substances extremely small concentrations change the entire solution properties. That is, the water supramolecular structure is modulated according to the dissolved molecule structure. This means that a micelle-like shell is set up around it.

Data on the hydrocarbons solubility γ in Fig. 1 are given in the function form $K_\gamma = 6\gamma^{0.1}$. In this form, γ of n-alkanes and n-alcohols in the range of $n_C=4–16$ behave identically, and for some compounds with the same carbon atoms number, they coincide, which made it possible to develop a generalized approximation dependence with R=0,988 and an error of 17 % [20, 21]. The curves similarity indicates the micelle-like structures similarity of considered hydrocarbons solutions with the same carbon chain length; it also turns out that the "OH" group of alcohols takes the water molecule place between monomers in the hydrocarbon cluster linear structure (compared to alkanes). For high concentrations of short n-alcohols, the micelle-like structures absence can be predicted – which can explain the unlimited solubility, and for long n-alkanes –

globulization, which shortens the carbon chain and causes the overall dependence fluctuation. The single peak for n-alkanes at $n_C=13$ is interesting, which is similar to the single peak for n-alcohols at $n_C=15$. This can be explained by the fact that, according to the accepted model, the alkane monomer is surrounded on both sides along its length by water molecules, and in the alcohol case, by OH bridges. Then, for the monomer length of «15», another "pentane" effect can occur due to the addition of one more freedom degree. On the other hand, the final OH group changes the electron density distribution along the molecule length.
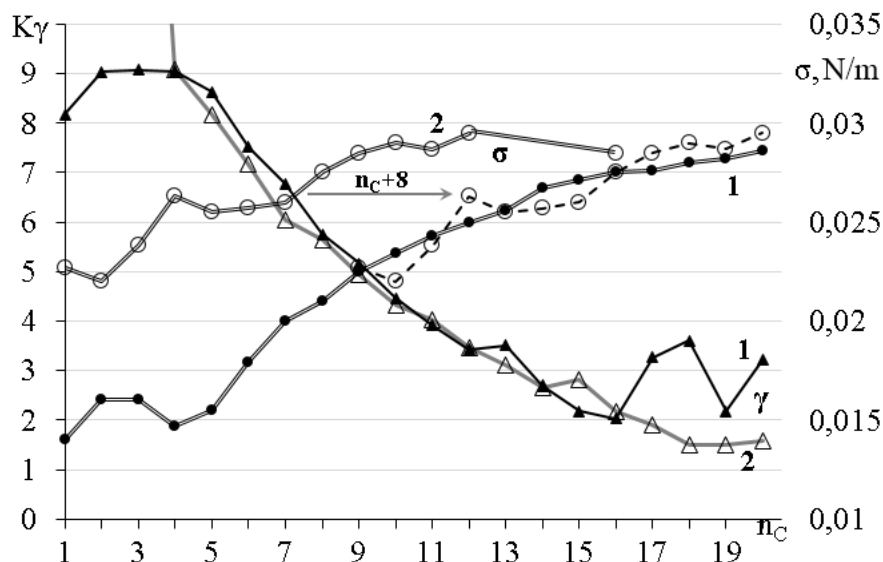

Fig. 1. Solubility in water (γ) and surface tension (σ) of alkanes (1) and alcohols (2)

For the investigated homologous classes of liquids, the opposite anomaly is noticeable in the region $n_C=1–3$, namely: unlimited γ for n-alcohols, and underestimated relative to the general trend of γ for n-alkanes. This can be explained by the fact that for alkanes solutions, as well as for the t_{mp} [1], for methane and ethane, a model with a higher coordination number worked; at the same time, for the first three n-alcohols homologues – a monomeric model.

In the same length range, there is an inversely proportional anomaly for the surface tension σ – slightly lower values relative to the trend for n-alcohols, and slightly higher values for n-alkanes, Fig. 1. Also, pronounced fluctuation of σ is noticeable for n-alcohols and less noticeable for n-alkanes. Separate data for hexadecanol, in addition, indicate the growth cessation of σ (or dependence fluctuation) in the n-alcohols homologous series, which correlates with a simultaneous decrease in the density. For σ n-alkanes and n-alcohols, a generalized calculation formula can be proposed, assuming that the alcohol carbon chain is 8 links longer than the molecular structure suggests:

$$\sigma=6 \cdot 10^{-7} n_C^4 - 3 \cdot 10^{-5} n_C^3 + 4 \cdot 10^{-4} n_C^2 - 1,3 \cdot 10^{-3} n_C + 0,0158, \text{ N/m}. \tag{1}$$

The formula approximates the dependence for σ with $R^2=0,98$, but does not reflect vibrational features, since it takes into account the molecule length, not the cluster

The vaporization heat growth (H_{vap}) in the studied hydrocarbons series turned out to be the most linear dependence, Fig. 2. But anomalies are also noticeable for the H_{vap} change: for light alkanes (similarly to γ and σ) there are slight deviations for alcohols according to the «pentane» effect principle, for long alcohols – starting from $n_C=13$ (while t_{mp} already exceeds the standard temperature).

The dependences inclination angle for alkanes and alcohols is the same, which makes it possible to superimpose them and establish a calculation permanent correction relative to n-alkanes for n-alcohols: a) «n_C+6», b) 2 «$H_{vap\ alk}+30$». The dependence for n-alkanes can be described by the equation: $H_{vap}=5,0076n_C+0,9121$, kJ/mol, which provides $R^2=0,99$. But this approach does not approximate the dependence anomalies for n-alcohols, because it does not take into account the peculiarities of their supramolecular structure (for n-alkanes no significant anomalies were noticed).
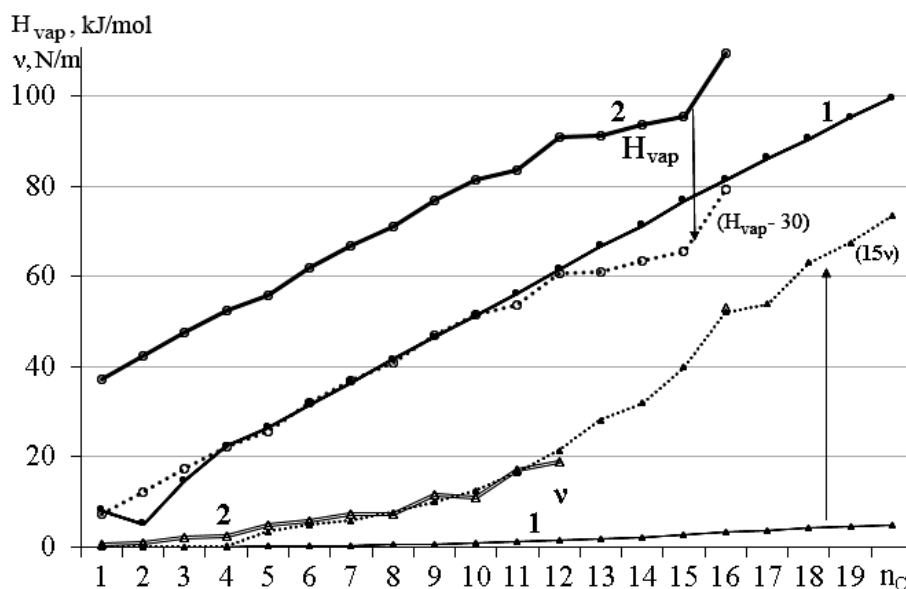

Fig. 2. Proportionality of viscosity and vaporization heat of n-alkanes and n-alcohols

The n-alkanes and n-alcohols viscosity ν has a significant difference, as well as fluctuations and the both dependences linear nature absence. Taking into account the proportionality between them, the formulas system can be proposed: for n-alcohols $v_{alc}=0,2498n_C^2-1,2536n+2,1192$, recalculation for n-alkanes $v_{alk}=v_{alc}/15$, with $R^2=0,99$. This formula also does not describe oscillations in homologous series.

Substances characteristic temperatures and their description are of the particular interest for the fire and man-made safety areas, (Fig. 3): t_{mp} and t_{bp} determine the substances behavior during emergency situations or fire, and t_{fp} and t_{ai} are directly fire hazard parameters. These temperatures ratio for n-alkanes and n-alcohols is given.

Of n-alkanes and n-alcohols t_{mp} has an identical character with synchronous fluctuations, but with a higher value for n-alcohols by 30–60°C and a more intense overestimation of t_{mp} for the first two homologues (methanol and ethanol). This relationship can be described by the equation, K: $T_{mp_{alc}}=T_{mp_{alk}}^{0,97}+79$, with R=0,996 and an average error of 3,7 K, the largest for methanol – 17,1 K. The methanol anomaly for t_{mp} can be explained by that it has a higher molar mass than methane. The methane anomaly for t_{mp} was previously explained by the clusters hexameric structure in contrast to other homologues [15]. The curves synchronicity indicates these substances supramolecular structure principles similarity in the solid state.

Within the n-alkanes and n-alcohols homologous series, t_{mp} and t_{fp} have an identical character. For n-alcohols, three areas of the dependence change are noticeable: $n_C=1–10$ (almost linear), $n_C=10–15$ (almost linear with a different slope angle), $n_C=15–20$ (oscillating), but with R=0,99 a linear approximation works, K: $T_{bp_{alc}}=18n_C+318$ and $T_{fp_{alc}}=0,6T_{bp_{alc}}+77$.
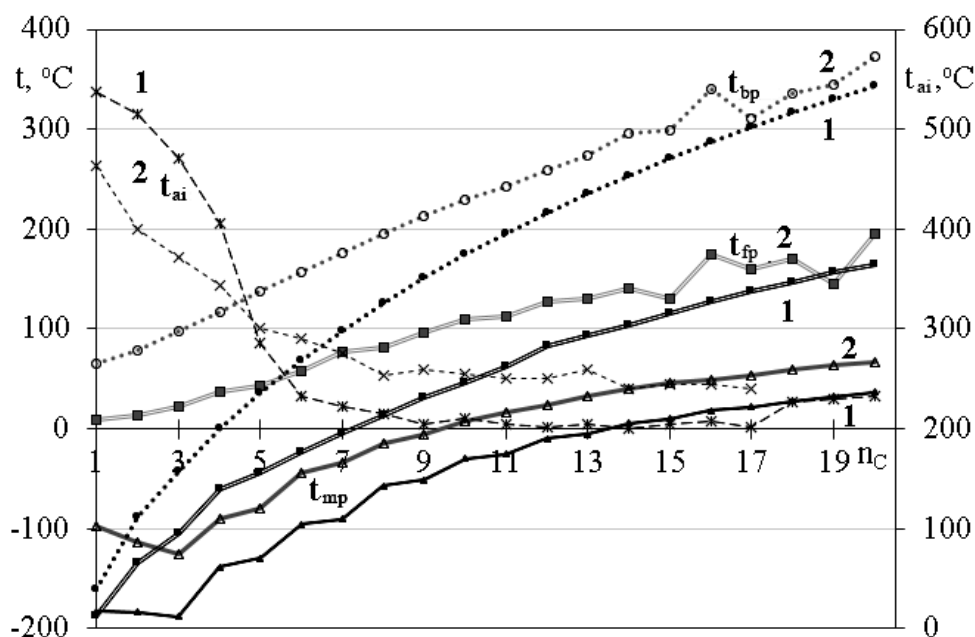
Fig. 3. N-alkanes (1) and n-alcohols (2) characteristic temperatures

The t_{fp} change in the n-alkanes homologous series has features relative to t_{mp} and t_{bp}: there is a slight fluctuation up to $n_C=4$, but without overestimated values for the t_{mp} methane and ethane; the graph is smoother, but there are also two linear segments (more pronounced than for n-alcohols) with $n_C=4–12$ and with $n_C=12–20$ (and for $n_C=4–12$ the t_{fp} slope angle coincides with the n-alcohols t_{bp} slope angle). Regardless of the t_{bp} n-alkanes dependence smoothness, it was possible to describe it only by a 3rd degree polynomial: $t_{bp}=0,0567n_C^3–2,7741n_C^2+60,515n_C–206,75$ with $R^2=0,999$, an average error of $3,5$ °C, the largest – $12,6$ °C (methane); then $t_{fp}=0,7t_{bp}–75$ °C with $R=0,99$ and an average error of $4,4$ °C, the largest – $18,8$ °C (butane). The n-alcohols t_{mp} fluctuation becomes less noticeable after $n_C=8$, for n-alkanes – after $n_C=17$.

The change in t_{bp} and t_{fp} in the n-alkanes and n-alcohols homologous series turned out to be the fundamentally different: methane and methanol t_{bp} and t_{fp} differ by approximately 200 °C. In addition, t_{bp} and t_{fp} of alcohols grow according to a dependence close to linear (which is logical – as proportionality to the molar masses growth in the homologous series); n-alkanes characteristic temperatures approach these lines asymptotically. Moreover, for n-alkanes, these dependences fluctuations are almost not noticeable, and for heavy n-alcohols there is a strong oscillation.

With regard to t_{ai}, at first glance the dependences for n-alkanes and n-alcohols have a similar character, but with a values different gradient within the homologous series. A more detailed analysis shows that for n-alcohols the graph has greater oscillation, as well as linearity in segments up to and after $n_C=8$ (taking into account the OH group, the "framework" length is 9). For n-alkanes, the linear character is observed in the segment $n_C=9–17$.

It is possible to analyze the hydrocarbons characteristic temperatures differences, Fig. 4: $\Delta t_{bp\text{-}fp}= t_{bp}–t_{fp}$, $\Delta t_{bp\text{-}mp}=t_{bp}–t_{mp}$, $\Delta t_{fp\text{-}mp}=t_{fp}–t_{mp}$. The presence of Δt close values can become the basis for creating a generalized calculation dependence. But cross-dependencies $\Delta t_{bp\text{-}mp}(n_C)$, $\Delta t_{fp\text{-}mp}(n_C)$ have significant differences and begin to approximately coincide only after $n_C=9$. And dependencies for t_{bp} and t_{fp} coincide quite closely, so they can be described by a general equation: $\Delta t_{bp\text{-}fp}=6,7105n_C+55,069$ with

$R^2=0,9575$. From this equation, a dependence can be obtained for predicting the n-alkanes and n-alcohols t_{fp} based on the values of t_{bp} and the molecule length n_C: $t_{fp}=t_{bp}-(6,7105n_C+55,069)$, but this dependence does not reflect the fluctuations of the t_{fp} change in homologous series.
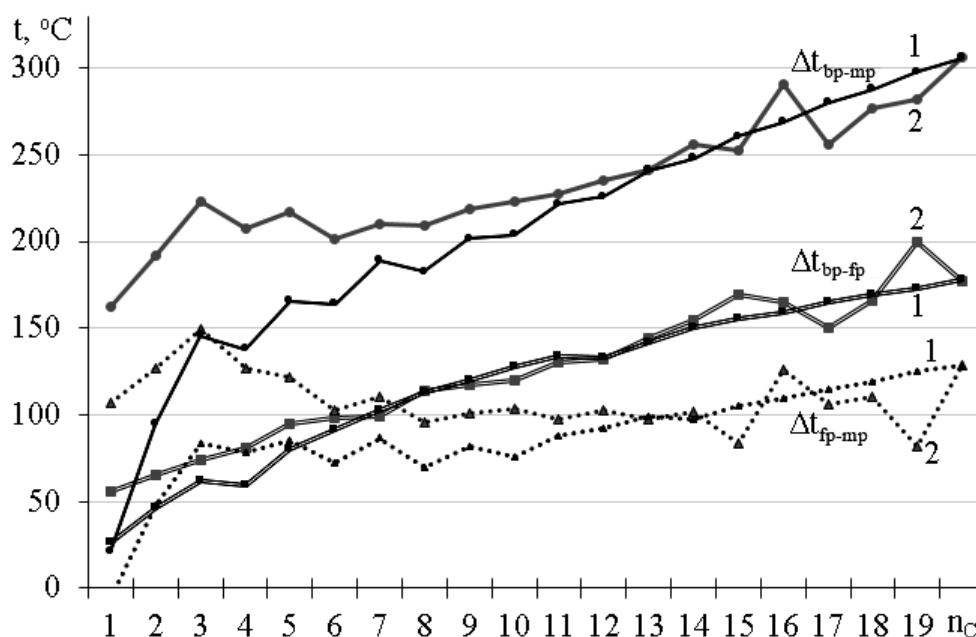

Fig. 4. The differences ratio in the n-alkanes (1) and n-alcohols (2) characteristic temperatures

There is another analysis direction of characteristic temperatures cross-dependencies, which concerns the air mixtures minimum temperature for initiating combustion (t_{ai}), Fig. 5: $\Delta t_{ai-bp}=t_{ai}-t_{bp}$, $\Delta t_{ai-mp}=t_{ai}-t_{mp}$. It turned out that starting from $n_C=6$, the dependences for "$t_{ai}-t_{bp}$", "$t_{fp}-t_{mp}$" behave identically for n-alkanes and n-alcohols, but a greater values coincidence is observed for the dependence «$t_{ai}-t_{mp}$».
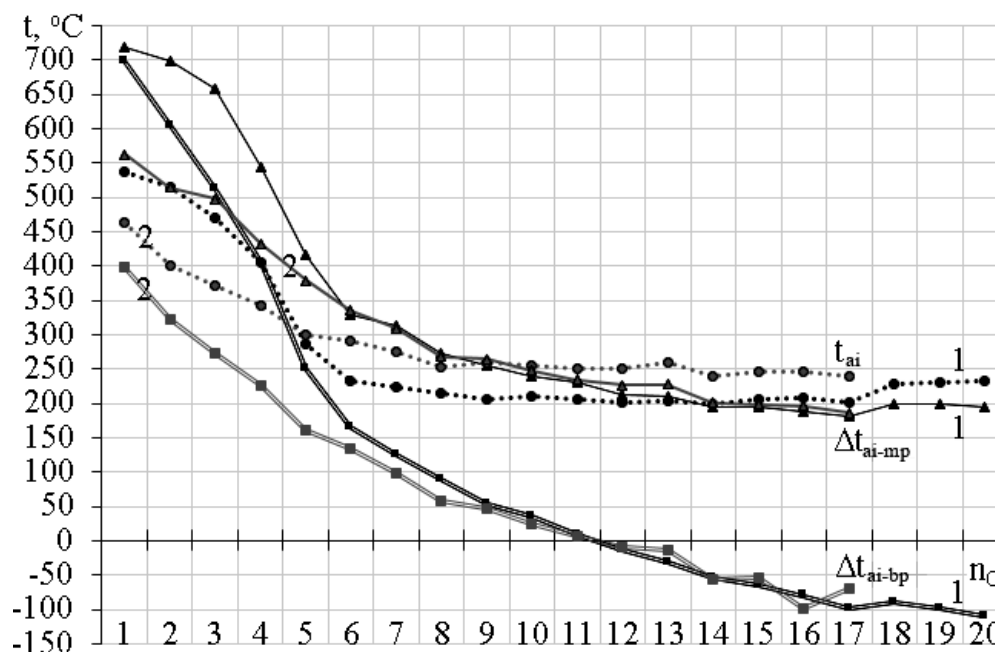

Fig. 5. Correlation between temperatures of the physical state change and combustion initiation for n-alkanes (1) and n-alcohols (2)

For n-alcohols, this dependence can be represented by a polynomial $\Delta t_{ai-mp}=1,852n_C^2 - 56,113n_C+620,84$ with $R^2=0,9885$. This dependence also works for n-alkanes with $n_C > 5$ (the standard technique also offers dependences for $n_C<5$ and $n_C>5$ [18]). Then the function $t_{ai}(t_{mp}, n_C)$ for n-alcohols, as well as for n-alkanes with $n_C>5$, is described by the equation: $t_{cc}=t_{пл}+1,852n_C^2-56,113n_C+620,84$, ^oC.

The dependence $\Delta t_{ai-bp}(n_C)$ for n-alcohols (and for n-alkanes with $n_C>5$) can be approximated by a polynomial $\Delta t_{ai-bp}=1,4631n_C^2-55,313n_C+426,57$ with $R^2=0,9863$. Then prediction of t_{ai} by t_{bp} and n_C for n-alcohols, as well as n-alkanes with $n_C>5$, can be carried out using the equation: $t_{ai}=t_{bp}+1,4631n_C^2-55,313n_C+426,57$, ^oC. Fig. 5 does not show the $\Delta t_{ai-fp}(n_C)$ dependences for substances under study, they are similar to those shown, but differ in the amplitude: for n-alcohols, as well as n-alkanes with $n_C>5$, $t_{ai}=t_{fp}+1,2949n_C^2-45,651n_C+472,41$, ^oC.

The predicting possibility the autoignition temperature (at which the chemical oxidation reaction rate in the combustible substance air mixture is sharply accelerated) based on the phase transitions temperature can be explained only by the fact that the oxidation process is accompanied by the similar supramolecular structures formation compared to the substance condensed state.

6. Results of taking into account the hydrocarbons supramolecular structure in calculations

The n-alcohols density ρ reflects the liquid state supramolecular structure peculiarities, as it has significant fluctuations of dependence, Fig. 6. For n-alkanes, this parameter has a smooth change. Both dependences grow exponentially, but for n-alcohols after $n_C=13$ an anomalous decrease in ρ is observed.
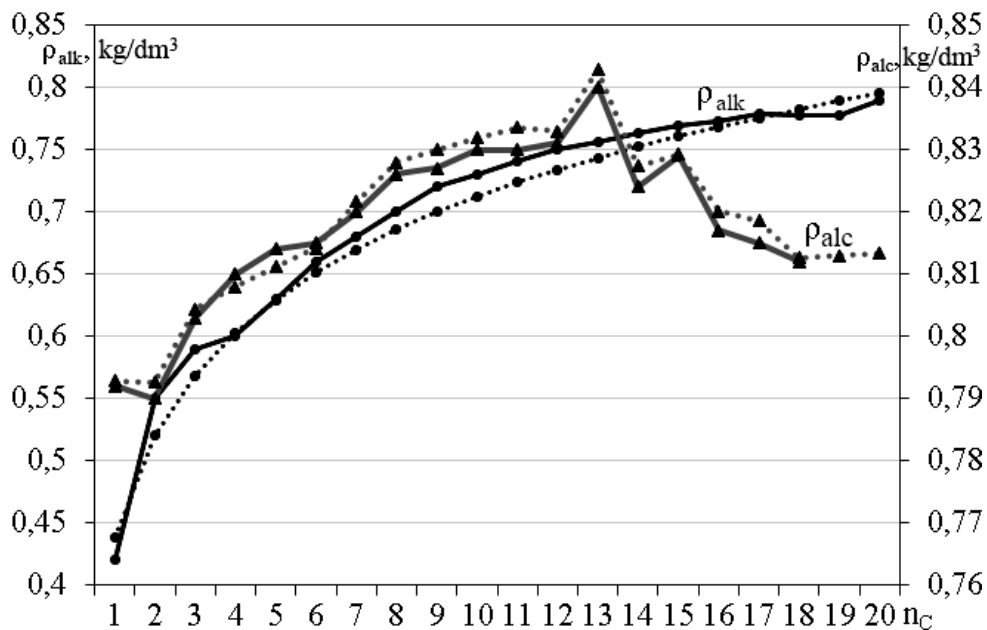

Fig. 6. Reference (—) and calculated (•••) n-alkanes and n-alcohols density values

For the solid state of alkanes, alkenes, alkynes, and cycloalkanes, we have developed a system for modeling supramolecular structures [2], Tabl. 1. This technique has been adapted to estimate the hydrocarbons solubility in a water [1]. For n-alcohols and n-alkanes in aqueous solutions, cyclic clusters are accepted, where monomers are combined by water molecules: for n-alcohols, the first three homologs are accepted as mon-

omers; for longer n-alcohols, the clusters coordination number increases with a maximum for octadecanol; for some clusters it is accepted shortening scheme; for n-alkanes to n-octane, the cluster scheme remained close to the solid state, later, as for n-alcohols, the coordination number increased with a maximum for penta- and hexadecane.

Tabl. 1. Hydrocarbons supramolecular structures models[1] for different states

n-alcohols																				
n_{C+OH}	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	19	20	21
water solution	1/3	1/4	1/5	2/-2	2/-2	2/-1[3]	2/9	2/10	3/-2	3/12	3/13	4/14	5/-1	6/16	5/17	8/18	11/19	17/20	16/21	14/22
liquid state	6/2	4/3	4/4	4/-1	4/-2	4/-3	4/-3	4/-3	4/-4	4/-5	4/-6	4/-5-1[4]	4/-6	4/-6-4	4/-6-5	4/-10-3	4/-12-2	4/-13-3	4/-14-3	4/-15-3
solid state	6/2	4/-1	3/-1	3/-1	3/-2	3/-2	3/-3	3/-2	3/-3	3/-3	3/-4	3/-4	3/-5	3/-5	3/-6	3/-7	3/-8	3/-9	3/-10	3/-10
n-alkanes																				
n_C	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	19	20
water solution	6/2[5]	3/3	2/4	2/-1	2/-2	2/-2	2/-2	2/9	3/-2	3/-1	4/-2	4/13	4/-1	6/15	9/16	9/17	3/18	2,5[2]/19	7/20	3/-1
liquid state	2/1	2/2	2/3	2/4	2/5	2/6	2/7	2/8	2/9	2/10	2/11	2/12	2/13	2/14	2/15	2/16	2/17	2/18	2/19	2/20
solid state	6/1	3/2	2/3	2/4	2/-1	2/6	2/-1	2/8	2/-1	2/10	2/-1	2/12	2/-1	2/14	2/-1	2/16	2/-1	2/18	2/-1	2/20

[1] – coordination number / monomer length or its shortening principle;
[2] – fractional number – a clusters mixture; [3] – clustering at site "2", monomer shorter at "1";
[4] – chain shortening due to molecule globulization and clustering (according to note 3);
[5] – n-alkanes aqueous solutions are calculated as cyclic clusters, which length takes into account H_2O

N-alcohols clusters modeling in the liquid state was carried out according to the change nature in their density in the homologous series and was based on developed models for the solid state, Tabl. 1.4 and Tabl. 1.5 [1]. H-alcohols in the solid state are modeled as trimers with a clustering point near the molecule center (except for methanol and ethanol – the linear hexamer and tetramer scheme worked for them). The main difference for the liquid state was the need to adjust the monomers length for long n-alcohols clusters with $n_C > 11$ to account for bending or molecules globulation. For an alcohols aqueous solution, this turned out to be unnecessary – no conformal changes occur, water molecules prevent this.

Since the n-alkanes density has no significant anomalies, this indicates the identity of the liquid state supramolecular structure. Therefore, there is no difference in the character between dependence profiles for t_{bp} and t_{mp}, Fig. 3, except for methane and ethane; for them, the difference between these parameters is reduced; in addition, there is no noticeable fluctuation of the dependence for t_{bp}. For the alkanes solid state, we previously proposed the models of smallest clusters: methane – hexamer, ethane – trimer, others – dimers with alternating clustering points for «even» and «odd» molecules [2]. The «odd» molecules, starting with pentane, turned out to be shortened by "1". Then, for the liquid state, only a dimeric structure can be proposed with an identical clustering principle – by terminal methyl groups. An instantaneous transition from dimers to the monomeric state is unlikely, as it would be accompanied by evaporation sharp intensification or by sublimation.

In order to take into account, the cluster structure influence on the hydrocarbons properties, we have developed the indicator "melting ease" [15]: $n_M = n_{C_{eq}} M^{0.2}$, where

$n_{C_{eq}}$ and M – the cluster equivalent length and its molar mass. Based on it, a formula was developed to describe ρ, which works with different constants for n-alkanes and n-alcohols: for n-alkanes $\rho=0,23\log_{10}n_M+0,3$, for n-alcohols $\rho=0,08\log_{10}n_M+0,67$, кг/dm^3, which provides a total R=0,992.

The n-alcohols t_{mp} can be calculated using the previously developed formula for n-alkanes [1]: $t_{mp}=102,46\ln(n_M) - 455,22$, ^oC. However, the «oscillating» model for n-alcohols did not work, the «stepped» model worked, as well as for aqueous solutions, Table 1; moreover, the option when the clustering point is moved further from the final group for long molecules turned out to be closer. For n-eicosanol ($n_{C+OH}=21$) in Table 1, it is proposed to shift the clustering point to «10» along the carbon chain, since «11» is already more than half the chain, although this would reduce the calculation error from 3 ^oC to 1,5 ^oC. Most likely, this is possible because there is a strong substituent at the molecule end. The coordination number for most n-alcohols turned out to be «3» (trimeric structure is typical for many hydrocarbon liquids, for example, nitromethane [22]), for ethanol «4», for methanol «6».

The n-alcohols t_{mp} calculation according to the above formula with reference to the clusters specified structure and using the indicator «melting ease» has R=0,997, the average deviation – 3,7 ^oC, the maximum – 13,2 ^oC (for $n_C=2–5$). The deviations presence indicates the model incompleteness. For example, if for ethanol we take 2 instead of 3 points of shortened clustering in the tetramer (or a cyclic tetramer with 2 points of shortened clustering out of 4), then the cluster length increases to 10, and the error decreases from 9 ^oC to 1,7 ^oC; if a cyclic trimer is accepted for n-propanol, then the cluster length decreases to 9, and the error – from 13,2 ^oC to 2,4 ^oC; the cyclic structure reduces the error for n-butanol and n-pentanol as well. Such measures increase the correlation with reference data [20, 21] to R=0,999, reduce the average deviation to 1,8 ^oC, and the maximum to 5 ^oC.

If we return to the graphs for t_{bp}, t_{fp} and H_{vap} of n-alcohols in Fig. 2 and 3, a synchronous deviation from linearity is noticeable for molecules with $n_C > 10$. To take into account such an anomaly within the dependence limits on the carbon atoms number in the molecule, it is possible to apply a cluster length reduction from the maximum possible as an amendment to the calculation of $\Delta n_{Ceq}=K·n_C - n_{Ceq}$ (varies from «0» to «69», K is the clustering coefficient): $T_{bp}=20n_C+316–\Delta n_{Cек}$, K ($t_{fp}$ related to t_{bp} proportionally); $H_{vap}=5,6n_C+31- 0,4\Delta n_{Ceq}$, kJ/mol, which provides R=0,99.

Thus, taking into account the substance supramolecular structure by calculating the cluster equivalent length improves the result of approximating various methods a certain actual dependence for hydrocarbons different homologous series.

7. Research results discussion of correlations hydrocarbons properties

According to research results, based on the curves synchronicity, the physico-chemical dependencies parameters were identified, which can be used for mutual forecasting. On some dependencies oscillation basis, an assumption is made regarding the substance cluster structure with a clustering different principle of hydrocarbons homologous series various representatives. Such substance parameters become a supramolecular structure indicator, which allows for its simulation. Based on this method, 14 mathematical expressions were obtained, which work with a good correlation, taking into account the molecule length (carbon atoms number) and using mutual correlations between parameters. The developed approach main difference is the search for ways to take into account the substance supramolecular structure. For this, a developed

melting ease index is used, which takes into account the length and molar mass of the simulated cluster. The cluster length is not always proportional to the monomer length, and the clustering coefficient may differ for homologues. This approach becomes more sensitive to substance properties than basing calculations on monomer state parameters. The dependences pulsating nature of certain properties made it possible to model the n-alkanes and n-alcohols clusters lengths for liquid and solid states, as well as for their aqueous solutions. This approach made it possible to describe the pulsating dependence for the liquid state density.

The correlations between n-alkanes and n-alcohols physicochemical properties both within the homologous series and between them were studied: t_{mp}, t_{bp}, t_{fp}, t_{ai}, ρ, γ, ν, σ, H_{vap}, using the molecule or possible supramolecular formations (clusters) length as a basic parameter. At the analysis first stage, general correlations and their description were subject, at the second – the correlations search taking into account the dependencies anomalies in the pulsating deviations form from the general trend. This question was solved on the basis of supramolecular structure features modeling based on a certain parameter of the substance properties, which has pronounced manifestations of dependence certain anomalies. The specified approach has given the positive results number.

An urgent issue is ensuring the converting possibility of known values of a certain physicochemical parameter of a substances certain class to an another homologous class similar indicator. This is possible if this parameter change profile coincides for two or more substances classes with repetition of all or most of anomalies of dependence, but differs in the absolute value. The similarity can be traced for t_{mp}, H_{vap}, γ, σ and ν of n-alkanes and n-alcohols; and for water solubility γ, the dependences almost overlap, Fig. 1 (deviation areas are for short alcohols and long alkanes). The generalized calculating method γ, taking into account the water solution cluster structure, was developed in a previous work [1], and the cluster models are listed in the Tabl. 1.

For the viscosity ν, the 15-fold proportionality $\nu_{alk}=\nu_{alc}/15$ works, and the ν calculation of n-alcohols can be carried out by the equation, which provides the total $R^2=0,99$ for alkanes and alcohols: $\nu_{alc}=0,2498n_C^2-1,2536n+2,192$ Н/м. But this equation does not take into account values fluctuations in homologous series.

Changes in H_{vap} values of n-alkanes and n-alcohols without taking into account fluctuations have linear parallel dependencies. A dependency works for n-alkanes: $H_{vap}=5,0076n_C+0,9121$, kJ/mol. Then n-alcohols H_{vap} can be recalculated based on n-alkanes H_{vap} by horizontal or vertical dependence shift with $R^2=0,99$. Principle «1» provides consideration in the n-alkanes formula of the n-alcohol imaginary length $n_{Cim}=n_{Calc}+6$, principle «2» provides a correction for the difference in amplitudes $H_{vap\cdot alc}=H_{vap\cdot alk}+30$. But the linear approach does not take into account supramolecular structure peculiarities and the graphs corresponding pulsations. Also, with the «horizontal shift» help, it is possible to generalize the surface tension calculation for n-alkanes and n-alcohols homologous series: in equation (1) to calculate σ of n-alcohols, apply $n_{Cim}=n_{Calc}+8$, which provides $R^2=0,98$.

The differences in the t_{mp} parameter are larger values for n-alcohols, a slightly smaller oscillation amplitude than in n-alkanes, and a more pronounced negative temperature effect for methanol and ethanol relative to methane and ethane. This similarity is reflected by the formula, K: $T_{mp.\ alc}=T_{mp.\ alk}^{0,97}+79$, with $R=0,996$, an average error of 3,7 K, which is the largest for methanol – 17,1 K. This equation modulates the oscillatory dependence for n-alcohols due to the oscillatory dependence profile for n-alkanes.

There are no coincidences for t_{fp} and t_{bp} between alkanes and alcohols homologous series. Within homologous series, they are similar: for n-alcohols they are almost linear, for n-alkanes they are exponential. The linear approximation for n-alcohols can be represented by equations: $T_{bp.\,alc}=18n_C+318$, $T_{fp.\,alc}=0{,}6T_{bp.\,alc}+77$, K, which provides R=0,99. These dependences do not have oscillations similar to t_{mp}, and both are correlated with H_{vap} with deviation areas repetition from the general linearity. For t_{bp} n-alkanes: $t_{bp}=0{,}0567n_C^3-2{,}7741n_C^2+60{,}515n_C-206{,}75$; the 3rd degree polynomial works with R= 0.999, the average error – 3,5 $^{\circ}$C and the maximum for methane – 12,6 $^{\circ}$C (but for $n_C>20$ this formula will give inflated values); conversion to tsp: $t_{fp}=0{,}7t_{bp}-75$ $^{\circ}$C with R=0,99, average error – 4,4 $^{\circ}$C, maximum for butane – 18,8 $^{\circ}$C. The last dependence peculiarity for n-alkanes is that the methane t_{fp} is lower than its t_{mp}. This phenomenon is cyclic compounds characteristic, for example, benzene and cyclohexane, which indirectly confirms the assumption about the methane cluster hexameric structure in the solid state [2].

A method for building general cross-dependencies that works for both n-alkanes and n-alcohols has been developed: graphical dependences are constructed for the characteristic temperatures differences and if they coincide between homologous series and a general calculated dependence is established. The change in the difference between the characteristic temperatures in one homologous series was investigated Δt (t_{mp}, t_{fp}, t_{bp}, t_{ai}). As modulating parameters for practical calculations, t_{bp} or t_{mp} are usually used. From the fire safety view point, it is of the interest to find new ways of forecasting and increasing the calculating certain parameters accuracy, for example, t_{fp} and t_{ai}. Corresponding convergences were found. During the analysis, we looked for cross-dependencies, which will have a close character for alkanes and alcohols of the normal structure. In the «triangle» «$t_{mp}-t_{fp}-t_{bp}$» such closeness was revealed only by the dependence Δt_{bp-ai}. This makes it possible to create a universal dependence for the t_{fp} studied substances predicting, based on the t_{bp} and the carbon atoms number in the molecule n_C: $t_{fp}=t_{bp}-(6{,}7105n_C+55{,}069)$, $^{\circ}$C, $R^2=0{,}95$. The equation disadvantage is the t_{fp} pulsations indirect description in homologous series, which works only for cases when the pulsations are synchronous with the dependence for t_{bp}. Existing mathematical models for this [18], based on the t_{bp} value, use the individual homologous series coefficients, therefore they are not universal.

It was also established that the t_{ai} of n-alkanes and n-alcohols can be expressed in terms of t_{mp}, t_{fp} or t_{bp} with $R^2=0{,}98$: $t_{ai}=t_{mp}+1{,}852n_C^2-56{,}113n_C+620{,}84$; $t_{ai}=t_{bp}+1{,}4631n_C^2-55{,}313n_C+426{,}57$; $t_{ai}=t_{fp}+1{,}2949n_C^2-45{,}651n_C+472{,}41$, $^{\circ}$C. But for n-alkanes, these formulas work for molecules with a carbon chain length of $n_C>5$ (the standard method also cannot describe the curve for t_{ai} of n-alkanes with one dependence, so separate formulas are proposed for $n_C<5$ and $n_C>5$ [18]). The developed formulas are not only of practical interest – as a method of estimating t_{ai}, but also of scientific interest, since the relationship existence between completely different parameters is shown: the oxidation reaction self-acceleration temperature, the vapor formation temperature in the lower flammability limit, phase transitions temperatures. Such a relationship testifies to the principles similarity of the supramolecular structures formation in substance different phase states and during the oxidation processesi nitiation in a combustible substance mixture with air. Parallel studies showed that the n-alkanes and n-alcohols water solubility also correlates with similar structures. Then a combustible air mixture at temperatures close to t_{ai} can be compared with an oxygen «solution» ac-

cording to clustering mechanisms.

The cluster structure modeling of n-alkanes and n-alcohols in water solutions, liquid and solid states was carried out, Tabl. 1. For n-alkanes in the solid state, we proposed a dimeric structure, except for methane and ethane (hexamer and trimer) with alternating structure of «even» and «odd» molecules with clustering on the last or penultimate carbon, starting with pentane [2]. For the n-alkanes liquid state, we assume only a dimeric structure with clustering by the final carbon. On the basis of the previously developed indicator of «ease of melting», molar masses and cluster lengths of studied hydrocarbons in the liquid state, the dependence for density ρ is described, which provides R=0,992: for n-alkanes $\rho=0,23\log_{10}n_M+0,3$, for n-alcohols $\rho=0,08\log_{10}n_M+0,67$, кг/дм^3. These calculations correlation increases if the trimeric model of the cluster cyclic structure is applied to the ethane and propane liquid state. One can also consider "shortened" clusters trimeric schemes for the following homologues of n-alkanes.

Regarding the t_{mp} formation of a substance, we previously had assumed that substances with the same equivalent length and molar mass of the cluster will have the same t_{mp} [2]. This means that to each t_{mp} of a substances given homologous class corresponds to a cluster with a certain coordination number and a aggregating molecules way into some smallest structure. Based on this principle, the "ease of melting" index and a universal formula for predicting t_{mp} were developed. The problem of such calculation is the cluster structure modeling. Taking into account the n-alkanes and n-alcohols curves synchronicity it was expected that the supramolecular structure same feature that was predicted for alkanes would work for calculating the t_{mp} of n-alcohols using the universal formula. But for better modeling, a step scheme for clusters structure changing with the clustering point gradual shift closer to the molecule middle worked, Tabl. 1.

In order to take into account, the underestimated relative to the values linear dependence of t_{fp}, t_{bp} and H_{vap} of long n-alcohols (Fig. 2 and 3), a correction was applied, which describes a decrease in the cluster length due to clustering not by molecule finite group or long molecule globulization: $\Delta n_{Ceq}=K \cdot n_{C+OH}-n_{Ceq}$ (varies between 0–69 for $n_C=1–20$). Based on this indicator and the proportional dependence on the carbon atoms number in the molecule, formulas have been developed that provide R=0,99: $T_{bp}=20n_C+316-\Delta n_{Ceq}$, K; $H_{vap}=5,6n_C+31-0,4\Delta n_{Ceq}$, kJ/mol; t_{fp} can be obtained through t_{fp} using cross-dependency. It was also found that ρ pulsations for n-alcohols are shifted by one molecular length link relative to pulsations of t_{fp}, t_{bp} and H_{vap}, as if ρ is modulated by the carbon chain length, and t_{fp}, t_{bp}, H_{vap} are modulated by the hydroxyl-carbon chain length. If for the last case a molecule length correction by one position is applied, then the calculation correlation can be increased.

The application limitations of this researche results are due to the fact that only 2 organic compounds main classes were studied – n-alkanes and n-alcohols with n_C up to 20. At the same time, the drawback is the hypotheticality of substance supramolecular structure applied models. The developed models, on the one hand, require experimental confirmation, on the other hand, they already work and provide acceptable coefficients of correlation and deviation during calculations. In addition, proposed solutions are based on individual experimental facts, namely, on the investigated some liquids cluster structure. Thus, in nitromethane and alcohols, the trimeric and tetrameric structures presence, as well as certain intermolecular bonds types, on which these structures are built, was found [13, 22]. But even these researches only hypothetically

describe the corresponding clusters structure [22]. Therefore, at the moment, we consider the developed technique primarily as a way of predicting the substance properties and an alternative to the liquids statistical associative theory, which uses a molecule coarse-grained model that is not directly related to the molecules or supramolecular formations structure.

The formation reasons of linear or exponential trends of changes in the actual dependences for physicochemical quantities indicators in homologous series, the supramolecular structures non-equal influence on different indicators, the alcohols some indicators modulation according to the carbon chain length, and others – to the carbon-hydroxyl chain length, have not been finally established, which requires the further research. The hydrocarbons «melting ease» indicator is most likely not correct to use for the liquid state, water solution, «zero» moment of the combustion initiation, but the similarity of the supramolecular structures organization principles for same molecules allows using such an approach. During current research, it was not possible to describe the density change in n-alkanes and n-alcohols homologous series using supramolecular structure indicators with one calculated dependence. The structure and length modeling method of clusters, for example, the linearity or cyclicity of supramolecular structures, also needs clarification.

The development of this research can involve several directions: experimental confirmation or refinement of the applied models for the supramolecular structure, methodology improvement for the smallest cluster length determining, approximation dependencies improvement for the description of substance physicochemical properties.

8. Conclusions

1. The changes analysis in 9 physicochemical properties parameters in n-alkanes and n-alcohols homologous series using a selection of 40 compounds revealed similarities between some parameters, as well as oscillatory and pulsating features that cannot be explained and taken into account by the direct correlation. The n-alcohols viscosity described by the 2nd degree polynomial with the recalculation possibility to n-alkanes due to the reduction coefficient «15», characterized by the general $R^2=0,99$. The n-alkanes and n-alcohols vaporization heats are described by a linear function with $R^2=0,99$ provided that the n-alcohols length n_C is substituted into the formula as "$n_C +6$" or the correction "+30 kJ/mol" is applied. The dependence for surface tension has an exponential character, which is described for n-alkanes by the 4th degree polynomial with $R^2=0,98$, this formula also allows predicting the dependence for n-alcohols, if their length n_C is considered greater than 8. Based on the melting points changes synchronicity in alkanes and alcohols homologous series, an equation was developed that allows calculating the n-alcohols melting points of with $R=0,996$ based on the data for n-alkanes, taking into account the dependence oscillation. The common dependence existence for n-alkanes and n-alcohols between melting and flash points, autoignition and other characteristic temperatures of liquids, taking into account the carbon atoms number has been proven, which provides $R^2=0,95–0,98$. These calculations take into account substance supramolecular structure peculiarities only indirectly.

2. Based on the relationship existence between the autoignition temperature and the melting and boiling points, a conclusion was made about the fundamental similarity of corresponding supramolecular structures. Such structures models have been developed for the solid, liquid state, and water solubility, taking into account different coordination numbers, changes in the clustering point according to the carbon chain length,

and long molecules globulization. On the basis of the supramolecular structure index «melting ease», the dependences for the n-alkanes and n-alcohols density with R=0,99, the change in the n-alcohols melting points with R=0,999 are described. The anomalies for the boiling point, flash point and vaporization heat of long n-alcohols in the values decrease form relative to the general linear dependence is described by taking into account the cluster structure through the cluster length decrease parameter relative to its linear structure, which provided R=0,99. Supramolecular structures modeling showed that no globulization effect occurs in aqueous solutions for long molecules.

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СПІВВІДНОШЕННЯ НЕЛІНІЙНОСТЕЙ ФІЗИКО-ХІМІЧНИХ ВЛАСТИВОСТЕЙ Н-АЛКАНІВ ТА Н-СПИРТІВ

Встановлено відповідності між нелінійністю зміни фізико-хімічних параметрів речовини та механізми впливу на них надмолекулярної будови речовини у вигляді розрахункових залежностей для н-алканів та н спиртів. Досліджено подібність, особливості зміни та кореляції між параметрами: температури плавлення, кипіння, спалаху, самоспалахування, густина, розчинність у воді, в'язкість, теплота випаровування, поверхневий натяг. Отримано 14 розрахункових залежностей, які прогнозують ці параметри на підставі встановленої подібності між ними та довжини молекули або кластеру з достатніми коефіцієнтами кореляції. Для в'язкості, теплоти випаровування та поверхневого натягу встановлено загальні залежності зміни, але без врахування коливальних відхилень. Отримано розрахункові крос-залежності між характерними температурами речовини: між температурами плавлення н-алканів та н-спиртів, між температурами кипіння та спалаху для гомологічний рядів, між температурою самоспалахування та плавлення (або спалаху, або кипіння). Пояснено таку кореляцію тим, що у різних станах речовини та під час ініцію-

 вання горіння формуються надмолекулярні структури за близьким принципом. Проведено моделювання таких структур для твердого, рідкого стану та розчинності у воді з урахуванням різного координаційного числа, глобулізації та зміни точки кластеризації за довжиною молекули. На базі такого моделювання та показника «легкість плавлення» розроблено залежності для розрахунку густин алканів та спиртів, описано температури плавлення спиртів з відбиттям нелінійностей залежностей. Для температури кипіння, спалаху і теплоти випаровування н-спиртів відхилення від лінійності враховано впровадженням параметру зменшення довжини кластеру. Дослідження показало, що модулювання розглянутих залежностей за довжиною кластеру дозволяє описати їх аномалії та підвищує збіжність розрахунку.

Ключові слова: н-спирти, н-алкани, фізико-хімічні властивості, кластер, модель, нелінійність, збіжність розрахунку

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