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Oscillation and Stepwise of Hydrocarbon Melting Temperatures as a Marker of their Cluster Structure

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Abstract. The presence of melting temperatures oscillatory and stepwise changes for hydrocarbons four homologous series is demonstrated and analyzed. The oscillating dependence is manifesteds on the principle of «even-odd» molecules with different deviations from linearity. According to the working hypothesis, this is due to the presence of the matter smallest structural unit in the cluster form of with a certain coordination number. The oscillation of melting temperatures in hydrocarbons series is explained by the fact that clustering can occur both at the site of the final carbon in the molecule and at other carbons in the molecule chain, and this fact depends on the «even-odd» effect. Based on the known values of melting temperatures in homologous series, the clusters probable structure is assumed. It is shown that graphs for the calculated values of equivalent lengths of these clusters correlate with corresponding graphs for hydrocarbons melting temperatures. An approximation formula has been developed to predict melting temperatures of hydrocarbons based on the values of the equivalent length and the cluster molecular weight, which operates with an approximation coefficient of 0.997 and a mean deviation of 4.2 K.

1 Introduction

All uses of substances are based on certain parameters of their physical and chemical properties. For example, the melting temperature is an important parameter for the refractory lining of steel smelting furnaces [1]. But it is noticed that many of these properties have an oscillating nature of growth in each hydrocarbons homologous series [2]. Such features can be manifested as alternation of the parameter values for «even-odd» molecules and are observed for the melting point t_{mp}, boiling point t_{bp} and for mass burnout rate [3, 4]. But a number of the values of t_{mp} have greater nonlinearity than t_{bp}. X-ray analysis revealed for odd n-alkanes less dense packing of molecules with larger intermolecular distances [5]. Known calculations using the Atoms series and molecular weight, which predict t_{mp} with a mean deviation of 4 ^{o}C (a selection of 10 compounds) [6]. A typical calculation is to take into account the contribution of individual functional groups in the formation of substance properties, for example, for t_{mp} [7]. For ethane, propane, n-butane in the solid state, layered structures with a molecular geometry in the form of a rectangle, pentagon, hexagon were found [8]. This allows the propane to be packed more densely and therefore have the smallest t_{mp}. One explanation for the discrepancy t_{mp} may be the substance cluster structure and its differences for «even» and «odd» molecules [3]. For example, in the formation of strong metal coatings electrochemically form alloys of heavy metals as a target cluster structure [9]; for the n-hexanol liquid state the presence of di-, tri- and tetramers is shown [10]. It is known that cyclobutane can be formed by dimerization of ethylene, vinyl acetylene – by dimerization of ethine, benzene – by trimerization of ethine, trimethylbenzene – by trimerization of propinion (that is, the appropriate dimers or trimers exist in liquids, and in the case of the temperature influence and the catalysts presence, the reaction ends with chemical transformations), cyclododecan is obtained by the hydrogenation of butadiene cyclotrimerization products in the presence of catalysts. It is also interesting to note that cyclohexane has the smallest tension in the molecule [11]. Therefore, it can be expected that instant cluster structures exist in a

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