

Possibility of Predicting Activation Energy for Viscous Flow in Five-Membered Naphthenes by Means of Structural Descriptors

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Abstract: In this paper, the possibility of predicting values apparent activation energy for viscous flow in five-membered naphthenes by the calculation method, namely, using the two-parameter dependence of structural descriptors, is investigated. We explore structural descriptors of the molecular graph, namely, a topological index and the sum of eigenvalues squares of the topological matrix. Interchangeability checking of topological descriptors was performed. We performed regression analysis, and constructed dependences of apparent activation energy on the sum of squares of eigenvalues and topological indices. This paper presents data for calculating apparent activation energy of viscous flow from the experimental data and from the dependence on the Wiener topological index and the squares sum of eigenvalues. It is shown that for compounds under consideration there is a kinetic compensation effect. Based on the studies carried out for compounds considered, it can be assumed that, the apparent activation energy of viscous flow and the associated Arrhenius constant (frequency factor) is determined by the topological characteristics of the molecules.

Keywords: Five-Membered Naphthenes, Activation Energy of a Viscous Flow, Topological Indices, Topological Matrix

1. Introduction

Naphthenes (e.g., cycloalkanes) are an important class of organic compounds, as they are part of all oils and hydrocarbon fuels without exception. Naphthenes of a series of cyclopentane with long branched side chains are components of lubricating oils, diesel and jet fuels, and cause their operational properties. Five-membered naphthenes play an important role as reaction intermediates in the dehydrocyclization of paraffins into aromatic hydrocarbons [1]. This paper describes the viscosity characteristics of monocyclic hydrocarbons representing a number of naphthenes with a five-membered ring and alkyl side chains (Table 1). One of the main characteristics of molecules, which largely determine the nature of intermolecular interactions, is the chemical structure of molecules [2, 3].

According to A.M. Butlerov's theory, the nature of the molecule is determined by the chemical structure, which implies the existence of molecular structures and the energy inherent in these structures. To obtain these parameters, the classical structural formula of the molecule, which can be considered as a labeled graph, is used as the basis. Note that in QSPR models of the structure-property communication models, the use of the calculated parameters of molecules, on which their properties (descriptors) depends, makes it possible to predict the properties and carry out organic synthesis in a given direction.

A small number of studies are known concerning the QSPR prediction of kinetic properties of molecules, such as viscosity [4]. According to the classical Eyring's theory fluids, the viscous flow is an activation process [5]. If temperature dependence is included, it is expressed through

the zero shear viscosity which is calculated from an Arrhenius expression, specifically known as the Arrhenius-Frenkel-Eyring formula [6]

$$\eta = A \exp\left(\frac{E_a}{RT}\right) \quad (1)$$

Where η - dynamic viscosity, Pa·s; E_a - apparent activation energy of viscous flow, J/mol; R - universal gas constant, J/mol·K; A is a constant which does not depend on the temperature T in very first approximation, Pa·s and calculated by the formula

$$A = \frac{Nh}{V} \quad (2)$$

Where N is Avogadro's number, $N = 6.022 \cdot 10^{-23} \text{ mol}^{-1}$; V is molar volume, m^3/mol ; h is Planck constant, J·s; N is numbers of molecules.

Therefore, the task of further research is to apply the quantitative structure-property relationship (QSPR) method to five-membered naphthenes.

The aim of the work is to study and use the relationship of the energy parameter (apparent activation energy of viscous flow) of five-membered naphthenes with structural descriptors (topological indices and the eigenvalues squares sum of the molecular graph) to predict the values of the apparent activation energy of viscous flow.

2. Method

We consider the relationship between the activation energy of a viscous flow and topological descriptors for molecular graphs. It is known [7] that the energy of intermolecular interactions is significantly influenced by correct estimates of the size of the molecule and the degree of their branching. Consider the structure of a molecule as a physical quantity, which we characterize numerically using topological indices from graph theory [8]. To obtain these parameters, the classical structural formula of the molecule is used as the basis, which can be regarded as a labeled graph. As a topological descriptors the Wiener index, the Balaban centric index, the Randic index (the index of molecular connectivity), Gutman (Szeged) index, Platt index and the Harary index were considered. The formulas for calculating these indices are given below.

For a graph G , let $d_G(u, v)$ be the number of edges on any shortest path joining vertex u to vertex v . The Wiener index is defined as:

$$W = \frac{1}{2} \cdot \sum_{u, v \in V(G)} d_G(u, v) \quad (3)$$

Where the sum runs over all ordered pairs of vertices.

The Harary index of a simple connected graph G is defined as follows:

$$H(G) = \sum_{u, v \in V(G)} \frac{1}{d_G(u, v)} \quad (4)$$

Where the summation goes over all pairs of vertices $\{u, v\}$ of G .

Hyper-Wiener Descriptor:

$$W^* = \frac{1}{2} \cdot \sum_{u, v \in V(G)} d_G(u, v) + \frac{1}{2} \cdot \sum_{u, v \in V(G)} (d_G(u, v))^2 \quad (5)$$

Where the summation goes over all pairs of vertices u and v .

The Platt number $F(G)$ of a graph G is defined as the total sum of degrees of edges in a graph,

$$F = \sum_{f=1}^n \deg e_f \quad (6)$$

Where $\deg e_f$ denotes degree of the f_i , i.e., number of edges adjacent to e_f and n denotes the number of edges.

Balaban distance connectivity descriptor (also called distance connectivity descriptor or average distance sum connectivity):

$$J = \frac{N}{\mu + 1} \cdot \sum_{i=1}^{n-1} \sum_{j=i+1}^n \frac{1}{\sqrt{D_i D_j}} \quad (7)$$

Where the summation runs over all the molecular bonds, D_i and D_j are the vertex

Distance degrees of the adjoining atoms, μ is cyclomatic number representing number of rings in the graph and N is the number of bonds in the molecular graph G .

The Randic connectivity index was defined as:

$${}^1\chi = \sum_{k=1}^n \frac{1}{\sqrt{v_i \cdot v_j}} \quad (8)$$

Where v_i and v_j represent the degrees of the vertices i and j ; the term $\sqrt{v_i \cdot v_j}$ for each pair of adjacent vertices is called edge connectivity.

Let $e=(u, v)$ be an edge of the graph G . The number of vertices of G whose distance to the vertex u is smaller than the distance to the vertex v is denoted by $n_u(e)$. Analogously, $n_v(e)$ is the number of vertices of G whose distance to the vertex v is smaller than the distance to the vertex u .

Szeged descriptor:

$$Sz_e = \sum_{e=uv} n_u(e) \cdot n_v(e) \quad (9)$$

If there are no side branches in the molecular graph, then for n even we have

$$n_u(e) = n_v(e) = \frac{n}{2}$$

If n is odd, then we can express n as $n_u(e) = n_v(e) = \frac{n-1}{2}$

Accordingly, the formula for calculating the Szeged (Gutman) index will take the form

$$Sz = n \cdot \left[\frac{n}{2} \cdot \frac{n}{2} \right] = \frac{n^3}{4} \quad n \text{ is an even number}$$

$$Sz = n \cdot \left[\frac{n-1}{2} \cdot \frac{n-1}{2} \right] = \frac{n \cdot (n-1)^2}{4} \quad n \text{ is an odd number}$$

Early studies [9, 10] showed the dependence of molecular properties on the spectral characteristics of molecular graphs, which were determined by the adjacency matrix. We construct an adjacency matrix A for molecular graph, i.e. we will convert the graph of the molecule into a matrix form. Then we write the characteristic polynomial as:

$$P(\lambda) = (-1)^n \det(A - \lambda E) = \lambda^n + a_1 \lambda^{n-1} + \dots + a_{n-1} \lambda + a_n \quad (10)$$

Where E is the n -by- n unit matrix, the coefficients $a_i, i=1, \dots, n$ are to be computed by evaluating the determinant, λ_i are the eigenvalues (the roots of the polynomial)

The roots of the characteristic polynomial are the eigenvalues of the adjacency matrix, which are interpreted as the energy levels of the electrons in the molecule [11]. Characteristic polynomials and spectra of graph, is independent of the choice of the adjacency matrix. We consider the sum of the eigenvalues squares of the topological matrix as a characteristic of the spectrum. The choice of the eigenvalues squares of the molecular graph are due to the consequence of the theorem of Sachs [11, 12], according to which the sum of the roots of the characteristic polynomial (10), i.e. the eigenvalues sum of the topological matrix of the molecular graph is zero.

The eigenvalues squares sum of the molecular graph indirectly reflects the energy spectrum of the electronic States of

molecules and is calculated by the formula

$$L = \sum_{i=1}^n \lambda_i^2 \quad (11)$$

Where λ_i is eigenvalues of the molecular graph.

It was shown earlier that the activation energy of viscous flow is related to the topology molecules [13]. Assuming that such a dependence exists, it would need to be present for the compounds under consideration. We write

$$E_a = E_a(L, TI) \quad (12)$$

Where TI is topological index (topological parameter).

We decompose E_a into a Taylor series by powers $(L - L_0), (TI - TI_0)$ in the vicinity of a point $(0, 0)$ and write the linear form of the formula:

$$E_a(L, TI) = E_{a0} + L \frac{\partial E_{a0}}{\partial L} + TI \frac{\partial E_{a0}}{\partial TI} = \gamma + \alpha \cdot L + \beta \cdot TI \quad (13)$$

Where γ, α, β is constants.

3. Result

The experimental values of hydrocarbons viscosities (Table 1) were selected from reference data [14-16]. The apparent activation energies of viscous flow and the logarithms of the Arrhenius constant (coefficients depending on the molecular nature of the liquid) were calculated by the least squares method according to equation (13) (Table 1).

Note that the value E_a makes sense of the activation energy of viscous flow only under condition of complete identity of the particles shape, size and other characteristics. When calculating the value $\ln A$ used by multiplication numerical value of viscosity on 10^6 . According to one widespread of Frenkel's Theory viscosity [6], the appearance of the viscosity force in case of liquids is associated with overcoming of potential barrier.

Table 1. Topological indices, apparent activation energy of the viscous process and logarithms of the Arrhenius constant (frequency factor) for hydrocarbon liquids of five-membered naphthenes.

No	Name	Dynamic viscosity		Topological indices							L
		$\ln(\eta_0)$	$E_a, \text{J/mol}$	Platt	Randic	Balaban	Harary	Hyper-Wiener	Szeged	Wiener	
1	cyclopentane	-11.004	7961.40	10	2.5	2.08	7.5	20	20	15	10
2	methylcyclopentane	-11.123	8590.88	14	2.89	2.18	10.17	39	33	26	12
3	ethylcyclopentane	-10.89	8300.44	16	3.43	1.83	12.83	75	52	43	14
4	propylcyclopentane	-10.782	8504.45	18	3.93	2.06	15.57	135	78	67	16
5	butylcyclopentane	-11.045	9790.01	20	4.43	1.76	18.38	227	112	99	18
6	pentylcyclopentane	-11.194	10788.04	22	4.93	1.91	21.29	360	155	140	20
7	hexylcyclopentane	-11.408	11955.60	24	5.43	1.69	24.27	544	208	191	22
8	heptylcyclopentane	-11.435	12564.72	26	5.93	1.81	27.34	790	272	253	24
9	octylcyclopentane	-11.615	13613.44	28	6.43	1.64	30.48	1110	348	327	26
10	nonylcyclopentane	-11.679	14205.95	30	6.93	1.75	33.69	1517	437	414	28
11	decylcyclopentane	-11.851	14972.96	32	7.43	1.61	36.96	2025	540	515	30
12	isopropylcyclopentane	-10.891	8842.67	20	3.8	2.24	16	114	73	62	16
13	1,3-Dimethylcyclopentane	-11.13	8647.39	18	3.29	1.93	13.08	68	51	41	14

For five-membered naphthenes from Table 1, a kinetic compensation effect with a determination coefficient was

established, which is described by the equation [13]

$$\ln A = k \cdot E_a + m \quad (14)$$

Where k, m are constants in equations.

In our case, $k = -0.0001 \text{ mol} / \text{kJ}$, $m = -9.8702$.

All the connections discussed in this article contain only simple bonds. Since all TI characterize the molecular structure and are a mathematical abstraction, a tests for their interchangeability were carried out. Linear and exponential

correlations between indices were constructed for this purpose. The x-axis was postponed value of TI No. 1, and the y – axis TI No. 2, in other words, we checked the dependence of TI n 2 TI No. 1. Sample values TI No. 1 were postponed on the horizontal axis X and sample values TI No. 2 were postponed on the vertical axis Y. In other words, we checked for the dependence of TI No. 2 on TI No. 1. The largest coefficient of determination (R2) is shown in Table. 2.

Table 2. Interchangeability of topological indices (TIs).

	Platt	Randic	Balaban	Harary	Hyper-Wiener	Szeged	Wiener
Platt	1	0.97	0.21	0.97	0.82	0.97	0.88*
Randic		1	0.31	0.997	0.87	0.98*	0.98*
Balaban			1	0.29	0.34	0.34	0.35
Harary				1	0.97 *	0.95	0.94
Hyper-Wiener					1	0.99	0.99
Szeged						1	0.999
Wiener							1

* Logarithmic (exponential) dependence.

4. Discussion

According to the data given in Table 1, dependences were of activation energy on the eigenvalues squares sum and topological indices constructed. Regression analysis was performed for the confidence level set to 0.95. Correlations with different TI were constructed according to equation (13). The results are shown in Table 3. For significance contributions verification of TI and L to equation (13), we used the dependences of the activation energy on L (TI) and the dependence of TI on L (Table 3).

The magnitude of the reliability of the approximation when considering the dependence of the activation energy of the viscous flow on the eigenvalues squares sum has $R^2 = 0.01$. The coefficients of determination for other dependencies are presented in Table 3. Namely, coefficients by linear dependences of the viscous flow activation energy (E_a) from the sum of squares of eigenvalues (L) and topological indices (TI) (Column 2), E_a from TI (Column 3) and TI from L (Column 4).

Table 3. The coefficients of determination for dependencies.

TI	Coefficient of determination (R^2)		
	$E_a(L, TI)$	$E_a(TI)$	$TI(L)$
1	2	3	4
Platt	0.970	0.91	0.977
Randic	0.965	0.96	0.999
Balaban	0.965	0.61	0.290
Harary	0.970	0.97	0.999
Hyper-Wiener	0.971	0.91*	0.981*
Szeged	0.974	0.94	0.982*
Wiener	0.974	0.95	0.979*

* Logarithmic (exponential) dependence.

As can be seen from the table, all indices well describe the activation energy.

We examined the Wiener index, analyzed the standard errors of the coefficients and calculated the interval estimates of the regression equation $E_a(L, TI) = 0$. In our case, the coefficients for equation (13) are presented in the Table 4.

Table 4. Coefficients for equation (13) and their characteristics.

	Regression coefficients	Standard error	t-statistics
Y-intercept	5277.69	984.88	5.36
Variable X 1	222.15	75.25	2.95
Variable X 2	6.65	2.94	2.26

We found that the standard error is less than the absolute value of the coefficient. This allowed us to say that all coefficients in the equation (including the free term) are significant. This conclusion is confirmed by t-statistics, which gives a more accurate assessment of the significance of the coefficients. Namely, with a standard 95% level of reliability, the corresponding t_i criterion should fall into the 5% two-way critical area. For our case, the boundary of the critical area can be written as: $t_{cr}(1 - 0.95; 13 - 1 - 2) = 2.23$. All coefficients are significant.

We will estimate the activation energy of the viscous flow using the Wiener index by the formula (13) and calculate the $\ln A$ by the formula (14). The values obtained are shown in Table 5. Comparative analysis of the above energy and molecular characteristics of experimental data available in the literature and by proposed formula is performed. Comparison results in the form of relative errors are given in Table 5.

Table 5. Activation energy for viscous flow and logarithms of Arrhenius constant (pre-exponential or frequency factor) for hydrocarbon liquids.

No	Hydrocarbon liquids	$E_a \cdot 10^{-3}$, J/mol by formula (13)	$\ln A$ by formula (14)	Relative error. for $E_a \cdot 10^{-3}$, %	Relative error. for $\ln A$, %
1	2	3	4	5	6
1	cyclopentane	8044.00	-10.67	1.038	2.99
2	methylcyclopentane	8561.49	-10.73	0.34	3.57
3	ethylcyclopentane	9118.89	-10.78	9.86	0.99
4	propylcyclopentane	9722.87	-10.84	14.33	0.56
5	butylcyclopentane	10380.07	-10.91	6.03	1.24
6	pentylcyclopentane	11097.14	-10.98	2.87	1.91
7	hexylcyclopentane	11880.75	-11.06	0.63	3.07
8	heptylcyclopentane	12737.54	-11.14	1.38	2.55
9	octylcyclopentane	13674.17	-11.24	0.45	3.25
10	nonylcyclopentane	14697.28	-11.34	3.46	2.90
11	decylcyclopentane	15813.54	-11.45	5.61	3.37
12	isopropylcyclopentane	9689.60	-10.84	9.58	0.48
13	1,3-Dimethylcyclopentane	9105.59	-10.78	5.30	3.14
Average value				4.68	2.31

As it can be seen from the data of Table 5, the relative errors of estimating for values of the apparent activation energy of the viscous flow do not exceed 14.5%, and the average error is 4.7%, for logarithms of pre-exponential factor 3.57% and 2.3%, respectively.

5. Conclusion

It is established from the conducted studies that for the compounds of a number of five-membered naphthenes, the apparent activation energy of the viscous flow and the associated preexponent of the Arrhenius are determined by a pair of descriptors. Namely, one of the descriptors is the topological structure index, and the other is a descriptor reflective hueckel spectrum of the molecular graph. The reliability of the established regularities is confirmed by a high coefficient of determination (ca 0.97) and t-statistics.

Topological descriptors e.g. the Wiener index, the Balaban index, the Randic index, Gutman (Szeged) index, Platt index and the Harary index influences of the activation energy of viscous flow of cyclopentanes.

For five-membered naphthenes a kinetic compensation effect was established.

Established dependencies can be used to predict the viscosity characteristics of synthesized and natural five-membered naphthenes.

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