

Spectral Moments of Polycyclic Aromatic Hydrocarbons. Solution of a Kinetic Problem

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



















The relationship between the rate of supercritical fluid extraction of polycyclic aromatic hydrocarbons (PAHs) from coal-tar pitch and some topological invariants are examined. The aim is to explain the appearance of a minimum value on the activation energy/molar mass curve of the PAHs. Rate constants are approximated using spectral moment expansion. It is shown that the size of the PAHs determines more than 95% of the extraction rate. Activation energy for the extraction of the PAHs was found to increase with increasing molar mass. The appearance of a minimum value on the activation energy/molar mass curve is the consequence of experimental difficulties resulting from the tendency of lower members of the PAHs to sublime.

1. INTRODUCTION

Supercritical fluid extraction (SFE) has become an accepted alternative to traditional solvent extraction methods, due mainly to its speed and the reduced amount of liquid solvent required.^{1,2} In general, the rate determining step in the extraction of solutes from a matrix is either the desorption or the solubility/elution step.^{2–6} The “hot-ball model” was put forward in order to describe desorption as the diffusion of homogeneous spherical particles into a medium, where their concentration is infinitely dilute.³ This model was further developed, so that the effect of solubility of the analytes in the solvent was also included.⁴ For many dynamic SFE experiments, the rate of overall extraction is limited by the rate of diffusion or a similar process or by that of transfer out of the matrix. In an extraction of polycyclic aromatic hydrocarbons (PAHs) from soil, the effect of flow rate on SFE rate was used in order to elucidate the mechanism of the extraction process.⁵

In recent literature,^{6,7} extraction of coal-tar pitch with supercritical carbon dioxide was examined. Some of the PAHs were identified in appreciable amounts in the extracts (see Table 1). In addition, some minor PAHs were also detected in the extracts (Table 4). Experimental concentration–time data were utilized to determine the rate constants, and the temperature dependence of the extraction rates was used to calculate the activation energies for the extraction of the components given in Table 1.⁶ Naphthalene and 2-methylnaphthalene were identified in the extracts at significant concentrations, but their rate constants and activation energies were not determined, because the loss of these compounds, due to their sublimation, was unavoidable.^{6,8} It was found that the activation energies of PAHs slightly decreased with increasing molar mass up to molecules of mediate molar masses and then increased with further increase in molar mass. Such behavior of the molecules of lower molar masses was unexpected, and it

Table 1. Molecular and Line Graphs, Rate Constants, and Activation Energies of the Major Components of Coal-Tar Pitch^a

N°	Molecular graph	Line graph	Rate constant [$\times 10^3 \text{ min}^{-1}$]			Activation energy [kJ/mol]
			70 °C	90 °C	125 °C	
1*			150.5	164.7	187.7	4.6
2*			100.8	116.9	137.1	6.5
3			43.5	56.1	67.6	9.6
4			38.2	51.9	56.8	9.0
5			21.1	25.5	31.5	8.4
6			20.3	26.4	30.7	9.1
7			7.4	10.6	12.2	11.2
8			6.4	8.7	10.4	10.7
9			3.1	4.6	7.4	18.2
10			3.0	6.2	6.3	17.8

^a 1 – naphthalene, 2 – 2-methylnaphthalene, 3 – acenaphthene, 4 – fluorene, 5 – phenanthrene, 6 – anthracene, 7 – fluoranthene, 8 – pyrene, 9 – benzo(a)anthracene, and 10 – chrysene. * Rate constants and activation energies approximated by eq 1, $p = 2$.

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was not explained in the ref 6. In this work we attempt to clarify this problem by means of theoretical methods.









Table 2. Data Showing the Quality of the Approximations 1–3^a

<i>p/q</i>		eq 1						eq 2						eq 3
		0	2	4	6	8	10	0	2	3	4	5	6	
70 °C	R	0.994	0.997	0.997	0.997	0.9990	0.9998	0.997	0.997	0.997	0.997	0.998	0.9990	0.98
	ARE	3.70	2.54	2.54	2.37	1.55	0.64	2.60	2.54	2.54	2.83	1.73	1.41	7.03
	f		0.26	0.14	0.18	0.38	0.75		0.14	0.14	0.17	0.26	0.22	
90 °C	R	0.98	0.988	0.988	0.990	0.992	0.993	0.988	0.988	0.988	0.991	0.995	0.995	0.97
	ARE	5.20	4.97	4.97	4.71	3.99	4.01	4.94	4.97	4.97	3.40	3.38	3.29	7.41
	f		0.19	0.14	0.18	0.20	0.15		0.14	0.14	0.19	0.27	0.16	
125 °C	R	0.985	0.992	0.992	0.998	0.998	0.998	0.991	0.992	0.992	0.992	0.998	0.9987	0.98
	ARE	4.35	3.32	3.32	1.20	1.29	1.31	3.24	3.32	3.32	3.32	2.70	1.50	6.46
	f		0.25	0.14	0.57	0.16	0.15		0.15	0.14	0.14	0.78	0.17	

^a R – correlation coefficients, ARE – average relative errors, and f – results of the F-test.**Table 3.** Fitting Parameters for the Eq 1, $p = 2$

	a_0	a_2	a_4
70 °C	−0.05976	−0.17081	9.36963
90 °C	0.02742	−0.18488	8.89717
125 °C	0.11784	−0.21607	8.81020

Table 4. Molecular Graphs, Rate Constants, and Activation Energies of the Minor Components of Coal-Tar Pitch^a

N°	Molecular graph	Rate constant [$\times 10^3 \text{ min}^{-1}$]			Activation energy [kJ/mol]
		70 °C	90 °C	125 °C	
1		224.9	231.9	257.1	2.6
2		100.8	116.9	137.1	6.5
3		67.5	83.0	100.1	8.4
4		67.5	83.0	100.1	8.4
5		45.2	59.0	73.1	10.4
6		21.5	28.9	34.7	10.5
7		14.4	20.5	25.3	12.4
8		9.6	14.6	18.5	14.4

^a 1 – indene, 2 – 1-methylnaphthalene, 3 – ethylnaphthalene, 4 – dimethylnaphthalene, 5 – methylbiphenyl, 6 – methylfluorene, 7 – methylphenanthrene, and 8 – phenylnaphthalene. Rate constants and activation energies were approximated by means of eq 1, $p = 2$.

Chemical graphs are the basic tools used in applying the techniques of mathematical graph theory to the specific problems of chemistry.^{9–11} The molecular graph of a conjugated hydrocarbon is a graph representing the carbon atom skeleton of the corresponding molecule. Consider a molecular graph G with n vertices and m edges. The line graph of G (L) can be constructed in the following manner: a vertex of the line graph is associated to each edge of G . The edges of L are now obtained by connecting those vertices of L which represent adjacent edges in G . Molecular graphs represent the adjacency of carbon atoms (existing of chemical

bonds), whereas line graphs reflect the adjacency of these bonds. The graphs G and L can be represented by their adjacency matrices A and E , respectively.

It is well-known that the physicochemical behavior of PAHs is highly dependent on molecular topology,^{9–12} and it can be successfully described by topological invariants such as spectral moments and topological indices.

Spectral moments of G and L , M_k , and μ_k , are equal to the numbers of self-returning walks of length k contained in molecular and line graphs, respectively. They are defined as

$$M_k = \text{Tr}[A^k]$$

and

$$\mu_k = \text{Tr}[E^k]$$

where Tr denotes the traces of the matrices A and E . Spectral moments of molecular graphs have been employed in the physical chemistry of solid state^{13–15} and in the theoretical chemistry of conjugate hydrocarbons.^{16–26} Spectral moments of line graphs have found remarkable applications in quantitative structure–property (QSPR) and structure–activity (QSAR) relationship studies and in the theoretical chemistry of aromatic compounds.^{27–32}

An important structural descriptor of organic molecules is the Wiener index (Wiener number), that is defined as the sum of the distances between all pairs of vertices of the molecular graph G

$$W(G) = \sum_{i < j} d(v_i, v_j)$$

where d denotes the distance between the vertices v_i and v_j . The Wiener number measures the branching of the carbon atom skeleton of an organic molecule. It is correlated with a variety of physicochemical properties of hydrocarbons: boiling point, heat of isomerization, heat of vaporization, surface tension, chromatographic retention indices, ultrasonic sound velocity, etc. More details on the applications of the Wiener number can be found in the review³³ as well as in the recent paper.³⁴

In this work, the relationships between kinetic quantities of extraction of the coal-tar pitch and topological invariants mentioned above are examined. It is expected that the study will shed some light on the dependence of these kinetic properties on molecular structure, and, hopefully, explain the

appearance of a minimum value in the activation energy/molar mass curve of PAHs.⁶

2. RESULTS AND DISCUSSION

In Table 1, PAHs extracted with the yields higher than 1% of the original sample mass⁶ are presented by their molecular and line graphs. The rate constants (k) and activation energies (E_a) for extraction of these compounds are also given in Table 1.

The results of investigation of the dependence of rate constants on both spectral moments of molecular and line graph as well as on Wiener index are reported below. For this purpose, k is approximated by the following three types of expressions:

$$\ln k \approx a_0 M_0 + a_2 M_2 + \dots + a_p M_p + a_{p+2} \\ p = 0, 2, 4, \dots, 10 \quad (1)$$

$$\ln k \approx b_0 \mu_0 + b_2 \mu_2 + b_3 \mu_3 + \dots + b_q \mu_q + b_{q+1} \\ q = 0, 2, 3, \dots, 6 \quad (2)$$

$$\ln k \approx c_0 \ln W + c_1 \quad (3)$$

The sample consists of the compounds **3–10** in Table 1, for which rate constants and activation energies were obtained experimentally.⁶ It includes both alternant molecules (5, 6, 8–10) and nonalternant hydrocarbons (molecules 3, 4, 7), i.e., bipartite and nonbipartite molecular graphs. As a consequence, all odd spectral moments M_{2k+1} of bipartite graphs are equal to zero. Since the molecules 3, 4, and 7 contain five-membered rings, their M_5 and higher odd moments are nonzero, but their numerical values are much lower than those of even spectral moments. In eq 1, only even spectral moments of molecular graphs are considered. All line graphs in Table 1 contain triangles, so that their odd spectral moments μ_{2k+1} , except μ_1 , are nonzero. In eq 2, the term $b_1 \mu_1$ is omitted for this reason.

The coefficients a , b , and c were calculated by the least-squares fitting for different values of p and q . The values of the coefficients are not reported in this work, but they can be obtained from the authors, upon request. The correlation coefficients and average relative errors for eqs 1–3 were determined. These results reflect the accuracy of the approximations, and their values are given in Table 2.

The introduction of a new fitting parameter a_p into 1 or b_q into 2 necessarily increases the correlation coefficients and decreases the average errors. To check if this improvement is statistically significant or not, the standard F -test was used.³⁵ The results of the F -test are presented in Table 2. The quantity f for eq 1 is equal to the ratio of the sample dispersion for a certain p and that for $p+2$, divided by the respective value of the F -distribution, at confidence level of 99%. Therefore, if f is greater than unity, then the change $p \rightarrow p+2$ significantly improves the quality of the respective approximation; if f is below unity, then, from a statistical point of view, the previous and the new equations are equivalent. The quantity f for eq 2 is defined analogously.

By inspecting the correlation coefficients and relative errors in Table 2, it can be concluded that the approximation 3 is of lower quality as compared to eqs 1 and 2. This indicates that the influence of the structural features on which the spectral moments depend is stronger than that of the

branching of the carbon atom skeleton. Approximations 1 and 2 produce very similar results. The accuracy of eq 2 for $q = 0$ is slightly better than that of eq 1 for $p = 0$, whereas for higher values of p and q , they yield almost identical results. The advantage of the approximation 2 over eq 1 is that, for similar accuracy, it requires moments of lower order. According to the F -test (Table 2), the increase in p - and q -values does not yield statistically significant improvements, so that a further increase in p - and q -values is immaterial.

It can be observed from Table 2 that the correlation coefficients and relative average errors for $p = 2, 4$ in eq 1 and for $q = 2, 3$ in eq 2 are all identical. Their sample dispersions are also identical (6.815×10^{-3}). These facts indicate that the moments M_2 , M_4 , μ_2 , and μ_3 of the given sample are mutually linearly dependent. This also implies that one can achieve the same quality of approximation for rate constants of PAHs by using either

$$\ln k \approx a_0 M_0 + a_2 M_2 + a_4$$

or

$$\ln k \approx b_0 \mu_0 + b_2 \mu_2 + b_3 \mu_3 + b_4$$

Both eqs 1 and 2 are surprisingly good approximations for SCF extraction rate of PAHs. They, in some way, elucidate the dependence of extraction rate of PAHs on their molecular structure. If only M_0 and M_2 are used in the spectral moment expansion (eq 1, $p = 2$), the relative error is less than 5%. Bearing in mind that M_0 of all molecular graphs equals to the number of C-atoms, whereas M_2 is equal to twice the number of C–C bonds, it turns out that more than 95% of the extraction rate of PAHs is determined by the size of the molecules. This conclusion is in agreement with kinetic models, according to which the rate of extraction decreases with increasing size of the molecules, because diffusion coefficient and solubility also decrease with increasing size of the molecules.

On the basis of the above, it may be concluded that eq 1, $p = 2$ is a reasonable approximation for the rate constant of extraction. The values of its fitting parameters are given in Table 3. As an illustration, a plot of experimental versus calculated values of $\ln k$ is presented in Figure 1. It is obvious that the molecules 3 and 4 significantly deviate from linearity.

Rate Constants and Activation Energies of Naphthalene and 2-Methylnaphthalene. The rate constants of naphthalene and 2-methylnaphthalene were calculated by means of the approximation 1, $p = 2$, and then these were used to approximate their activation energies by means of the Arrhenius equation. The values of the approximated rate constants and activation energies are listed in Table 1.

E_a of naphthalene is lower than that of 2-methylnaphthalene, and they are both lower than the experimental activation energies. This observation contradicts the experimental results, i.e., that E_a for fluorene and acenaphthene slightly increased with decreasing molar mass.⁶ As mentioned above, these molecules show significant deviation from linearity in the plot of experimental versus calculated values of $\ln k$. The method predicts lower E_a values for these molecules (6.6 and 8.6 kJ/mol for acenaphthene and fluorene, respectively).

An Application of the Method. Rate Constants and Activation Energies for Minor Components of the Pitch.

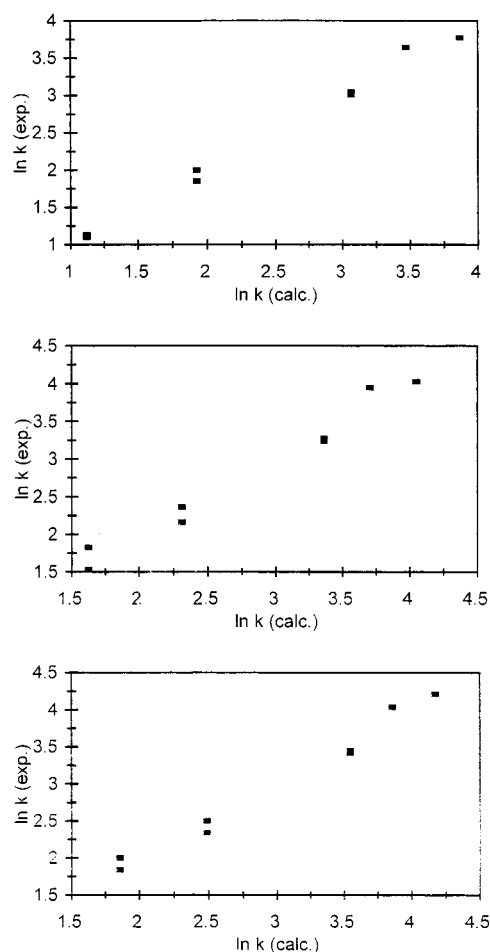


Figure 1. Experimental versus calculated values of the rate constants at (a) 70 °C, (b) 90 °C, and (c) 125 °C.

The PAHs presented in Table 4 were identified in the pitch in very low concentrations.⁷ For this reason, it was not possible to use the experimental concentration–time data and temperature dependence of the extraction rates to determine the rate constants and activation energies for the extraction of these compounds. In this work, these quantities were approximated in the same manner as for naphthalene and 2-methylnaphthalene (i.e. using eq 1, $p = 2$ and the Arrhenius equation). The calculated values for rate constants and activation energies are listed in Table 4.

As expected, the rate constants decrease, whereas the activation energies increase, with increasing molar mass. The approximated values of rate constants and activation energies for the compounds given in Table 4 are similar to the experimental values for the compounds of similar molar masses presented in Table 1 (for example, fluorene (Table 1, molar mass = 166 g/mol) and methylbiphenyl (Table 4, molar mass = 168 g/mol); phenanthrene and anthracene (Table 1, molar mass = 178 g/mol) and methylfluorene (Table 4, molar mass = 180 g/mol)). The method predicts identical values for isomers (compounds **3** and **4** in Table 4), whereas experimental values for isomers are not identical but very similar (compounds **5** and **6**, **7** and **8**, **9** and **10** in Table 1).

3. CONCLUDING REMARKS

It is well-known that the compounds **1–4** (Table 1) have a tendency to sublime, causing experimental difficulties.^{6,8}

In the case of the compounds **1** and **2** this problem is so pronounced that their rates of extraction were not determined in the ref 6. It may be supposed that the enhanced values for E_a of the compounds **3** and **4** can be attributed to an experimental error due to their sublimation. This assumption is confirmed by the theoretical method above, which predicts lower E_a values for the extraction of the compounds **1–4**. In other words, activation energy for the extraction of PAHs from coal-tar pitch increases with increasing molar mass. The appearance of a minimum on the activation energy/molar mass curve is the consequence of experimental difficulties due to a tendency of lower members of PAHs to sublime.

This theoretical method was applied to predict the rate constants and activation energies for the extraction of those PAHs whose values for k and E_a were not determined experimentally, due to their very low concentrations in the extracts. So far, the application of eq 1, $p = 2$ is limited to the extraction process examined in refs 6 and 7, but we suppose that the method itself is applicable to any extraction of PAHs from various matrices. This assumption is based on the well-known fact that physicochemical properties of PAHs are highly dependent on molecular topology.

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