

Calculation of Adsorption Energy and Henry Law Constant for Nonpolar Molecules on a Nonpolar Uniform Adsorbent

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A method for a priori calculation of the energy of interaction between an adsorbed molecule and an adsorbent accounting for the adsorbed molecule shape is developed. This method is incorporated in our model of adsorption on a uniform adsorbent (Dolgonosov, A. M. *Doklady* 1994, 338, 760). Relations between adsorption parameters, the nonpolar molecule structure, and three characteristics of the uniform nonpolar adsorbent are established. They allow us to easily calculate the adsorption energy and the Henry law constant for a wide range of temperatures with good accuracy. The calculation of the adsorption characteristics of hydrocarbons and other compounds on graphite is carried out.

Introduction

The approaches available in the adsorption theory for a priori calculation of adsorption characteristics meet with irresistible complexity of ab initio calculations or with imperfections in the models based on the principle of additivity of van der Waals atom–atom potentials. In the meantime, it is apparent that this principle is vicious for elements of rigid molecules because the potential energy of interacting objects in a superimposed field may be summed only when their binding energy is small compared to the summed quantities.

Our approach is based on the concept that the molecule is an indivisible, shaped, and structured object in the adsorbent field whose structural elements give nonadditive contributions into the total potential.

In order to describe the interaction of an adsorbed molecule with a uniform adsorbent, we introduce the following postulates determining the geometry of this system:

(1) *Its temperature is sufficiently high to make the molecule adsorption time to be much less than the time of relaxation to the most probable arrangement of the molecule on the adsorbent surface.* Such conditions are supposed to occur. In the adsorption practice, the temperature range used is wide and usually is in line with the high temperatures determined here. This postulate breaks down at small temperatures ($T \rightarrow 0$).

(2) *The probability density function for collisions of the molecule with the planar adsorbent is the same for any area of the convex surface of the molecule.* This statement makes the frequency of collisions with the adsorbent to be identical for every point of the surface of the ellipsoidal molecule. In virtue of the short-range behavior of van der Waals forces, the statement may serve a definition of the convex van der Waals surface of the molecule.

(3) *An object being in the shadow of the adsorbed molecule does not interact with the adsorbent.* The principle of shielding the adsorbent field reflects the short-range behavior of van der Waals forces. The shielded object (i.e. arranged behind the adsorbed molecule) does not interact with the adsorbent because the object–adsorbent distance exceeds the molecule size (i.e. it is very large).

Expression for the Henry Law Constant

Because adsorbate molecules fly into the adsorbent-affected zone under random angles, the first postulate allows us to regard the angular dependence of the molecule adsorption energy to be implicit and to express the energy through the average distance between the adsorbed molecule and the adsorbent surface that essentially simplifies the expression for the Henry law constant. On this basis, the Henry law constant K_{1i} and the average distance $\rho_i d$ between the i th adsorbed molecule and the adsorbent surface were expressed¹ through the molecular area w_i :

$$K_{1i} = \frac{A \rho_i \exp X_i}{X_i^{1/2}} \quad (1)$$

$$X_i = -a w_i \left(\frac{U_0}{RT} + \frac{1}{2} \right) \quad (2)$$

$$\rho_i = \frac{1}{2} + \frac{w_i^{1/2}}{F_i d} \quad (3)$$

where $A = d[2\pi/mn]^{1/2}$, d is the adsorbent constant characterizing the van der Waals size of adsorbent atoms (for graphite $d = 0.336$ nm is the minimum distance between carbon atoms lying in different atomic planes²), m and n are the power exponents for the Lennard-Jones potential ($mn = 72$), R is the gas constant, T is the temperature; U_0 the potential energy of a reference system (for the equilibrium interaction between a C(sp³) atom and the graphite surface $U_0/R = -877$ K), a is a constant characterizing the reference system (for the stated example¹ $a = 10.5$ nm⁻²), and

$$F_i = \frac{\cos \theta_i}{P_i} \quad (4)$$

$$P_i = \frac{1}{2\pi} \int_{-\pi}^{+\pi} p_i(\xi) d\xi \quad (5)$$

θ_i is the equilibrium angle between a principal section of the

TABLE 1: Properties of Rigid Molecules of Alkanes Employed for Determining the Generalized Charge and the Steric Factor

	alkanes (rigid molecules)											
	short			linear polygonal			isomeric			cyclic		
	methane	ethane	propane	butane	pentane	hexane	isobutane	isopentane	neopentane	cyclopropane	cyclohexane	adamantane
N_C-N_H	1-4	2-6	3-8	4-10	5-12	6-14	4-10	5-12	5-12	3-6	6-12	10-16
bonds												
total	4	7	10	13	16	19	13	16	16	9	18	28
remote	0	0	0	0	0	0	1	1	3	0	2	7
in cycles	0	0	0	0	0	0	0	0	0	3	6	6
	Calculation Results											
generalized charge	1.682	2.559	3.344	4.071	4.757	5.411	3.834	4.532	4.071	3.090	4.757	5.833
steric factor	0.748	0.895	1.01	0.707	0.595	0.500	0.707	0.595	0.595	0.951	0.595	0.297
Figure	1	2	3	4	5	6	7	8	9	10	11	12

TABLE 2: Properties of Rigid Molecules of Alkenes Employed for Determining the Generalized Charge and the Steric Factor

	alkenes (rigid molecules)											
	short							cyclic				
	ethylene			linear polygonal				cyclohexadiene-1,3			benzene	
	ethylene	propene	acetylene	butene-1	<i>trans</i> -butene-2	butadiene-1,3	hexene-1	cyclohexene	<i>a</i>	<i>b</i>		
N_C-N_H	2-4	3-6	2-2	4-8	4-8	4-6	6-12	6-10	6-8	6-8	6-6	
bonds												
single		4	7	2	10	10	7	16	15	12	12	9
double		1	1	0	1	1	2	1	1	2	2	3
triple		0	0	1	0	0	0	0	0	0	0	0
remote		0	0	0	0	0	0	0	2	2	1	0
in cycles												
total		0	0	0	0	0	0	0	5	5	5	6
without single ones		0	0	0	0	0	0	0	1	2	1	3
DPEs		0	0	0	0	1	2	0	1	2	2	3
	Calculation Results											
generalized charge	2.397	3.196	2.231	3.933	4.222	4.218	5.286	4.924	4.939	5.170	5.377	
steric factor	0.911	0.841	0.918	0.771	0.771	0.841	0.545	0.569	0.595	0.621	0.677	
Figure	13	14	15	16	17	18	19	20	21a	21b	22	

^a Molecule arrangement when the single bond does not touch the adsorbent. ^b Molecule arrangement when the double bond does not touch the adsorbent.

TABLE 3: Properties of Nonrigid Molecules of Hydrocarbons Employed for Determining the Generalized Charge and the Steric Factor

	hydrocarbons (nonrigid molecules)									
	saturated								unsaturated	
	octane		nonane		decane					
	rigid	Me-Hep	rigid	Me-Oct	Me-Non	Et-Oct	toluene	ethylbenzene	biphenyl	
segment no. 1										see segment no. 2
N_C-N_H	0-0	1-3	0-0	1-3	1-3	2-5	1-3	1-3		
bonds (total)	0	3.5	0	3.5	3.5	6.5	3.5	3.5		
segment no. 2										
N_C-N_H	8-18	7-15	9-20	8-17	9-19	8-17	6-5	7-7	6-5	
bonds										
single	25	21.5	28	24.5	27.5	24.5	8.5	11.5	8.5	
double	0	0	0	0	0	0	3	3	3	
in cycles										
total	0	0	0	0	0	0	6	6	6	
without single ones	0	0	0	0	0	0	3	3	3	
DPEs	0	0	0	0	0	0	1	0	1	
	Calculation Results									
generalized charge	6.648	7.458	7.238	8.069	8.662	8.968	6.521	6.878	9.852	
steric factor	0.354	1.16	0.297	1.15	1.14	1.24	0.982	0.823	1.14	
Figure	23a	23b	24a	24b	25a	25b	26	27	28	

molecule and the adsorbent surface. The principal section is *the section of maximum area through the body center of mass*. Bearing in mind that at zero temperature, when the frequency of molecule-adsorbent collisions tends to zero, the molecule stands at the most beneficial position for which $\cos \theta_i = 1$, we can define the **molecule principal section**: *it is the section by the plane parallel to the adsorbent surface through the molecule center of mass at the temperature $T \rightarrow 0$* . [For uniform bodies

with a smooth convex surface, this definition coincides with the above geometrical definition.]

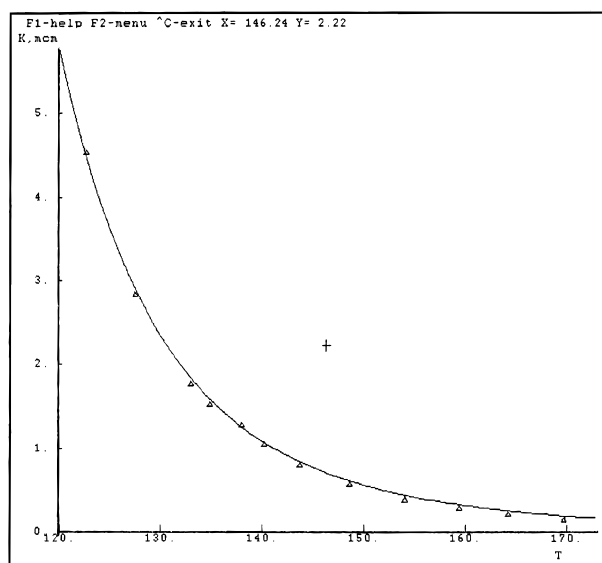
Further, ξ is the angle of rotation of the molecule in its principal plane, and $p_i(\xi)$ is a function characterizing the asymmetry and the polarity of the molecule so that the quantity $P_i = 1$ for a nonpolar molecule with the circular symmetry in its principal plane.

Expressions 1-3 indicate that to find the Henry law constant,

TABLE 4: Properties of Oxygen-Containing Organic Molecules Employed for Determining the Generalized Charge and the Steric Factor

	oxygen-containing molecules											
	esters			ketones			aldehydes			alcohols		
	diethyl ether	methyl acetate	vinyl acetate	acetone	methyl ethyl ketone	acetylacetone	propanal	butanal	isobutanal	propanal	2-propanol	propanol
segment no. 1 $N_C-N_H-N_O$	0-0-0	1-3-0	2-3-1	1-3-0	1-3-0	1-3-0 (for segments no. 1 & 3)	1-1-1	1-1-1	1-1-1	1-3-0	3-7-0	2-3-0
bonds												
single ^a	0	3.5	4.7	3.5	3.5	3.5	1.5	1.5	1.5	3.5	9.5	4.5
double	0	0	1	0	0	0	1	1	1	0	0	1
segment no. 2 $N_C-N_H-N_O$	4-10-1	2-3-2	2-3-1	2-3-1	3-5-1	3-2-2	2-5-0	3-7-0	3-7-0	2-5-1	0-1-1	1-3-1
bonds												
single ^a	14.2	5.7	4.5	4.5	7.5	5	6.5	9.5	9.5	7.7	1.7	4.7
double	0	1	1	1	1	2	0	0	0	0	0	0
remote	0	0	0	0	0	0	0	0	1	0	0	0
DPEs	1	0	0	0	0	0	0	0	0	0	0	0
						Calculation Results						
generalized charge	4.644	4.380	5.126	4.057	4.844	6.344	4.075	4.872	4.615	4.270	4.103	4.153
steric factor	0.771	1.23	1.33	1.17	1.21	1.39	1.17	1.26	1.23	1.17	1.15	1.18
Figure	29	30	31	32	33	34	35	36	37	38	39	40

^a Here, the oxygen π -electron in esters and alcohols is accounted for as 0.7 of single bond.

**Figure 1.** Methane (1.682/0.748).

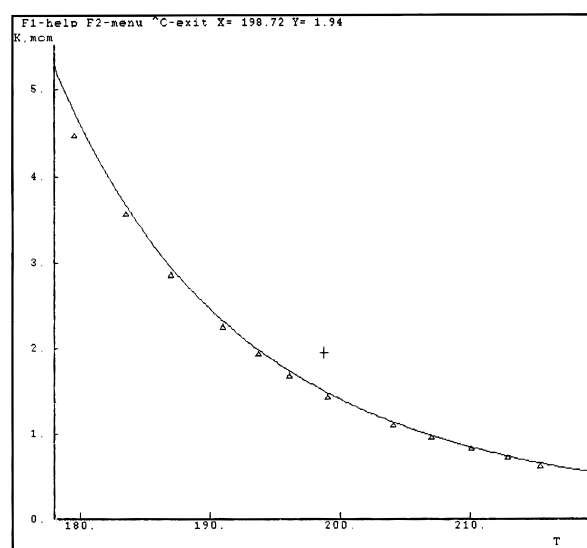
it needs to be able to calculate the molecular area w_j and the parameter F_i .

Calculation of the Adsorption Energy and the van der Waals Molecule Size

We consider a method of calculations of the adsorbent area w_i per adsorbed molecule based on the additivity of "volumes" of elements of a rigid molecule being a power function of the atomic potentials. As will be shown below, this method formally reminding the atom-atom potentials method is much more efficient than the latter because it uses only one parameter—the ratio of the "volumes" of π - and σ -electrons.

Relation between the Adsorption Energy and the Molecular Area. The generalized molecule charge¹ Q_i is defined through the minimum potential energy U_i of the adsorbed molecule as follows:

$$U_i = Q_i U_0 \quad (6)$$

**Figure 2.** Ethane (2.559/0.895).

where U_0 is the potential energy of an adsorbed object with a unit generalized charge (for the above reference system, it is the potential energy of an adsorbed carbon sp^3 atom on graphite so that the generalized charge of this atom is set equal to unity).

The third postulate was applied by Brunauer, Emmett, and Teller (BET) in their famous article,³ where the BET adsorption model was proposed. This postulate attaches particular significance to the concept of "a single layer of molecules on the adsorbent surface": any molecule added to this system does not interact with the adsorbent; i.e. it does not change the adsorbent surface potential. It means that the adsorbent surface potential in the monomolecular layer system reaches its absolute minimum independent of species of molecules.

The sense of the considered monolayer model consists of describing interrelations between the adsorbent and mutually independent molecules specific for the Henry law region. Therefore, in the stated inference we have implicitly supposed the insignificance of molecule-molecule interactions, which is usually important in reality and does not allow the layer to complete its formation.

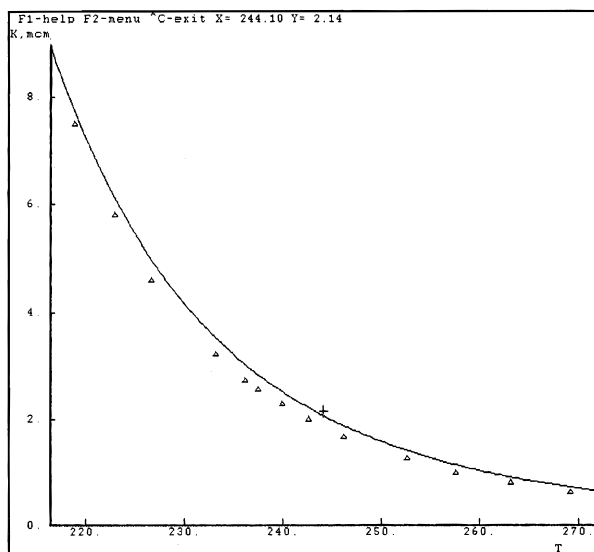


Figure 3. Propane (3.344/1.01).

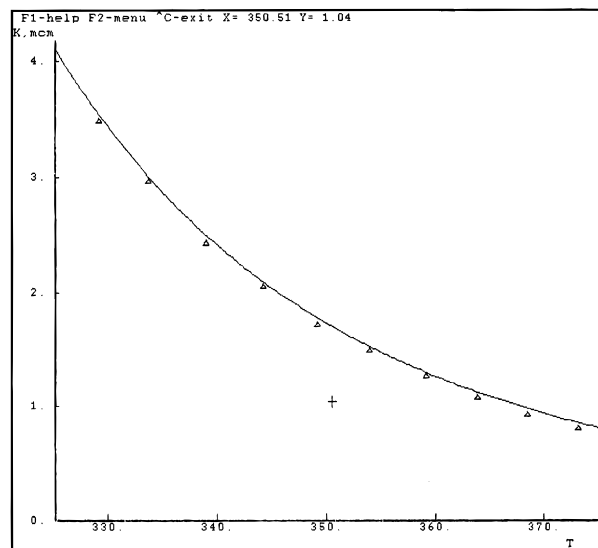


Figure 5. Pentane (4.757/0.595).

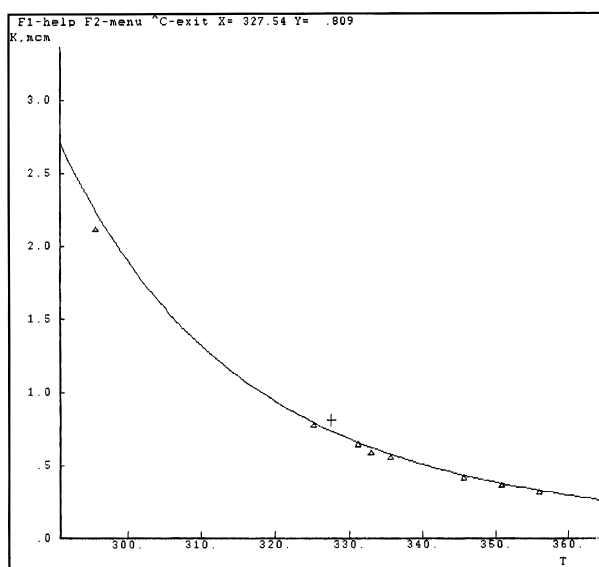


Figure 4. Butane (4.071/0.707).

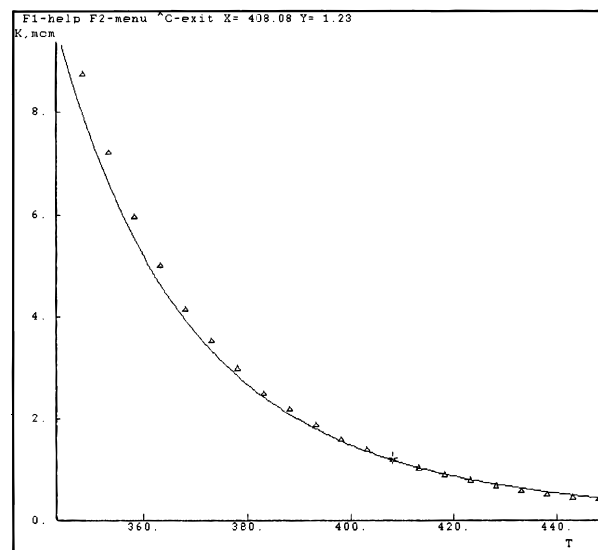


Figure 6. Hexane (5.411/0.500).

The property of the adsorbent surface to have an absolute minimum potential in the system with the monomolecular layer corresponds to the property of molecules occupying equal areas on the adsorbent surface to have equal energies of their interaction with the adsorbent. In general, this means that the adsorption potential energy of a molecule is proportional to its area on the adsorbent. This property is involved in the term of expression 2, describing the i th molecule adsorption potential energy:

$$U_i = aU_0w_i \quad (7)$$

Hence, in view of (6) we get

$$Q_i = aw_i \quad (8)$$

The above introduced empirical constant a is the reciprocal area of the adsorbed $C(sp^3)$ atom. Note that the area $a^{-1} = 0.0952 \text{ nm}^2$ of the carbon atom adsorbed on graphite corresponds to the area of a sphere with radius 0.166 nm in the regular close packing of the spheres on a plane with the coordination number 6. The close value $R_C = 0.17 \text{ nm}$, equal to half the thickness of aromatic hydrocarbon rings, is usually taken as the van der

Waals carbon atom radius.^{2,3} In this connection, it is convenient to characterize the adsorbent surface by the dimensionless quantity

$$\alpha = \pi R_C^2 a \quad (9)$$

which for graphite is close to unity—the theoretically maximum value specific for a uniform adsorbent. If an actual adsorbent can be represented as a uniform one partially dead with some adsorbate and if, in addition, the interaction between the molecule at hand (or the reference atom) and a modifier is much weaker than that between the molecule and the free surface, this adsorbent may be considered *conventionally uniform*, different from actually uniform adsorbents only by the value of α equal to the fraction of free surface. It follows that for conventionally uniform adsorbents the parameter α is independent of the nature of the atom taken for the reference system.

If the base face of graphite with the adsorbed atom (whose parameters will be marked by primes below) is chosen as the reference system, its physical properties such as the energy, the adsorbed molecule area, and the adsorbent parameter α must remain constant after the generalized charge to be redefined. Expressions 7 and 9 in accord with the invariant property of

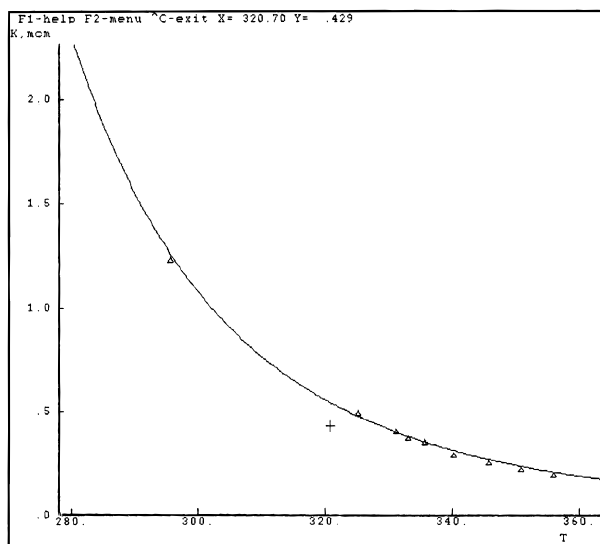


Figure 7. Isobutane (3.834/0.707).

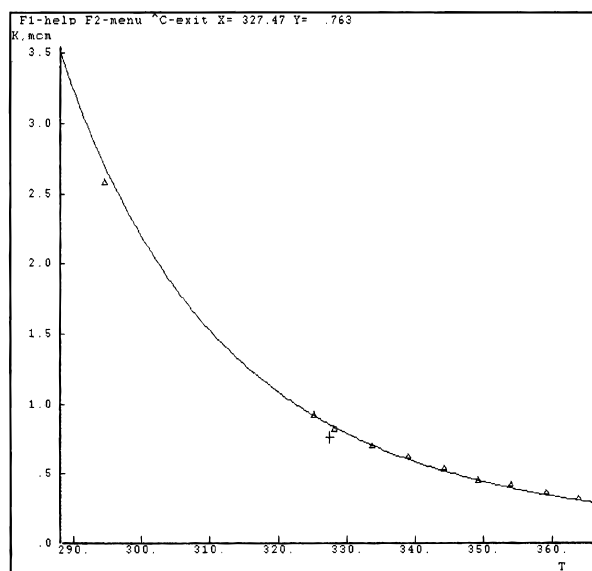


Figure 9. Neopentane (4.071/0.595).

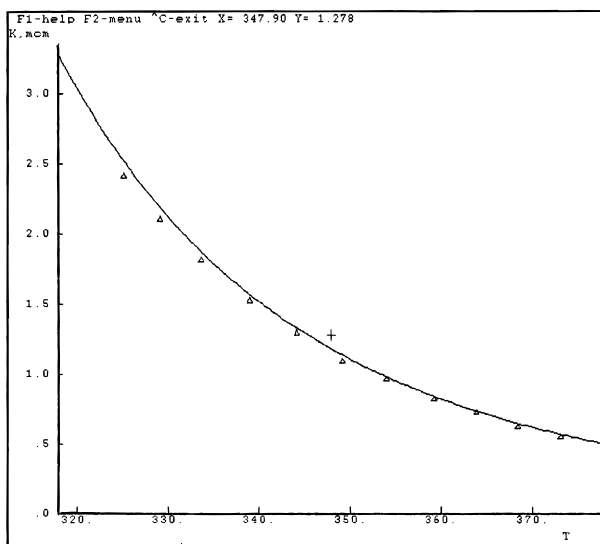


Figure 8. Isopentane (4.532/0.595).

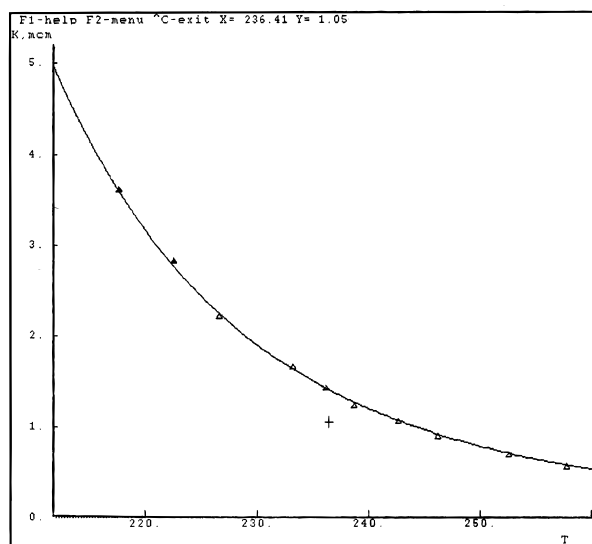


Figure 10. Cyclopropane (3.090/0.951).

U_i/w_i and α imply

$$U_0' a' = U_0 a, \quad a'(R')^2 = a R_C^2$$

That for the generalized charge of the chosen atom in the "carbon representation" yields

$$Q' = \frac{U_0'}{U_0} = \frac{(R')^2}{R_C^2} \quad (10)$$

The van der Waals radius of a hydrogen atom is taken as $R' \equiv R_H = 0.11$ nm. In view of the low accuracy of the data for atomic radii,⁴ we get an approximate estimate for the generalized charge of hydrogen: $Q_H = 0.4$. Substituting $R' \equiv R_O = 0.14$ nm in (10), we can estimate the generalized charge for oxygen: $Q_O = 0.7$.

Generalized Charge Calculation Method for Molecules.

We will demonstrate that the estimates found for the generalized charges of hydrogen and oxygen atoms are fitted in a simple framework which enables us to calculate the generalized charges of a wide class of molecules as well as to determine the molecular areas and the adsorption potential energies in accord with (6) and (8).

Similar to a rigid mechanical system additive with respect to volumes of its elements, rigid molecules and their elements also can be described by "volumes" (in a broad sense) as a power function of the area w . According to (8), the generalized charge is proportional to the adsorbent area per atom (or molecule). Hence, the relation between the properties of a rigid molecule and its atoms is, in general,

$$Q_i = \left(\sum_{j=1}^{N_i} Q_j^b \right)^{1/b} \quad (11)$$

where Q_j is the generalized charge of the j th atom in the i th molecule consisting of N_i atoms; $b = \text{constant}$. Relation 11 with regard to (8) gives the best fit to the data for molecular areas of n -alkanes at $b = 4/3$ (a discrepancy between the experimental data and the approximation is within 10%), not at $b = 3/2$ which corresponds to three-dimensional volumes.

The "volume" of the atom (or rigid molecule) is denoted as

$$V_i = 4Q_i^{4/3} \quad (12)$$

and it is found by using the estimates of (10) for hydrogen,

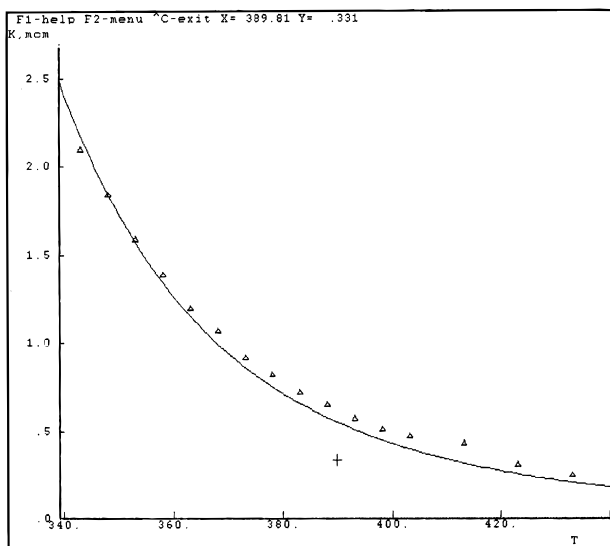


Figure 11. Cyclohexane (4.757/0.595).

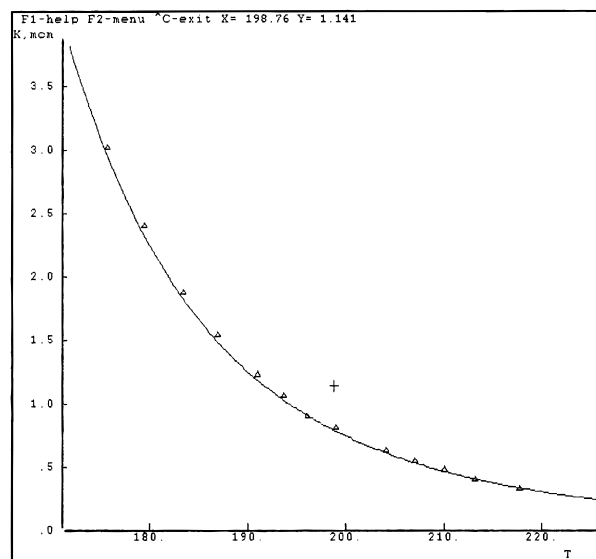


Figure 13. Ethylene (2.397/0.911).

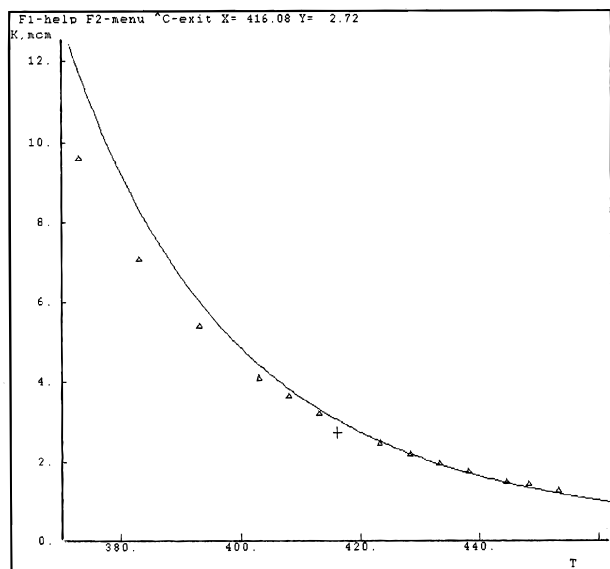


Figure 12. Adamantane (5.833/0.297).

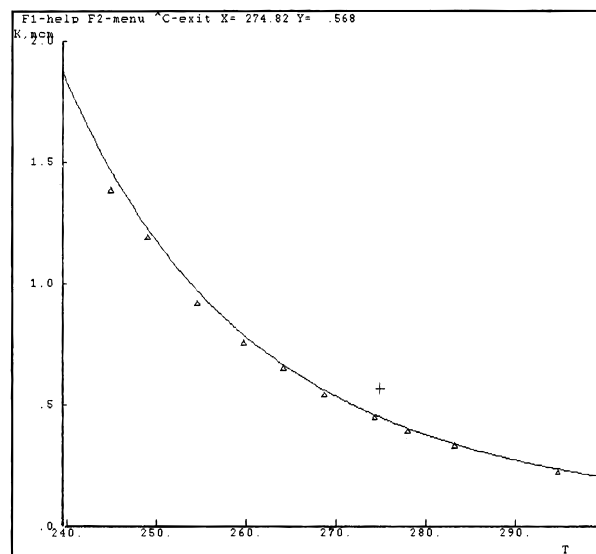


Figure 14. Propene (3.196/0.841).

oxygen, and carbon (sp^3) atoms: 1.2, 2.5, and 4, respectively. Further empirical refinement of the first two values yields 1 and 2.41. Atoms H, O, and $C(sp^3)$ in covalent compounds have σ -electron, one σ -electron and one π -electron, and four σ -electrons, respectively. Comparing to the “volumes” obtained, we conclude that the quantity V_i is the sum of the “volumes” of valent electrons, the “volume” of the σ -electron is equal to 1, and the “volume” of the π -electron is equal to 1.41. Equation 11 implies that the volume of a rigid molecule is equal to the sum of the volumes of its atoms and, consequently, to the sum of the volumes of all its valent electrons:

$$V_i = \sum_{j=1}^{N_i} V_j \quad (13)$$

As follows from (12), the generalized charge of the rigid molecule is

$$Q_i = (V_i/4)^{3/4} \quad (12')$$

Considering the generalized charge of the rigid molecule, we bear in mind that each covalent bond is formed with two valent

electrons: a σ -bond with σ -electrons of the total volume equal to 2 and a π -bond with π -electrons of the total volume of 2.82. If all of the valent electrons are involved in the molecule bonds,⁵ expressions 11 and 12 yield

$$V_i = 2(n_\sigma + 1.41n_\pi) = 2n_s + 4.82n_d + 7.64n_t \quad (14)$$

where n_σ and n_π are the numbers of σ - and π -bonds; n_s , n_d , and n_t are the numbers of single, double, and triple bonds in the molecule.

According to the third postulate, it needs to exclude from (14) bonds of remote (or “shaded”) atoms which do not affect the adsorption in virtue of the short-range behavior of van der Waals forces. The case of remote CH bonds is most simple. Small-sized hydrogen atoms are easily shaded with large atoms (of carbon, for example). In this case, the distance between a hydrogen atom and the adsorbent exceeds the carbon atom van der Waals diameter:

$$r_H > 0.34 \text{ nm}$$

For rigid molecules, this inequality can be realized in the

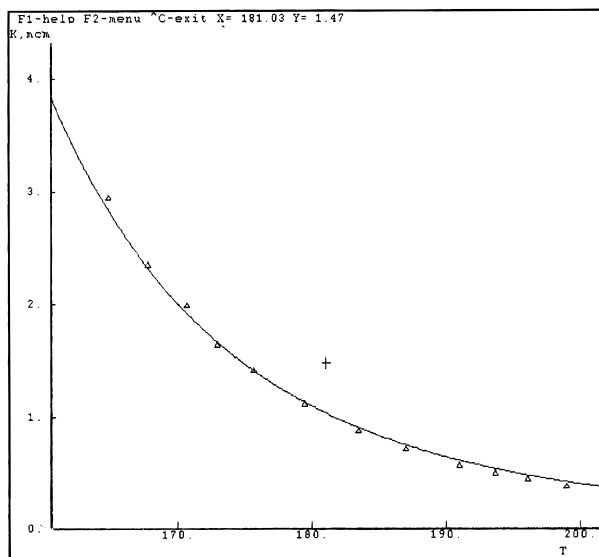


Figure 15. Acetylene (2.231/0.918).

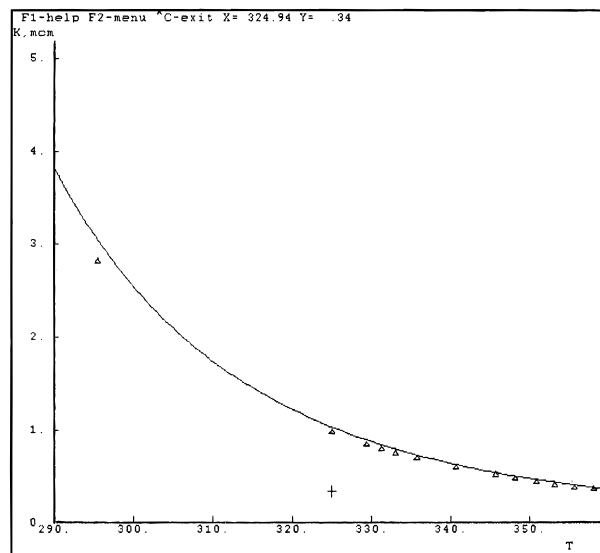
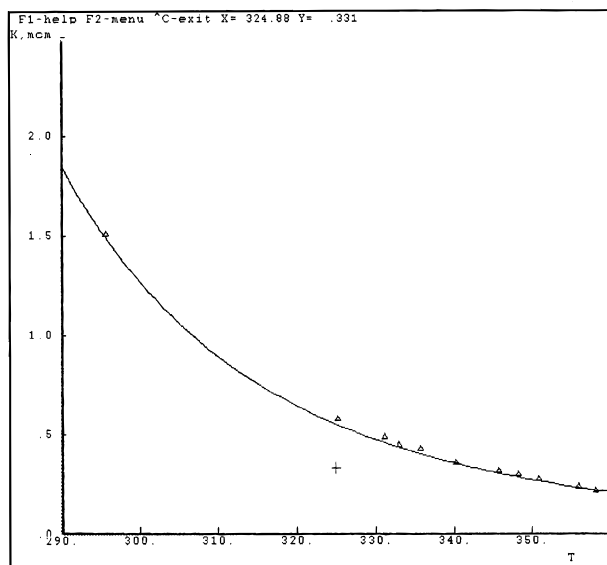
Figure 17. *trans*-butene-2 (4.222/0.771).

Figure 16. Butene-1 (3.933/0.771).

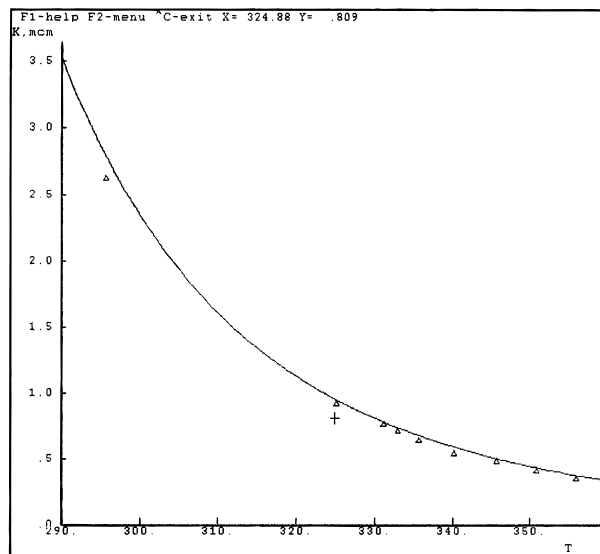


Figure 18. Butadiene-1,3 (4.218/0.841).

following cases:

(1) The vertical CH bond beginning from a carbon atom is spaced from the adsorbent not less than by 0.06 nm (the stated atom can be exemplified by a triple-carbon-bonded carbon).

(2) The CH bonds of the carbon atom lies at the end of a vertical CC bond (for example, CH bonds of methyls in neopentane).

A similar, but more seldom analogue is the case of excluding CC bonds: to be shaded with a more closely adjacent carbon atom, the atom in question must be spaced from the adsorbent surface by not less than three carbon atom van der Waals radii:

$$r_C > 0.34 + 0.17 = 0.51 \text{ nm}$$

This implies that the end atom of the vertical CC bond is not shaded with the lower atom touching the adsorbent. The carbon atom lying at the top of an *adamantane* molecule is spaced from the lower atomic plane by approximately the double CC bond length (0.31 nm); therefore its distance from the adsorbent cannot exceed 0.48 nm so that this atom is not shaded. This molecule has seven shaded atoms; thus, seven single (CH) bonds should be excluded in calculating the adsorption energy.

The case of *nonrigid molecules* is more complex. Molecules are regarded to be nonrigid when they have at least one *nonrigid bond*; i.e. a bond lost the torsional rigidity so that stresses appeared to exceed the rotation barrier. Parts of the molecule interconnected with nonrigid bonds, but not containing them, will be called *rigid segments* of the molecule. All the relationships needed to calculate the generalized charges and related adsorption properties for rigid segments have been derived above. Interactions of rigid segments with the adsorbent can be considered as independent; therefore, *the molecule potential energy can be found as the sum of potential energies of all its rigid segments*. [Similarly, the adsorbed molecule area is the sum of areas of its rigid segments.] *The rigidity of a bond breaks down, when the vibration-rotation energy of the adsorbed molecule segment involving the bond exceeds its rotation barrier*. According to (2), (6), and (8), the adsorbed molecule total energy is

$$E_i = X_i RT = Q_i (U_0 + \frac{1}{2} RT)$$

The vibration-rotation energy W_i of the molecule can be found

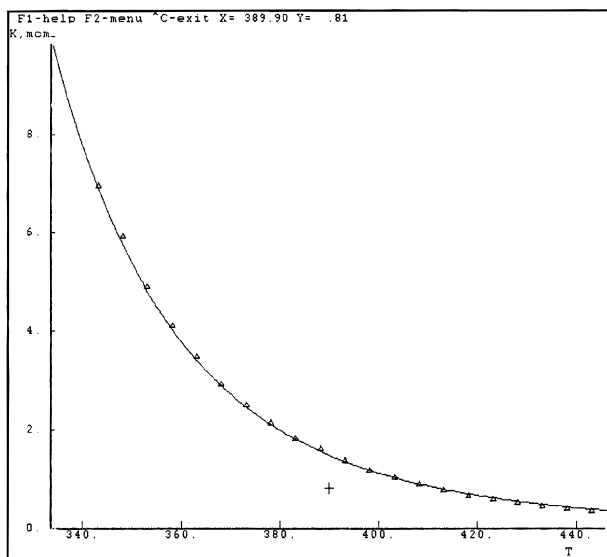


Figure 19. Hexene-1 (5.286/0.545).

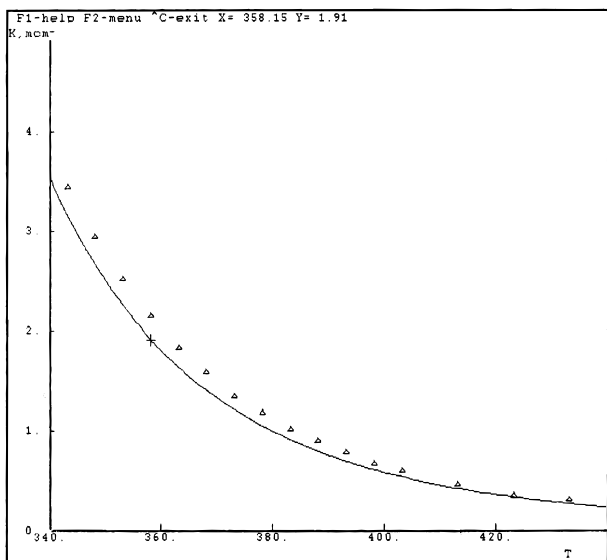
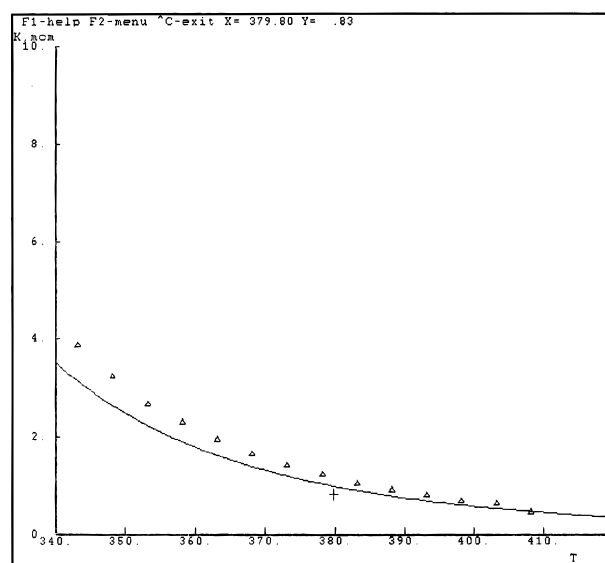


Figure 20. Cyclohexene (4.924/0.569).

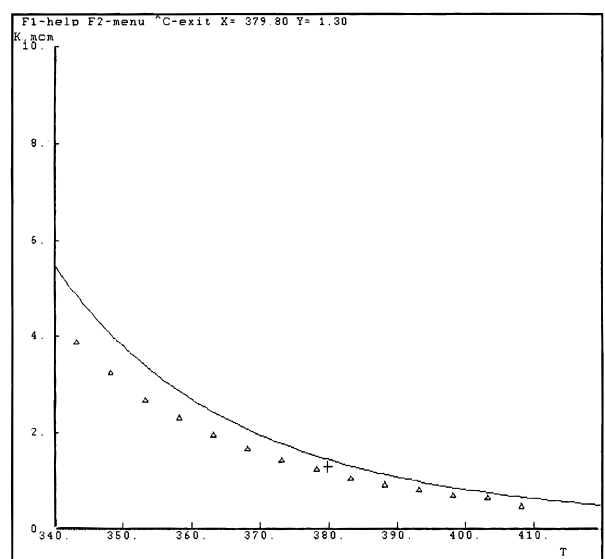


Figure 21. Cyclohexadiene-1,3 [offset single CC bond (a, top) (4.939/0.595); offset double bond (b, bottom) (5.170/0.621)].

as the difference

$$W_i = E_i - U_i = \frac{1}{2} Q_i RT \quad (15)$$

Note that the adsorbed molecule vibration–rotation energy is proportional to the temperature; therefore, any representation of the molecule as a set of segments is concerned only to a definite temperature range whose width and position determine the representation type. Below, we propose one of the possible algorithms for determining the *segment formula* of a nonrigid molecule.

At first, the molecule at hand is supposed to be rigid. Specifying required parameters of the molecule from its structural formula, we determine Q_i by eqs 13 and 14. For a given temperature and the minimum barrier W_0 of rotation around one of the molecule bonds, we compare $2W_0/RT$ and Q_i . If

$$Q_i > 2W_0/RT \quad (16)$$

the molecule is supposed to consist of two segments interconnected with the bond whose rotation barrier was considered. Then, inequality 16 is separately tested in each segment.

Iterating the segmentation of the molecule until inequality 16 breaks down, we find the segment formula of the molecule at the given temperature. Further, Q_i is again calculated as the sum of generalized charges of the rigid segments revealed. This algorithm can lead to several segment formulas for the molecule. However, by in virtue of the Boltzmann factor, for adsorption that formula is preferred which relates to the maximum generalized charge of the molecule.

We will illustrate this procedure for numerous *n*-alkanes. For rigid molecules, the generalized charge can be written as

$$Q_{alc} = (N_C + \frac{1}{4} N_H)^{3/4} \quad (17)$$

where N_C is the number of carbon atoms and N_H is the number of hydrogen atoms. For *n*-alkanes, the rotation barrier for the bond with methyl is 12.2 kJ/mol and for the bond with ethyl is 13.8 kJ/mol. Inequality 16, transformed in the first case at a temperature of 450 K into $(1.5N_C + 0.5)^{3/4} > 6.52$, yields $N_C > 7.7$; i.e. the rigidity violation for the bond with methyl in the *n*-alkane series begins from *octane* under the stated conditions. The rigidity violation for the bond with ethyl at 450 K

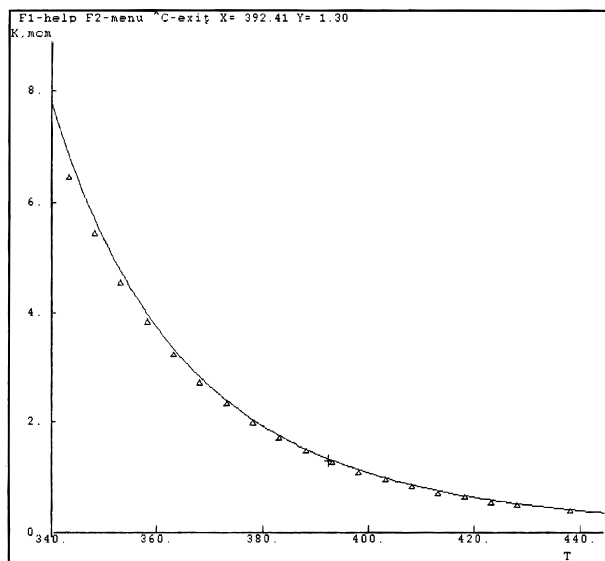


Figure 22. Benzene (5.377/0.677).

corresponds to the value 7.38 for the right-hand side of inequality 16. The latter yields $N_C > 9.2$. It means that the rigidity violation for the bond with ethyl in the *n*-alkane series can begin from *decane* under the stated conditions. The Boltzmann factor enhances this possibility.

Another example of the “freedom” of elements of a molecule is associated with delocalized π -electrons (DPE), mobile enough to not be included in the rigid segment containing parent atoms. The delocalized state of π -electrons is possible, when resonant patterns different from the initial pattern by positions of the π -electrons exist. Taking into account that electrons within a π -bond are not belonging to a definite atom, the apparent property of DPEs is their exchange interaction. The exchange interactions between DPEs make their motion to be correlated enough to consider the overall π -electron rigid segment for the molecule.

Exchange of two electrons with each other is only possible when their states are energetically identical with different spins (*para* states) or equal spins (*ortho* states). Their coordinate functions are symmetrical, in the first case, and antisymmetrical, in the second. In the molecule, the most probable regions of localization of its electrons (and paths of their motion) correspond to covalent bonds. The probability of *ortho*-electrons to be on the symmetry axis is zero. It means that the molecular structure has no bonds intersecting the symmetry axis. Hence, in the majority of cases when the symmetry axis intersects the molecule bonds, the only *para*-electrons may be considered as DPEs. The question rises: at what distance from the molecule symmetry axis there are atoms whose electrons are DPEs. If the atoms lie on the axis, the exchange of electrons does not lead to resonant patterns and their contribution in the number of DPEs is zero.⁶ Only symmetrical atoms with π -electrons can exchange them. Therefore, the route through bonds from the atom with π -electrons to the symmetry axis cannot include more than the half-length of a single bond. Recalling the freedom of π -electron transport within the π -bond, we may conclude that this route can contain any number of π -bonds. Finally, links between electrons in the DPE group (considered as a rigid segment) must be rigid. In particular, the probability of bringing any pair together must be equal to zero. It means that all electrons of the DPE group have equal spins. Hence, the number of DPEs is just the halved number of exchangeable π -electrons. So, if the symmetry axis of the molecule intersects its bonds, the number of DPEs is half the number of π -electrons

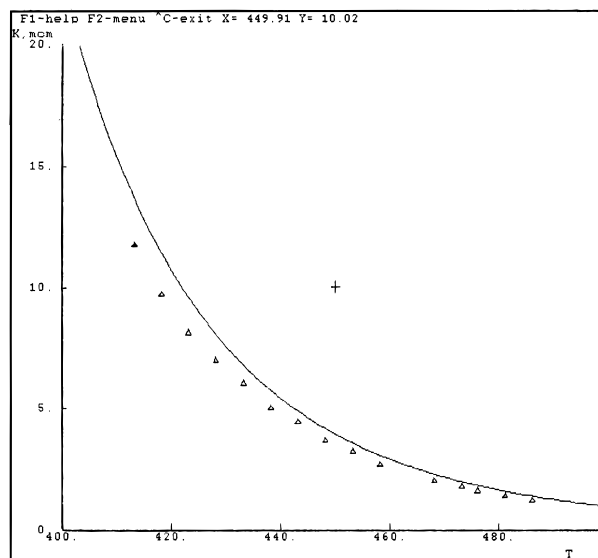
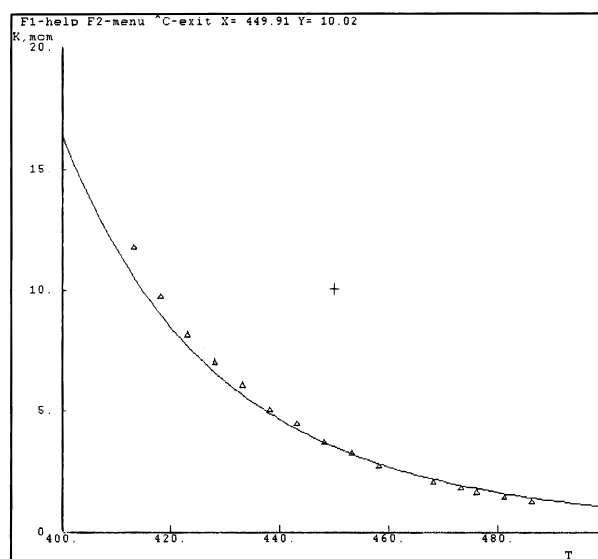


Figure 23. Octane: (a, top) [rigid] (6.648/0.354); (b, bottom) [*Me-Hep*] (7.458/1.16).

of all those atoms the route from which to the symmetry axis, drawn through bonds, is not equal to zero and contains no more than half the overall single bonds. Thus, the entire adsorbed molecule is represented as a mosaic structure whose elements are rigid segments and the DPE group. The behavior of each rigid segment is caused only by its own adsorption properties. The total generalized charge of the molecule is the sum of the generalized charges of its segments and delocalized electrons. Using (13), we get the expression for the generalized charge of the *i*th nonrigid molecule with the DPE group:

$$Q_i = 0.354 \sum_k V_k^{3/4} + 0.458 \left(\sum_k \pi_{dk} \right)^{3/4} \quad (18)$$

where k is the rigid segment summation index and $\sum \pi_{dk}$ is the number of DPEs in the molecule. The electron volume of the rigid segment is determined by formula 14 modified with regard to the above-mentioned comments (the index “ k ” is omitted):

$$V = 2(n_s - n_{ls}) + 4.82(n_d - n_{ld}) + 7.64(n_t - n_{lt}) - 1.41\pi_d \quad (19)$$

where π_d is the number of delocalized electrons and n_{ls} , n_{ld} ,

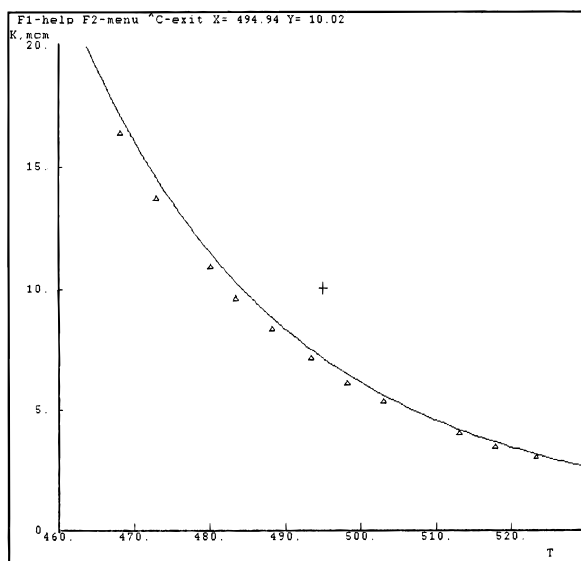
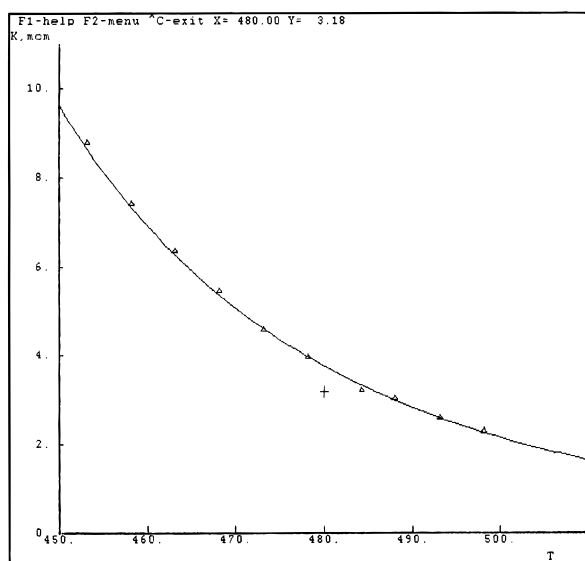
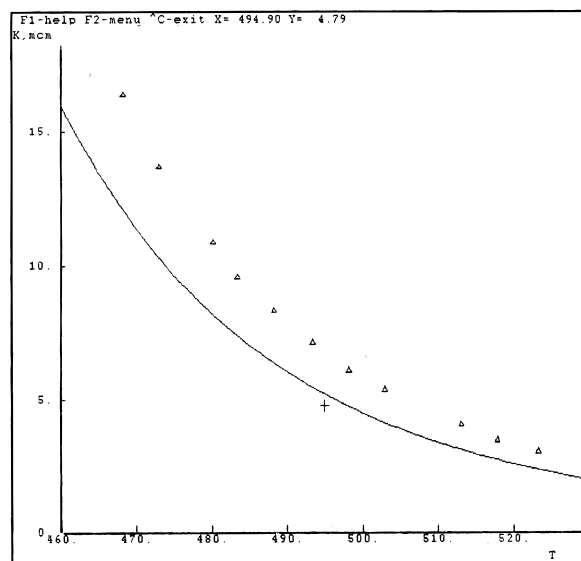
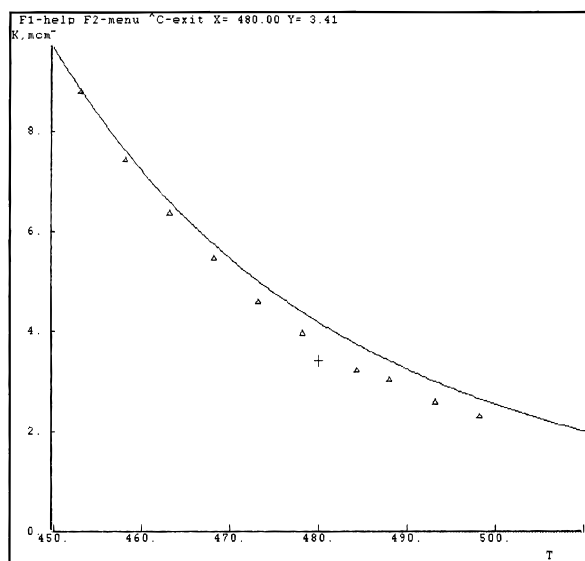


Figure 24. Nonane: (a, top) [rigid] (7.238/0.297); (b, bottom) [*Me-Oct*] (8.069/0.15).

Figure 25. Decane: (a, top) [*Me-Non*] (8.662/1.14); (b, bottom) [*Et-Oct*] (8.968/1.24).

and n_{it} are the numbers of excluded single, double, and triple bonds, respectively.

Calculation of the Steric Properties of an Adsorbed Molecule

We consider a method of calculation of the parameter F_i defined by expressions 4 and 5. According to (5), P_i is the absolute term in the Fourier expansion of $p_i(\xi)$ and, therefore, is unrelated to the angular distribution of parts of a uniform (nonpolar) body. Hence, for nonpolar molecules $P_i = 1$ independently of their shape. Substituting this value in (4) yields

$$F_i = \cos \theta_i \quad (20)$$

We express $\cos \theta_i$ as an equilibrium characterization of the slope of the molecule principal section to the adsorbent plane through the molecule structure parameters. For simplicity, we will consider the molecule as a uniform ellipsoid with the axes $a \leq b \leq c$. Its principal section is bounded with an ellipse with the axes b and c and in any instant is sloped to the adsorbent surface on the angle θ . The quantity $\cos \theta_i$ can be found by integrating its absolute value over the entire ellipsoid surface S_e with the

unit weight, the latter being the result of the second postulate formulated at the beginning of the paper. Because the projection of a small area of the ellipsoid taken at the point of contact with the adsorbent surface onto the principal section has the angle θ , it is easy to prove that the integral in question is equal to the doubled area Φ of the principal section:

$$\cos \theta_i = S_e^{-1} \int_{S_e} \cos \theta \, dS = 2\Phi/S_e \quad (21)$$

It is apparent that expression 21 refers not only to an ellipsoid but also to any body for which the convex part of the surface obeys the second postulate.

The principal section of an ellipsoid is its section of maximum area. Therefore, the quantity $2\Phi/S_e$ is maximum for the ellipsoid corresponding to the molecule. This quantity has the minimum value $2\Phi/S_e = 1/2$ for a sphere and the maximum value 1 for a double-sided elliptic area (i.e. at $a = +0$). For a narrow cylinder, the quantity $2\Phi/S_e$ equals $2/\pi$. A thin torus has the same value of the average cosine (in calculations, we should take the ratio of Φ to $S_e/2$ because the torus interior is inaccessible for collisions with the planar adsorbent).

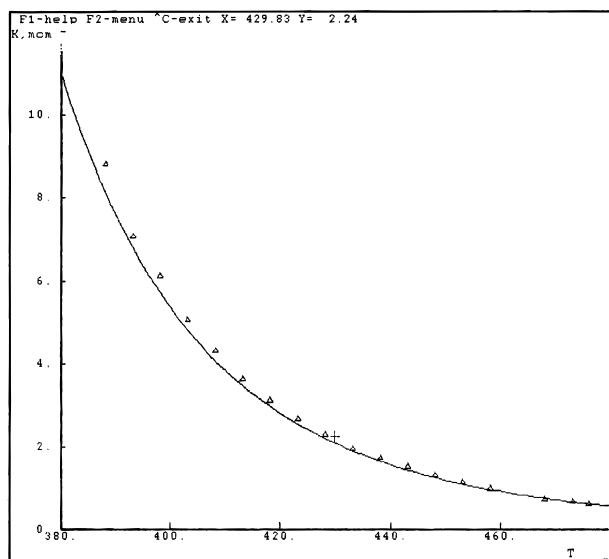


Figure 26. Toluene [Me-Ph] (6.521/0.982).

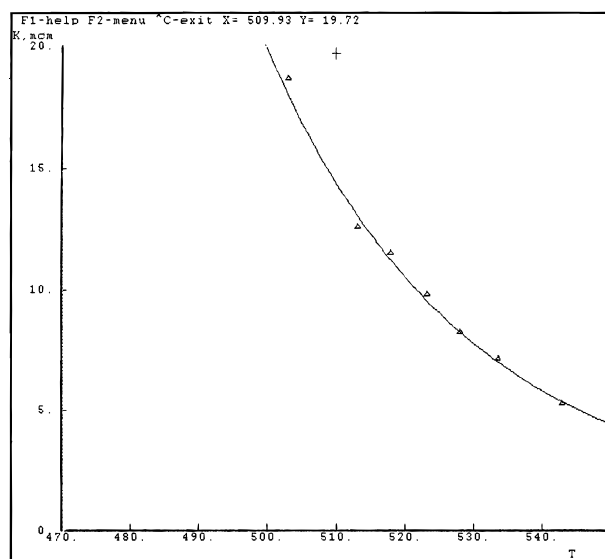


Figure 28. Biphenyl [Ph-Ph] (9.852/1.14).

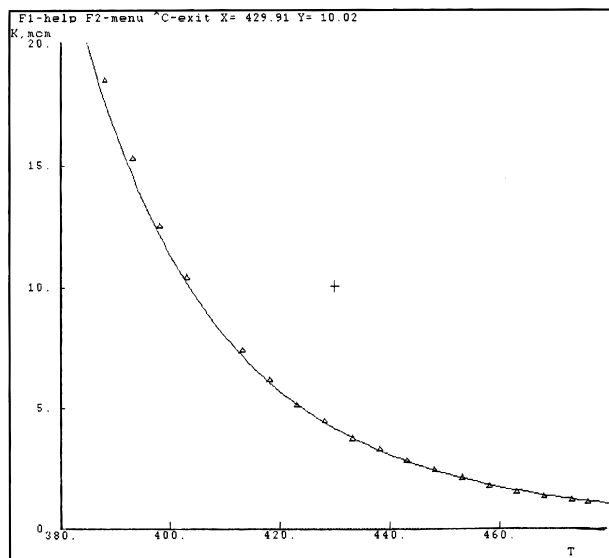


Figure 27. Ethylbenzene [Me-Bz] (6.878/0.823).

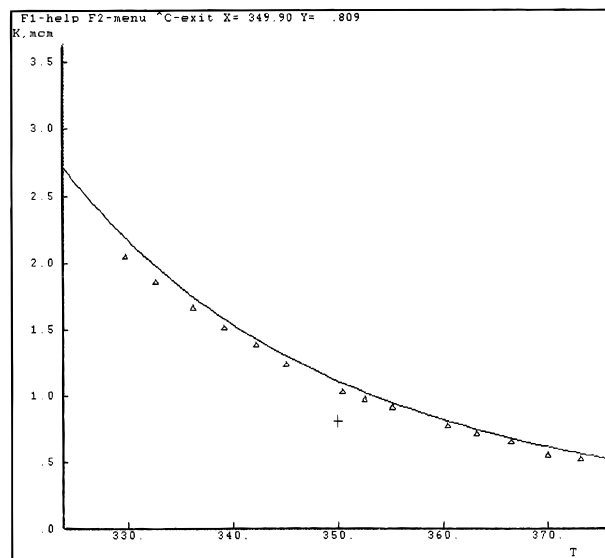


Figure 29. Diethyl ether (4.644/0.771).

Thus, the parameter $F_i = 2\Phi/S_e$ characterizes the shape of a geometrical body and may be called the steric factor of the molecule. In spite of the simplicity of expression 21, in order to apply it to calculations, we need reliable and exact procedures of “wrapping” molecules by the models filling the space and accounting for the nonuniformity of the molecules and dynamically associated model bodies. For example, a benzene molecule is known to be approximated by a torus; hence, the steric factor of benzene is close to $2/\pi$. However, in other cases the molecular stereometry is not so evident

Rigid Polygonal Molecule. We will consider the widespread case of the molecule representation as a linear chain of identical links with fixed valent and inner rotation angles. The latter are determined from the commonly used description of possible conformations of the molecule at lower temperatures for which inner rotation barriers are not overcome. In an ensemble of such molecules, different molecular conformations are distributed by the Boltzmann law. All the mostly repeated (“allowed”) conformations can be represented as elements of the figure built of an arbitrary conformation by the allowed rotations about each bond (the so-called retarded rotation) provided some bond of the molecule (e.g. the first) is fixed. The body bounded with

the surface on which end bonds of the conformers lie is the object (called the “molecule body”) which reflects the distribution and the steric factor of conformations of the rigid polygonal molecule. O denotes the chain initial link common for all molecule conformations. The end link of some conformer is on the angle θ to the link O . The familiar multiplicative property for the average cosine of this angle⁷ provided the average cosine of the inner rotation angle is equal to zero (that approximately fulfills for alkanes⁴) yields

$$\langle \cos \theta \rangle = \exp\left(-\frac{s}{c}\right)$$

where s is the chain length from the end of the link O (for which the cosine is identically equal to unity); c is the so-called persistent length of the chain—the average length of a nondeformable element of the molecule, i.e. the bond length c_0 multiplied by some constant k which can be determined from the properties of chain elements. The quantity s/c_0 is equal to the chain links number without unity, i.e. to the number of jogs of the molecule: $z = s/c_0$. As already mentioned in the deduction of (21), the quantity F_i subject to averaging by the

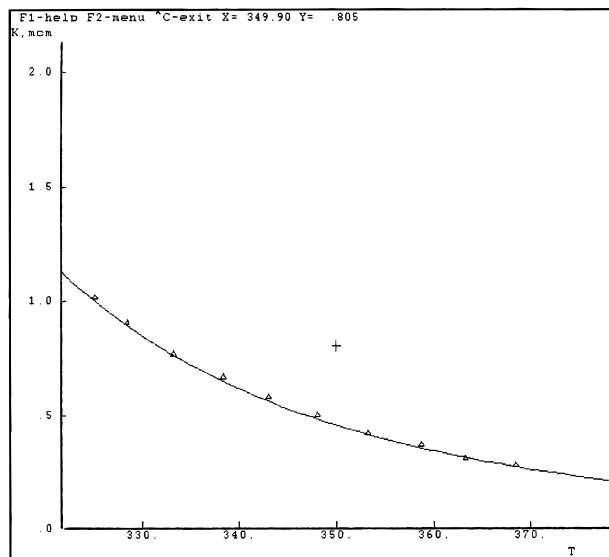


Figure 30. Methyl acetate [Me-Ac] (4.380/1.23).

angle ξ and to the second postulate is equal to the average modulus cosine of the angle between the surface element (i.e. the end link of the appropriate conformer) and the body principal plane (at which the first link lies). Hence,

$$F_i = \exp\left(-\frac{z_i}{k}\right) \quad (22)$$

where z_i is the number of jogs of the rigid polygonal molecule.

Provided the quantities F_a and F_b are known for sufficiently large parts a and b of the rigid polygonal molecule ab , expression 22 with regard to exclusion of two jogs in partitioning the molecule on links implies

$$F_{ab} = F_a F_b \exp\left(-\frac{2}{k}\right) \quad (23)$$

It follows from (23) that, in particular, *the steric factor of a branched molecule with long linear chains is equal to the steric factor of the isomeric linear molecule.*

The jogs number for a closed (cyclic) molecule are equal to its links number (l_c); however, a set of its conformations is equivalent to the set of conformations of a linear molecule with the halved jogs number (z_c):

$$z_c = l_c/2$$

An arbitrary link of the cycle vitally differs from an arbitrary link of the polygonal (linear) molecule because the former is an end link in the equivalent linear chain representation; i.e. it lies at the molecule body surface. When the molecule has no conformation in contact with the adsorbent by a given link of the cycle, this link lies at the concave area of the molecule body surface. Because concave areas of the molecule body surface do not affect the quantity S_e involved in expression (17) for the steric factor, cycle links never touching the adsorbent have no influence on the molecule steric factor different from the influence on an inner link of the polygonal molecule. Thus, *the number l_c involves only those links of the molecule cycles that touch the adsorbent.*

According to (22) and (23), when the linear part of the molecule contents z_1 jogs and the number of jogs in its cycles

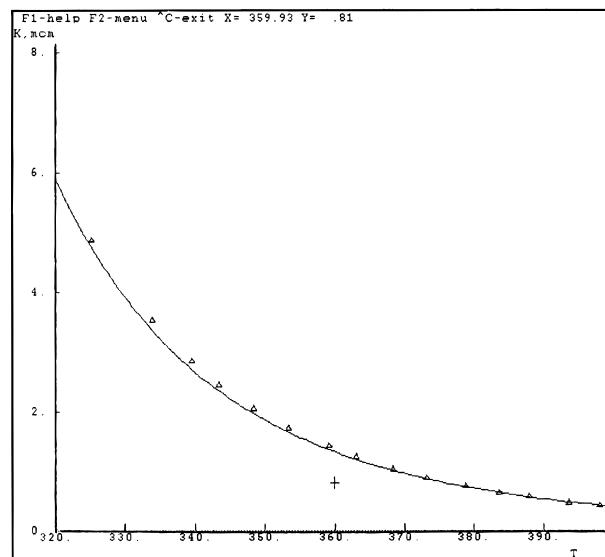


Figure 31. Vinyl acetate [VnO-Ac] (5.126/1.33).

is l_c , the number z_i can be determined as

$$z_i = z_1 + \frac{l_c}{2} + 2$$

Another consequence of the rigid polygonal molecule model (RPM model) is the account for *double* and *triple bonds* of the molecule. Representing the bonds as cycles containing only one link able to touch the adsorbent (σ -bond), we find

$$z_i = z_1 - \frac{n_{dl} + n_{tl}}{2} + \frac{1}{2}\left(l_c - \frac{n_{dc} + n_{tc}}{2}\right) + 2 \quad (24)$$

where n_{dl} , n_{tl} are the numbers of double and triple bonds in linear parts of the molecule and n_{dc} , n_{tc} are the numbers of double and triple bonds (which touch the adsorbent) in its cycles.

Expression 23 is asymptotic. If the parts of the molecule are *small*, we should average the products of their steric factors over all conformations (of the number N) like one manages in determining the macromolecule Green function:⁷

$$F_i = N^{-1} \sum (F_1 \dots F_n) \quad (25)$$

where F_1, \dots, F_n are the steric factors of n parts of the molecule provided the end of each part belongs to the convex surface of the molecule [this condition is used in the deduction of (22)]. It follows from (25) that the steric factors of isomeric molecules with short branches can noticeably be distinguished. Herein, we do not touch on this question in detail. The following calculations are limited by the conclusion, evident from (23), that the steric factors of isomeric molecules are equal in the first approximation.

The RPM model is not valid in the two cases: for short molecules whose length is less than the persistent one and for nonrigid molecules whose persistent length varies. However, both of these cases can be described *ab initio*.

Short Molecule. Each atom of the short molecule belongs to its convex surface. In this case, the principle of equal probability of collisions with the adsorbent for any point of the convex surface of the molecule (i.e. the second postulate) is equivalent to the principle of dynamic similarity in the adsorption of small particles: *the average distance between the particle and the adsorbent surface depends only on properties of this particle.* In other words, eq 3 is valid not only for the entire

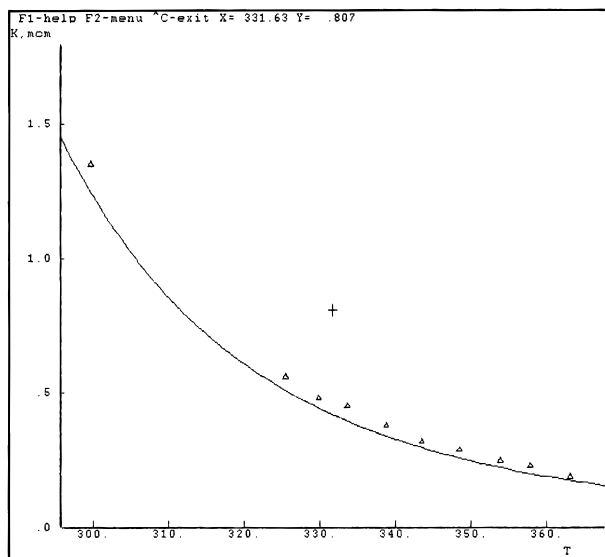


Figure 32. Acetone [Me-Ac] (4.057/1.17).

molecule but also for its parts (atoms j):

$$\rho_j = \frac{1}{2} + \frac{w_j^{1/2}}{F_j d} \quad (3')$$

Actually, if the quantity ρ_j depends on the properties of another atom of the same molecule, the frequency of collisions of the j th atom would analogously depend. For example, let a new ρ_j' be less than the ρ_j from (3'); then the j th atom more often enters the repulsive zone than the other atom giving rise to this process.

The i th molecule center-of-mass coordinate is defined as

$$\rho_i = \sum_j \mu_j \rho_j, \quad \sum_j \mu_j = 1 \quad (26)$$

where μ_j is the atom-to-molecule mass ratio. Substituting (3'), (8), (12), (13), and (26) in (3) yields

$$F_i = \frac{(\sum_j Q_j^{4/3})^{3/8}}{\sum_j \mu_j Q_j^{1/2} / F_j} \quad (27)$$

The use of masses of the molecule elements reflects the dynamic behavior of adsorption. In the RPM model, the more the massive atom, the greater its contribution in (27). This allows us to consider only the molecule skeleton consisting of massive atoms.

We consider for alkanes a simple and evident enough "sphere-needle" model in which the molecule is represented as a set of spheres ($F_j = 1/2$) corresponding by their mass ($m_j = 12$) and electron volume ($V_j = 4$) to C(sp³) atoms and a set of needles ($F_j = 2/\pi$) corresponding to bonds ($m_j = 0$) and hydrogen atoms ($m_j = 1$, $V_j = 1$). For these values, eq 27 gives the convenient formula

$$F_i = \frac{0.637(N_H + 12N_C)(N_H + 4N_C)^{3/8}}{N_H + 25.71N_C} \quad (28)$$

where N_H and N_C are the numbers of hydrogen and carbon atoms. Note that eq 3' implies that all the molecule atoms have equal probabilities of their collisions with the adsorbent. It is apparent that for simple molecules like methane, ethane, and propane this condition does not contradict the second postulate.

For a rigid molecule, eq 21 gives $F_i \leq 1$. When this condition breaks down in accord with (27), it needs to abandon the principle of identity of the dynamic conditions for each element of the molecule. Violation of this principle for linear molecules is caused by imperfections in the molecule shape (jogs) influencing the frequency distribution of collisions between its atoms and the adsorbent surface. Accounting for the different conformations of the molecule leads to the RPM model described above. For example, substituting the data $N_H = 10$ and $N_C = 4$ for an n -butane molecule in (28) yields $F_i = 1.111$ that contradicts the inequality $F_i \leq 1$. To determine the steric factor for n -butane, we use the RPM model. Expression 25 implies that the n -butane steric factor is equal to the half-sum of the squared steric factor for ethyl and to the product of the steric factors for propyl and methyl [cf. (28)]:

$$F_{n-But} = (F_{Et}^2 + F_{Me}F_{Pr})/2 = (0.857^2 + 0.690 \times 0.982)/2 = 0.706$$

Substituting the F_{n-But} value obtained and $z = 2$ in (22), we find the parameter k is the ratio of the persistent length to the single CC bond length: $k = -2/(\ln 0.706) = 5.74$. Note that in a good accuracy $k = 4/(\ln 2) = 5.77$; i.e. instead of (22) we get for alkanes the simple relation

$$F_i = 2^{-z/4} \quad (29)$$

Nonrigid Molecule. For nonrigid molecules consisting of several rigid segments, one can deduce a relation between the steric factors of the molecule and its segments. For this purpose, expressions 3, 8, and 26 should be substituted in the equation for the nonrigid molecule generalized charge:

$$Q_{is} = \sum_j Q_j$$

where is is the molecule index and j is the rigid segment index. This yields

$$F_{is} = \frac{[\sum_j Q_j]^{1/2}}{\sum_j \mu_j Q_j^{1/2} / F_j} \quad (30)$$

A distinctive feature of the nonrigid molecule steric factor is that it cannot, in general, be characterized by the cosine of any one angle. This implies that the upper bound for the steric factor is not already equal to unity, but in accord with (30) is equal to the square root of the segments number.

There exists another reason for increasing the nonrigid molecule steric factor. The energy needed to overcome the rotation barrier is the difference between the total energy of the adsorbed molecule (being constant in given conditions) and its potential energy depending on the distance from the adsorbent. Hence, the point, where the vibration-rotation energy reaches its maximum and the molecule rigidity breaks down, is located in the nearest vicinity of the adsorbent (roughly, the molecule touches the adsorbent at the point of rigidity violation). For molecules whose internal energy provides comparable amounts of rigid and nonrigid conformers, this statement is a tool for statistical selection. This needs to be explained. Because one of the bonds of a nonrigid conformer is the bond with violated rigidity and must be in continuous contact with the adsorbent, the conformation of the rigid polygonal residual bounded with the nonrigid bond must be planar with $F = 1$ (for alkyls this conformation is called the trans-zigzag). Otherwise, the contact point of the molecule with

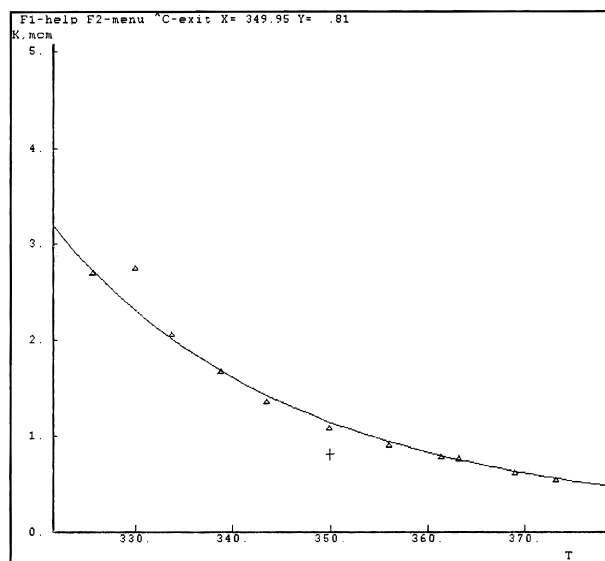


Figure 33. Methyl ethyl ketone [Me-X] (4.844/1.21).

the adsorbent would be random, while the point of the molecule rigidity violation appears to be *energetically determined*. Because of a good gain in the generalized charge of the nonrigid conformer compared to the rigid one (that is due to the different laws of adding the generalized charges of identical parts of the rigid and the nonrigid molecule), the adsorbed state of the nonrigid molecule characterizes, in large part, by planar conformations of its segments. Note that the condition for the adsorbent and the molecule to be in contact through its nonrigid bond relates to the temperature at which the internal energy nearly equals the rotation barrier. At well over these temperatures, this condition is not necessary.

Examples of Calculations

For each example, we will use the following order of calculations: generalized charge, formulas 18 and 19; steric factor, formulas 27, 24, 29, and 30; Henry law constant, formulas 1–3. All the data concerning the molecule properties needed for the calculations are commonly used, and the data for determining remote bonds, delocalized π -electrons, and the segment formula of the molecule are not in contrast with the conventional notion of molecular structure. The initial data and results of the calculations (for the generalized charge Q , the steric factor F , and the Henry law constant K (μm) as a function of the temperature T (K) are represented in Tables 1–4 and Figures 1–40. The figures show the calculated plots (solid curves) compared to the experimental data (dots) obtained by Prof. A. V. Kiselev and his colleagues^{2,8–12} and kindly extended to the author by Dr. N. N. Avgul' and Dr. N. V. Kalashnikova in the form of detailed tables. The figure captions present the generalized charge and the steric factor (in parentheses, through a slash) and also the segment formula of the molecule (in brackets).

Alkanes. Short Molecules. The calculation is based only on the numbers of atoms and bonds. Such molecules represented in Table 1 are *methane* (Figure 1), *ethane* (Figure 2), *propane* (Figure 3), and *cyclopropane* (Figure 10).

Rigid Polygonal Molecules: Linear, Branched, and Cyclic. Unlike short molecules, the steric factors for rigid alkanes beginning from *butane* (Figure 4) are determined from the RPM model. To illustrate the accuracy of this approach, Table 1 also contains the data and calculation results for *n-pentane* (Figure 5) and *n-hexane* (Figure 6). The calculation of branched

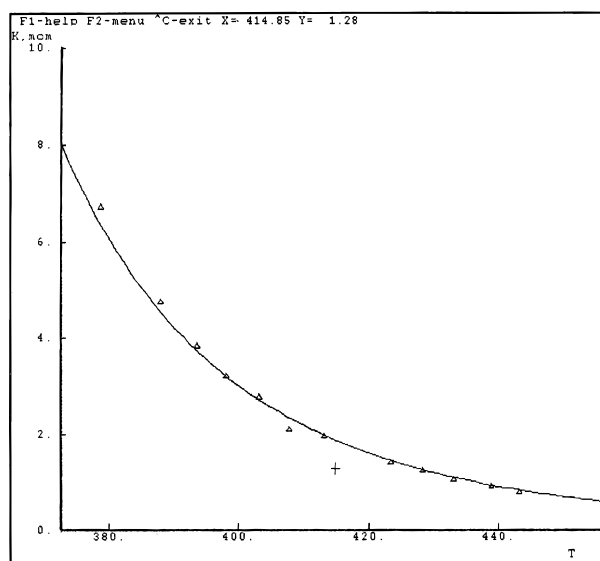


Figure 34. Acetylacetone [Me-X-Me] (6.344/1.39).

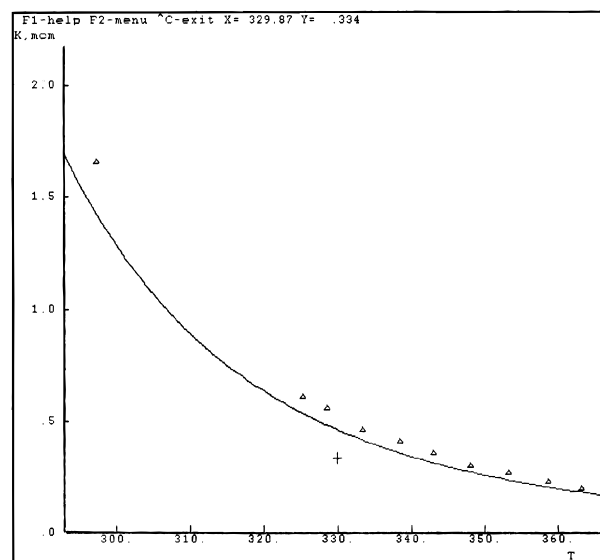


Figure 35. Propanal [Et-Ad] (4.075/1.17).

molecules such as *isobutane* (Figure 7), *isopentane* (Figure 8), and *neopentane* (Figure 9) involves remote bonds, i.e. bonds of shaded atoms. For the two former molecules, shaded atoms of the first type (see above) are the hydrogen atoms at the second carbon atoms. For the latter molecule, shaded atoms of the second type are the three hydrogen atoms at the vertically arranged methyl. In addition to the short cyclopropane molecules considered, there are other cyclic molecules in Table 1: *cyclohexane* (Figure 11) and *adamantane* (Figure 12). In any of the most probable conformations (“chair” and “bath”), the cyclohexane touches the adsorbent plane with each of the *six* links of the cycle, while shaded atoms (of the first type) are always *two* hydrogen atoms, not three, because not each angle of this cycle can be tetrahedral. The adamantane molecule during a single interaction with the adsorbent touches it with not less than the *six* links of the rings. This molecule has *seven* remote bonds (of the second type).

Alkenes. Short, Linear, and Cyclic Molecules. The calculation of the properties of many alkene molecules is similar to that for alkanes. This is also true for the following molecules represented in Table 2: *ethylene* (Figure 13), *acetylene* (Figure 15), *propylene* (Figure 14), *butene-1* (Figure 16), and *hexene-1*

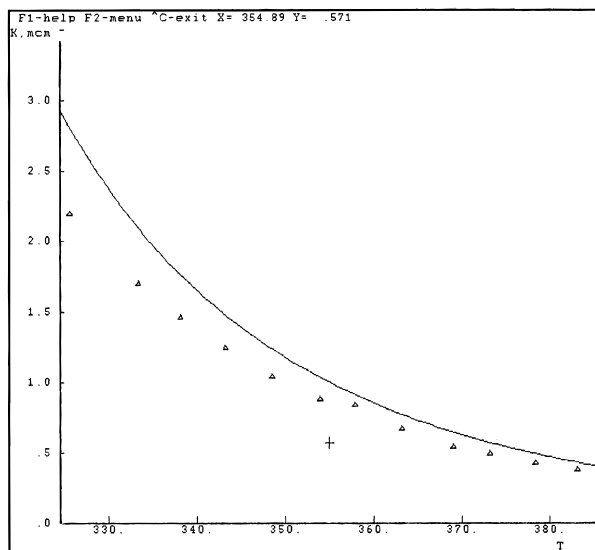


Figure 36. Butanal [Pr-Ad] (4.872/1.26).

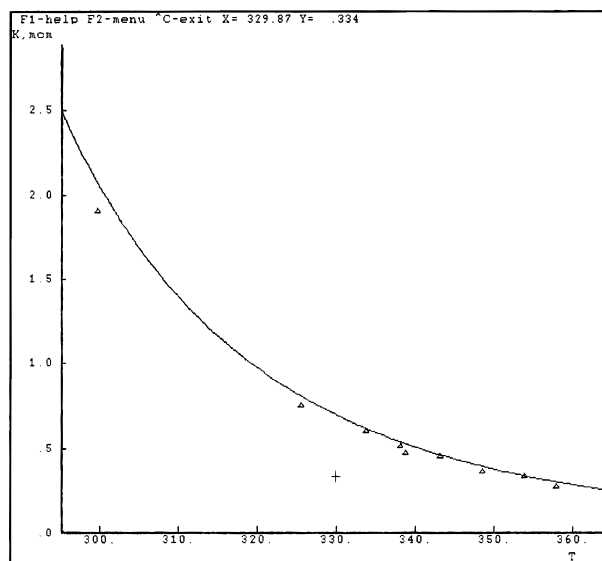


Figure 38. Propanol [Me-X] (4.270/1.17).

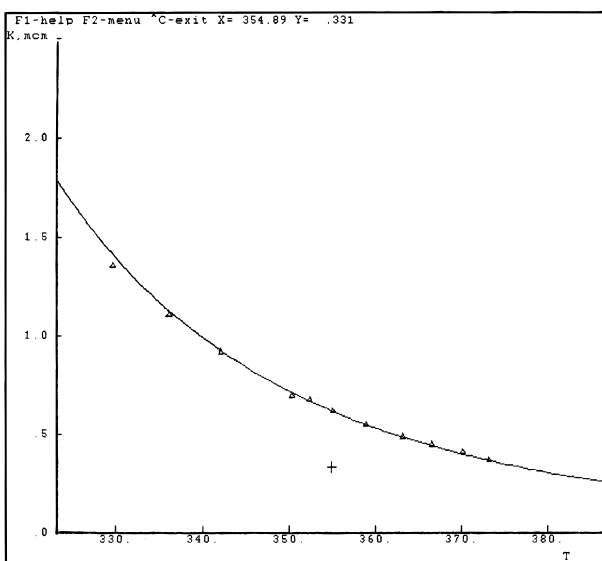


Figure 37. Isobutanol [Pr-Ad] (4.615/1.23).

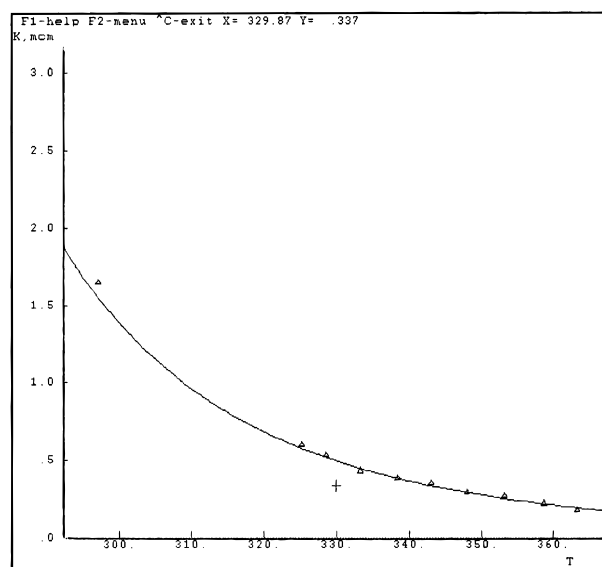


Figure 39. 2-Propanol [Pr-OH] (4.103/1.15).

(Figure 19). The rest of the molecules in Table 2 have the *symmetry axis* (not passing along the π -bond as in ethylene and acetylene). This property is reflected in the availability of delocalized π -electrons. According to the rule formulated above, *trans-butene-2* (Figure 17) has one DPE; *butadiene-1,3* (Figure 18), two DPEs; and *cyclohexene* (Figure 20), one DPE; *cyclohexadiene-1,3* (Figure 21), two DPEs; and *benzene* (Figure 22), three DPEs. Cyclohexene and cyclohexadiene molecules are nonplanar and, therefore, additionally characterized by *remote bonds* (with shaded hydrogen atoms of the second type) and *CC bonds not touching the adsorbent* (shortly, "offset bonds"). Depending on what bond—single or double—is an offset bond, we have different sets of initial data needed for the calculation. For cyclohexene the second case is seldom, but for cyclohexadiene with two double bonds both cases have comparable frequencies. For benzene, the steric factor calculated by the RPM model is 0.677 that is close to the value $2/\pi$ for torus. Note that this result is in agreement with the common notion of the benzene molecule shape.

Nonrigid Molecules. In this case, the calculation should be completed by representing molecules with sets of rigid segments. The key quantities for this purpose are the barriers of rotation about the molecule bonds, in particular, the barriers of rotation

of the molecule segments being found about the bonds between them. Using the well-known reference data, we took the following values for W_0 (kJ/mol): *Me-Alk*, 12.2; *Et-Alk*, 13.8; *Me-Ph*, 8.5; *Me-Bz*, 9; *Ph-Ph*, 15; *AlkO-Alk*, 11.4; *{Me-Ac, Me-Acl, VnO-Acl, Alk-Ad, Alk-OH, Vn-CH₂OH, Me-(CH₂)₂OH}*, 4.2–4.7 [*Alk* is alkyl].

For molecules of *octane* (Figure 23), *nonane* (Figure 24), and *decane* (Figure 25), Table 3 shows how important it is to make a correct segmentation of the molecule. The best convergence of the calculated and experimental data is achieved for the case which employs inequality 16 and the molecule segmentation algorithm developed. As can be seen, the temperature at which the molecule segment formula is changed according to (16) corresponds to close values of the Henry law constant on the plots of the competitive representations [Figure 23, (1) and (2); Figure 24, (1) and (2)]. It means that the barrier W_0 may not be preset too exactly. Physically, this fact means that changes in the segment formula (and the molecule energy state) cause smooth variations (without abrupt changes) of the Henry law constant in spite of a significant difference in the generalized charges. Molecules of *toluene* (Figure 26), *ethylbenzene* (Figure 27), and *biphenyl* (Figure 28) complete a series

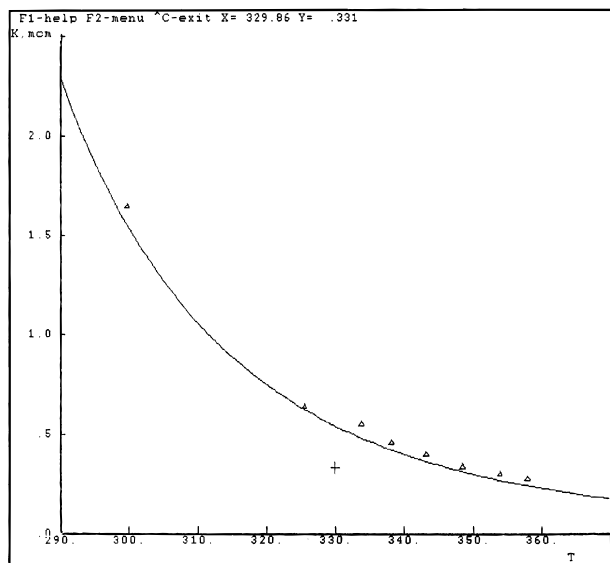


Figure 40. Propenol [Vn-X] (4.153/1.18).

of hydrocarbon molecules presented herein. The symmetry axis in a toluene molecule passes through $C(sp^2)$ atoms (and the carbon of methyl) that gives one DPE. An ethylbenzene molecule is nonsymmetric, and a biphenyl molecule has the symmetry axis which passes along its (nonrigid) single bond that corresponds to two DPEs.

Oxygen-Containing Molecules: Ethers, Esters, Ketones, Aldehydes, and Alcohols. The universality of the approach developed can be demonstrated by the calculation of oxygen-containing organic molecules. Substituting in all the formulas containing bonds the halved double bond characterizing an oxygen atom (as well as $m_O = 16$, $Q_O = 0.684$, $F_O = 0.5$) and employing all the above procedures, we determined the properties of the following molecules. *Diethyl ether* (Figure 29) is a rigid molecule under the given conditions and has the symmetry axis passing through the oxygen atom (by this cause the only π -electron is delocalized in the molecule). The rest of the molecules in Table 4—*methyl acetate* (Figure 30), *vinyl acetate* (Figure 31), *acetone* (Figure 32), *methyl ethyl ketone* (Figure 33), *acetylacetone* (Figure 34), *propanal* (Figure 35), *butanal* (Figure 36), *isobutanal* (Figure 37), *propanol* (Figure 38), *2-propanol* (Figure 39), and *propenol* (Figure 40)—are nonrigid under the given conditions. Of particular interest are the examples of the acetylacetone molecule (contains three segments) and branched molecules of isobutanal and isopropanol. Similar to isobutane, isobutanal has one shaded hydrogen atom of the first type, while an isopropanol molecule has no shaded atoms.

Conclusions

The postulates allowing us to develop the approach for describing van der Waals interactions are proposed. The

relationships between the energy and geometrical properties of molecules and the same properties of their atoms and bonds are established for the adsorption of nonpolar molecules on a uniform nonpolar adsorbent. The method for a priori calculation of adsorption properties such as the molecule area on the adsorbent, the adsorption energy, the internal energy of the adsorbed molecule, parameters of the molecule arrangement with respect to the adsorbent, and the Henry law constant. For the calculation, the following data are required: about the adsorbent, crystalline lattice parameter, degree of the surface uniformity, and energy constant characterizing the adsorption in a reference system; about the molecule, empirical formula, segment formula, numbers of single, double, and triple bonds, bonds in rings touching the adsorbent (single and double), remote bonds, and delocalized π -electrons. The rules for determining the molecule segment structure, numbers of remote bonds, and delocalized π -electrons are deduced (the remaining above-listed initial data are directly found from the molecule stereochemical formula). The accuracy and universality of the method are verified on the numerous examples.

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References and Notes

- (1) Dolgonosov, A. M. *Doklady* **1994**, 338, 760.
- (2) Avgul', N. N.; Kiselev, A. V.; Poshkus, D. P. *Gas and Vapor Adsorption on Uniform Surfaces*; Khimiya: Moscow, 1975. [All necessary information in English; see: Avgul', N. N.; Kiselev, A. V. In *Chemistry and Physics of Carbons*; Walker, P. L., Ed.; Dekker: New York, 1970; Vol. 6, p 1.]
- (3) Brunauer, S.; Emmett, P. H.; Teller, E. *J. Am. Chem. Soc.* **1938**, 60, 309.
- (4) Dashevskii, V. G. *Conformation Analysis of Organic Molecules*; Khimiya: Moscow, 1982. (van der Waals Radii, see: Bondi, A. *J. Phys. Chem.* **1964**, 68, 44.)
- (5) This condition is not suitable for all molecules. It breaks down, for example, for halogen derivatives of hydrocarbons: although a part of the valent electrons of halogens is not involved in the molecule bonds, their "volume" must be accounted for in calculating the generalized charge.
- (6) The case of a single atom and electron arranged on the molecule symmetry axis should separately be noted. Although electrons cannot be exchanged in this case, the π -electron becoming delocalized balances symmetrical bonds of the atom.
- (7) Grosberg, A. Yu.; Khokhlov, A. R. *Statistical Physics of Macromolecules*; Nauka: Moscow, 1989. (As analogous may be given: Doi, M., Edwards, S. F. *Theory of Polymer Dynamics*; Academic Press: New York, 1986.)
- (8) Kalashnikova, E. V.; Kiselev, A. V.; et al. *Chromatographia* **1971**, 4, 495.
- (9) Kalashnikova, E. V.; Kiselev, A. V.; et al. *Chromatographia* **1972**, 5, 278.
- (10) Kalashnikova, E. V.; Kiselev, A. V.; Shcherbakova, K. D. *Chromatographia* **1974**, 7, 22.
- (11) Makagon, A. M. Thesis, Chemistry Department, Moscow State University, Moscow, 1978.
- (12) Kalashnikova, E. V.; Kiselev, A. V.; Makagon, A. M. *Chromatographia* **1975**, 8, 399.