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ENERGY OF ADSORPTION OF HYDROCARBONS ON GRAPHITE

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Theoretical calculations of the energy of an adsorption bond can be checked experimentally by comparison with the heats of adsorption measured in a calorimeter. They are of important practical significance for understanding and solving questions that arise in adsorption chromatographic separation, in particular of mixtures of hydrocarbons. The simplest case is the adsorption of hydrocarbons on the surface of atomic lattices, for example on graphite.

Calorimetric measurements of the differential heats of adsorption of hydrocarbons on graphitized carbon blacks have been carried out in a few studies, namely in Biba' s laboratory ([1]) for 1-butene and n-butane and in our laboratory for n-pentane, n-hexane ([2]), n-heptane, and benzene ([3]). Therefore we have also made theoretical calculations of the energy of the adsorption bond for these and only a few other hydrocarbons. We attempted to elucidate the influence on the adsorption energy of the following factors: 1) lengthening of the carbon chain of n-alkanes; 2) branching of the chain in isoalkanes; 3) closure of the chain into naphthene rings; 4) a double bond; and 5) an aromatic ring. The calculations were made for the following hydrocarbons: n-butane–1-butene; n-pentane–neopentane–cyclopentane–1-pentene; n-hexane–1-hexene–benzene; n-heptane.

1. Methods of calculating the energy of the adsorption bond. We used the method for calculating the adsorption energy of complex molecules, applied in ([2]) for n-alkanes on the basal plane of graphite. In such a calculation the hydrocarbon molecule is divided into units, and the interaction energy of each unit with all atoms of the lattice in various mutual positions at the equilibrium distances r_0 is found. Summation over the units when they are equivalent (for example, the CH_2 groups in n-alkanes and in cyclopentane) is facilitated by the additive properties of the polarizability and diamagnetic susceptibility of hydrocarbons. The interaction of a given unit with the entire lattice is taken into account by summation over the 100 nearest lattice atoms, as in ([4]), and by integration over the remaining volume of the crystal ([2]):

$$\Phi = -C\left[\sum\left(\frac{1}{r^6} - \frac{r_0^6}{2r^{12}}\right) + \frac{\pi\nu}{6(r')^3}\right] = -Cf(r, r_0). \qquad (1)$$

The attraction constant is calculated for dispersion interactions by the quantum-mechanical Kirkwood formula

$$C = -6mc^2 \frac{\alpha_1 \alpha}{\alpha_1/\chi_1 + \alpha/\chi}, \tag{2}$$

where m is the electron mass, c is the speed of light, and α_1, χ_1 and α, χ are the polarizabilities and diamagnetic susceptibilities of the interacting centers.*

* Calculation of the constant C by the London formula using α and the ionization potential gives worse results, in accordance with the cruder approximation made in deriving that formula.

The quantity r in (1) represents the distance between interacting particles; the quantity r_0 is taken to be equal to the sum of half the interplanar distance in the graphite lattice, 1.70 Å, and the van der Waals radius of the molecular unit (for example, in the case of flat-oriented molecules of n-alkanes, 2.0 Å, and of the benzene molecule, 1.85 Å ([5])). Integration is carried out from $r' = 8.5$ Å, with ν being the number of carbon atoms in 1 cm^3 of graphite; this last term amounts to only about 4% of the total value of $f(r, r_0)$. The calculation performed in ([2]) showed that when r is changed by 0.05 Å (the possible error in the value of r_0), Φ changes by approximately 5%. Hydrocarbon molecules on the graphite surface at ordinary temperatures form mobile layers; therefore, in the calculations the values of Φ adopted are averages for different positions of the molecular units relative to the lattice atoms.

The properties of the units of the adsorbate molecule are reflected in the values of r_0 and C. For adsorption on the basal plane of the graphite lattice ($\alpha_1 = 0.937 \cdot 10^{-24}$ cm^3 and $\chi_1 = 10.54 \cdot 10^{-30}$ cm^3 ([4])

$$C = -6.58 \cdot 10^{-17} \frac{\alpha}{\alpha/\chi - 0.888 \cdot 10^5} \frac{\text{kcal} \cdot \text{cm}^6}{\text{mol}}, \tag{3}$$

where α and χ are the polarizability and diamagnetic susceptibility of the hydrocarbon or of its unit. For hydrocarbons of complex structure, the interaction energy is calculated by summation over the units

$$\Phi = \sum_i \Phi_i = \sum_i C_i f(r, r_{0i}). \tag{4}$$

2. Adsorption energy of n-alkanes and the effect of chain lengthening. This problem was solved in the form of a linear dependence of Φ on the number of carbon atoms in the molecule n ([2])

$$-\Phi = [2C_{\text{CH3}} + (n-2)C_{\text{CH2}}] f(r, r_0 = 3.7 \text{ Å}) =$$

$$= [2(C_{CH3} - C_{CH2}) + nC_{CH2}]f(r, r_0 = 3.7\ \text{Å}) = 0.9 + 1.85n\ \text{kcal/mol}. \quad (5)$$

3. Adsorption energy of isoalkane. Here the main factor is the displacement of part of the molecular units away from the surface of the adsorbent. We performed a calculation for the symmetric molecule neopentane. For three CH_3 groups $r_0 = 3.7$ Å, as for n-alkanes*, whereas for the quaternary carbon atom and especially for the fourth CH_3 group, r_0 is larger. For each r_0, the value of $f(r, r_0)$ was calculated. Proceeding from the additivity of α and χ, we divided the neopentane molecule into these units and, for each of them, determined the value of the constant C_i and Φ_i. Owing to the increase in r_0, the energy for some of the units is considerably smaller than for n-alkanes, which makes it possible to carry out their chromatographic separation on carbons.

4. Adsorption energy of cyclopentane. This molecule is planar and is oriented parallel to the surface of the adsorbent; therefore all 5 CH_2 groups are equivalent, and r_0 for them is the same and equal to 3.7 Å. The adsorption energy of cyclopentane is less than that of n-pentane, but considerably greater than that of neopentane.

5. Adsorption energy of α-monoolefins. In this case, with $r_0 = 3.7$ Å for the saturated part of the molecule and $r_0 = 3.6$ Å at the double bond, the calculation gives values somewhat smaller than for the corresponding n-alkanes. The dependence on n is given by the equation

$$-\Phi = 0.1 + 1.85n\ \text{kcal/mol}. \quad (6)$$

6. Adsorption energy of benzene. In this case $r_0 = 3.55$ Å; however, smaller average values of α and χ lead to the fact that the adsorption energy—

* The value of r_0 here may be somewhat different than for n-alkanes.

the adsorption of benzene on graphite is less than that of an n-alkane that also contains 6 carbon atoms in the molecule. Therefore, for the separation of aromatic and unsaturated hydrocarbons it is not expedient to use graphite bodies. One should use the ability of these hydrocarbons to form π-complexes with protonic acids, i.e., use acidic adsorbents (silica gels, aluminosilicagels) [6], which in fact give a good separation of these hydrocarbons.

7. Possible errors and necessary refinements. The repulsion constant was calculated from the condition of a minimum in the interaction potential with one atom of the adsorbent. Taking into account the interaction with the entire lattice increases it and somewhat lowers Φ. In the calculation only the dipole-dipole term in the attraction potential of nonpolar van der Waals forces was included, and the quadrupole-dipole and quadrupole-quadrupole terms were not taken into account—$\frac{D}{r^8}$ and $\frac{\varepsilon}{r^{10}}$. The latter term may be neglected for

$r_0 \geq 3.5$-3.7 Å. A calculation of the quadrupole-dipole term for the interaction of two CH_4 molecules at $r = r_0$ shows that it amounts to 20% of the dipole-dipole term [7]. Taking the interaction with the lattice into account considerably reduces the contribution of this term to the total adsorption energy*. More accurate calculations are needed here.

In the calculations presented, we used average values of the polarizabilities and magnetic susceptibilities, since the effect of additivity of the nonpolar van der Waals forces considerably exceeds the effect of anisotropy [8]. If, for benzene, which possesses a strong anisotropy of these properties, one takes the values of α and χ in the direction perpendicular to the plane of the ring ($6.35 \cdot 10^{-24}$ cm^3 and $189 \cdot 10^{-30}$ cm^3), then one obtains the value $C = 3.42 \cdot 10^{-45}$ kcal $\cdot$ cm^6/mol, close to the value calculated from the average values of α and χ, since changes in α and χ compensate each other. This question requires further study.

Next, the adsorption energy on the prismatic plane should be taken into account. The arrangement of carbon atoms on this plane is much more sparse. We made an approximate calculation of $f(r, r_0)$ for the case of adsorption on the prismatic plane at $r_0 = 3.7$ Å, the summation being carried out over the 65 nearest carbon atoms in a volume located at distances up to 9 Å, while the atoms located farther away were taken into account by integration. The value of $f(r, r_0)$ was $1.6 \cdot 10^{45}$ cm^{-6}, which is 40% smaller than the corresponding value for the basal plane; however, if the anisotropy of α_1 and χ_1 for graphite is taken into account, then for the prismatic plane one obtains a considerably larger value of the constant C than for the basal plane, which leads to a value of Φ close to that obtained for the basal plane.

8. Comparison of the calculated values of the energy of adsorption interactions with heats of adsorption. When comparing the energy of molecular interactions with thermodynamic quantities, a number of difficulties arise. For calculating equilibria, one interaction energy is insufficient—a molecular-statistical treatment is required. Therefore the molecular potential, in particular the adsorption potential, cannot be compared directly with the free energy of the process [9]. Comparison with the total energy, i.e., with the heat of adsorption, is possible, but with two reservations. First, the calculations of adsorption interactions presented refer to elementary acts, whereas the heat of adsorption, even the differential heat, is a macroscopic quantity. However, experiments show that, over a considerable interval of surface coverage of graphitized soot, the differential heat of adsorption practically does not change, and the adsorption isotherm is well described by the Langmuir equation [2]. This testifies to the homogeneity of the surface of graphitized soots and permits

* For adsorption on graphite, the magnitude of this term is considerably smaller than the magnitude of the repulsive term and does not compensate it, as was assumed in [8].

in the region of not very large coverages, to accept the equivalence of the elementary acts. Secondly, it must be assumed that the energy of the adsorption bond

does not depend on temperature; in the case of adsorption of hydrocarbons on graphite this is approximately justified. Further investigations are also needed here.

Table 1

Comparison of the calculated values of the adsorption energy $-\Phi$ of various hydrocarbons on the basal plane of graphite and the values of the differential heats of adsorption Q_a on graphitized carbon blacks

Hydrocarbons	r_0, Å	$f(r, r_0)\cdot 10^{-45}$ cm^{-6}	$\alpha \cdot 10^{24}$ cm^3	$\chi \cdot 10^{30}$ cm^3	$C \cdot 10^{45}$ $\frac{\text{kcal}\cdot\text{cm}^6}{\text{mol}}$	$-\Phi$ $\frac{\text{kcal}}{\text{mol}}$	Q_a $\frac{\text{kcal}}{\text{mol}}$
n-Butane	3.7	2.86	8.12	85.2	2.9	8.3	8.6
1-Butene	3.7; 3.6	2.98	7.8	68.0	2.51	7.5	8.2
n-Pentane	3.7	2.86	9.95	104.1	3.54	10.1	10.0*
Neopentane: $3CH_3$	3.7	2.86	6.78	71.0	2.41	6.9	–
Neopentane: C	4.2	1.75	0.961	12.3	0.379	0.66	–
Neopentane: CH_3	5.7	0.59	2.26	23.8	0.809	0.48	–
Cyclopentane	3.7	2.86	9.10	94.7	3.24	9.3	–
1-Pentene	3.7; 3.6	2.94	9.75	86.8	3.19	9.3	–
n-Hexane	3.7	2.86	11.78	123.0	4.19	12.0	11.9
1-Hexene	3.7; 3.6	2.92	11.55	106.0	3.84	11.2	–
Benzene	3.55	3.20	10.32	92.0	3.37	10.8	10.0
n-Heptane	3.7	2.86	13.61	141.9	4.84	13.8	13.4*

* The heat of adsorption of vapors of *n*-pentane and *n*-heptane was measured, as in (2), by G. I. Berezina and I. A. Lygina jointly with the authors of this work.

Table 1 compares the results of calculations of the energy of the adsorption bond and the values of the differential heats of adsorption on graphitized carbon blacks.

It is seen from Table 1 that the theoretical calculation gives not only the correct qualitative regularities in passing from some hydrocarbons to others, but

also good quantitative agreement with the measured differential heats of adsorption. Thus, the energy of the adsorption bond of hydrocarbons with graphite is satisfactorily described by the theoretical calculation made.

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Note: Figure translations are in progress. See original paper for figures.