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Application of Kinetic Investigations for Interpretation of *n*-Hexane and Benzene Adsorption on Active Carbon

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Differencies between the mechanism of *n*-hexane and benzene adsorption on active carbon were investigated on the ground of kinetic measurements. As it has been stated, the kinetic measurements show fundamental differencies between the mechanism of adsorption in spite of analogy existing in the state of adsorption equilibrium. Within the range investigated, only the adsorption of *n*-hexane follows the model of volume filling of micropores. Existence of those differencies is also confirmed by measurements of effective diffusion coefficient values as well as changes of activation energy of the diffusion—adsorption process.

(Keywords: Adsorption; Diffusion, carbon adsorbents; Kinetic adsorption)

Anwendung kinetischer Untersuchungen zur Interpretation des Adsorptionsverhaltens von n-Hexan und Benzol an Aktivkohle

Mittels kinetischer Messungen untersuchte man die Unterschiede im Mechanismus des Adsorptionsverlaufes von *n*-Hexan und Benzol an Aktivkohle. Man stellte fest, daß trotz der Analogie im Adsorptionsgleichgewichtszustand die kinetischen Messungen auf prinzipielle Unterschiede im Adsorptionsmechanismus hinweisen. Im untersuchten Bereich verläuft nur die Adsorption von *n*-Hexane nach dem Modell der Mikroporenvolumenausfüllung. Die auftretenden Unterschiede wurden auch durch die Berechnungen der Werte der effektiven Diffusionskoeffizienten sowie Änderungen der Aktivierungsenergie des Diffusions-Adsorptionsprozesses bestätigt.

Introduction

Almost complete absence of systematic kinetic studies on porous adsorbents is observed in the literature till today. Existing papers[1–6] are mostly fragmentaric and they are giving relatively scarce explanations for the mechanism of adsorption. The general rate of adsorption is decided by the slowest stage of the sorption process. This stage is the transport of adsorbate molecules into adsorbent pores. Then follows the diffusion mechanism. Kinetic measurements should give a more complete description of the adsorption process.

In this paper we apply kinetic measurements for the interpretation of the mechanism of adsorption on active carbon taking *n*-hexane and benzene as examples.

Experimental

The measurements were made on active carbon E prepared from chemically pure saccharose by the so-called chemical activation method using $ZnCl_2$ as the activator [$\alpha = 2$]. The detailed preparation of carbon E and its texture parameters are given in previous papers[7, 8]. The adsorption measurements for chromatographically pure *n*-hexane and benzene were made with an electronic vacuum microbalance Sartorius 4410 coupled with an analogue-to-digital converter and a recording system. The temperature range was 298.2–323.2 K. The detailed method of the measurements is described in Ref.[9]. Examples of kinetic curves for different pressures of *n*-hexane and benzene are given in Ref.[10].

Examples of isochrones obtained from the kinetic curves (at constant T and τ) are presented in Figs. 1 and 2.

The measurement method used does not eleminate thermal effects of adsorption. However, according to papers[11–13] the lack of thermal equilibrium in the first stage of adsorption influences not the results of the kinetic measurements. The activation energy of the diffusion—adsorption process has been calculated[14] from the known diffusion coefficients[10] for given instantaneous degrees of filling of adsorbent at different temperatures.

Figs. 3 and 4 present the values of the activation energies in dependence on mean adsorption values and on assumed shapes of carbon samples.

In accordance with the absolute reaction rate theory, it is possible to calculate the entropy of the diffusion—adsorption process from the kinetic measurements of adsorption[14, 15] using the equation

$$D_e = D_0' \cdot e^{\Delta S^*/R} \cdot e^{-\Delta H^*/RT} \qquad (1)$$

where D_e is the effective diffusion coefficient, ΔS^* and ΔH^* are the activation entropy and enthalpy of the diffusion—adsorption process, and D_0' is a pre-exponential coefficient independent on temperature and calculated from the formula[14]

$$D_0' = \frac{\Delta^2 \cdot \nu}{C} \qquad (2)$$

where Δ is the mean free path of adsorbate molecules in the adsorbent, ν is the frequency of atomic vibrations in the crystal lattice of the porous solid, and C is a constant related to the number of possible directions for molecular transport in the given adsorbent.

The calculated changes in activation entropy for *n*-hexane and benzene as a function of both the adsorption value and the mean free path of adsorbate molecules are presented in Tables 1 and 2.

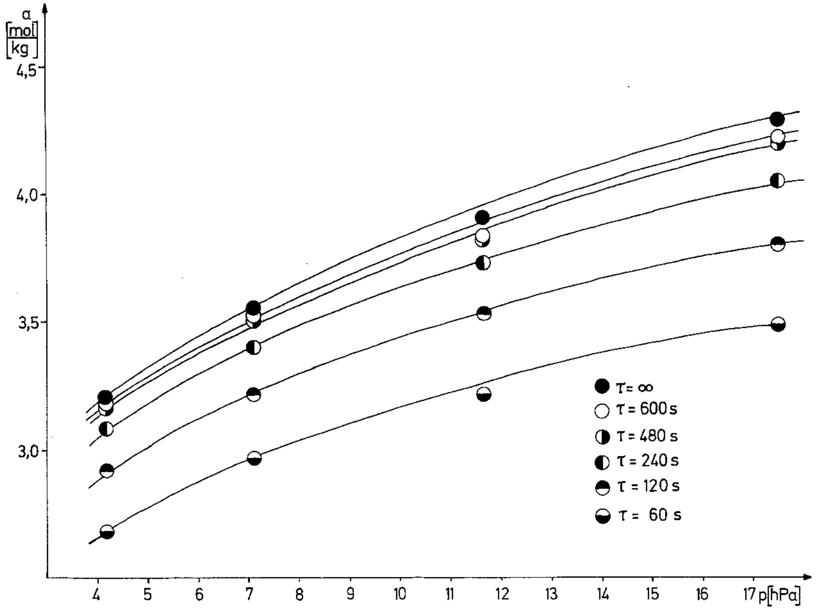

Fig. 1. Isochrones for *n*-hexane on active carbon at a temperature of 306.2 K

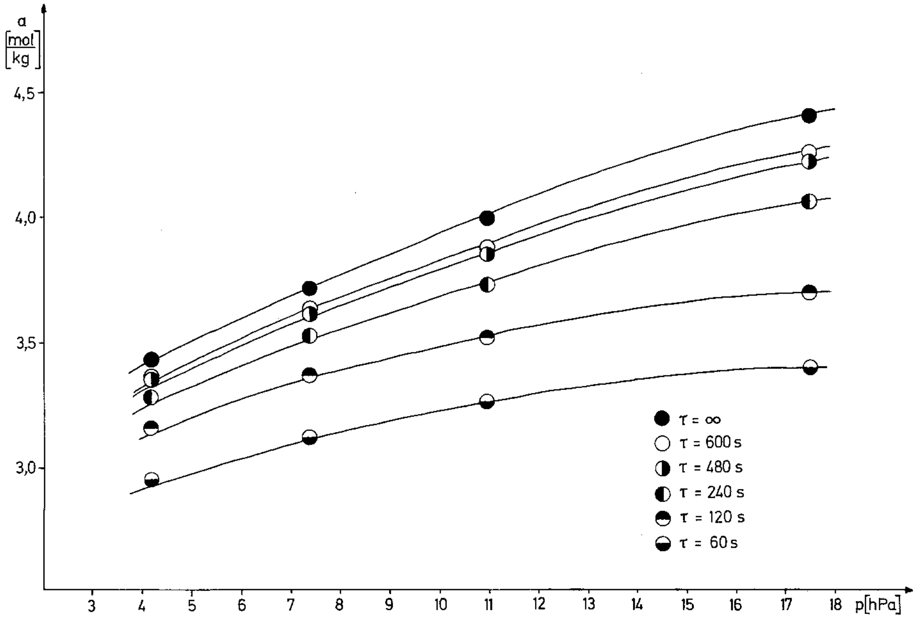

Fig. 2. Isochrones for benzene on active carbon at a temperature of 306.2 K

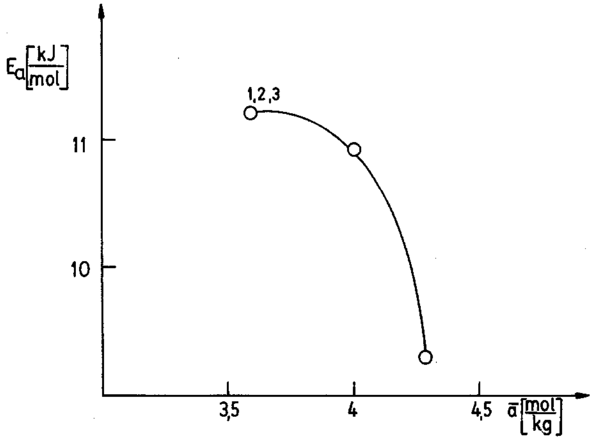

Fig. 3. Values of the activation energy of the diffusion-adsorption process for *n*-hexane on active carbon studied as a function of the mean adsorption value and assumed shape of adsorbent samples. *1* $L = R$; *2* $L = 2R$; *3* $L = 4R$

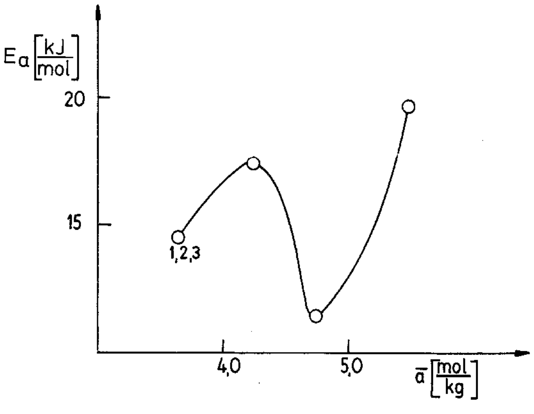

Fig. 4. Values of the activation energy of the diffusion-adsorption process for benzene on active carbon studied as a function of the mean adsorption value and assumed shape of adsorbent samples. *1* $L = R$; *2* $L = 2R$; *3* $L = 4R$

Results and Discussion

Assuming that every stage of the diffusion process reaches a quasi-equilibrium adsorption state, some kinetic data description with equations corresponding to the equilibrium adsorption state may be accepted. The obtained isochrones presented as examples in Figs. 1 and 2 are described in all cases by the *BET*[16] equation. Analysis of constant

Table 1. *Changes of values of activation entropy for n-hexane in dependence on the adsorption value a, adsorbent shape, and free path of adsorbate molecules*

a [mol/kg]	$-\Delta S_{L=R}$ [J/mol K]		$-\Delta S_{L=2R}$ [J/mol K]		$-\Delta S_{L=4R}$ [J/mol K]	
	$D'_{0\max}$	$D'_{0\min}$	$D'_{0\max}$	$D'_{0\min}$	$D'_{0\max}$	$D'_{0\min}$
3.595	38.47	29.76	37.85	29.14	35.20	26.49
3.600	38.94	30.23	38.32	29.61	35.76	26.96
3.630	37.96	29.25	37.34	28.62	34.69	25.98
3.680	39.45	30.74	38.83	30.12	36.18	27.47
3.940	40.43	31.71	39.81	31.09	37.16	28.44
3.990	39.45	30.74	38.83	30.12	36.18	28.47
4.018	39.54	30.83	38.91	30.20	36.27	27.65

$D'_{0\max} = 1869.33 \cdot 10^{-8}$.
$D'_{0\min} = 655.66 \cdot 10^{-8}$.

Table 2. *Changes of values of activation entropy for benzene in dependence on adsorption value a, adsorbent shape, and free path of adsorbate molecules*

a [mol/kg]	$-\Delta S_{L=R}$ [J/mol K]		$-\Delta S_{L=2R}$ [J/mol K]		$-\Delta S_{L=4R}$ [J/mol K]	
	$D'_{0\max}$	$D'_{0\min}$	$D'_{0\max}$	$D'_{0\min}$	$D'_{0\max}$	$D'_{0\min}$
3.770	34.58	29.84	32.83	28.09	31.36	26.62
3.800	29.41	24.67	28.75	24.01	26.10	21.36
3.870	29.07	24.33	28.48	23.74	25.83	21.09
4.200	23.80	19.06	23.17	18.44	20.51	15.77
4.280	28.09	23.35	27.46	22.72	24.77	20.03
4.365	30.38	25.64	30.97	25.01	27.11	22.37
4.438	31.57	26.84	30.97	26.23	28.30	23.56
4.938	42.74	38.00	42.09	37.35	39.43	34.69
4.990	41.53	36.79	40.93	36.19	38.25	35.51
5.070	40.09	35.35	39.42	34.68	36.78	32.04

$D'_{0\max} = 2013.11 \cdot 10^{-8}$.
$D'_{0\min} = 1138.56 \cdot 10^{-8}$.

values resulting from the *BET* model (Table 3) shows that a formal value of the constant $a_m[\tau]$ corresponding to the amount of adsorbate necessary for adsorbent covering by compact monolayer increases with the adsorption time τ.

For these cases, the value of constant C for benzene decreases what shows that adsorption of benzene molecules, as opposed to *n*-hexane, occurs in course of time on centers of lower and lower energy. It would be

Table 3. *Parameters from the BET equation characteristic for adsorption of n-hexane and benzene on active carbon E for proper isochrones*

T [K]	τ [s]	*n*-hexane C_i[a]	*n*-hexane a_{mi}[b] [mol/kg]	benzene C_i[a]	benzene a_{mi}[b] [mol/kg]
298.2	60	128.71	3.700	202.14	3.534
298.2	120	131.21	4.012	115.26	4.566
298.2	240	245.50	4.073	65.14	5.482
298.2	480	269.10	4.129	51.81	6.031
298.2	600	269.10	4.129	57.28	6.020
298.2	∞	150.03	4.761	51.83	6.653
306.2	60	164.67	3.572	151.46	3.668
306.2	120	127.10	3.934	73.56	4.668
306.2	240	133.80	4.152	55.93	5.418
306.2	480	137.61	4.275	50.04	5.887
306.2	600	137.61	4.275	62.02	5.759
306.2	∞	266.25	4.195	56.31	6.124
314.2	60	216.52	3.299	153.04	3.439
314.2	120	235.74	3.535	89.68	4.289
314.2	240	166.47	4.029	69.97	4.929
314.2	480	191.84	4.030	73.00	5.074
314.2	600	191.84	4.030	68.46	5.217
314.2	∞	198.63	4.173	62.30	5.535
323.2	60	488.80	2.923	170.15	3.265
323.2	120	394.70	3.167	75.79	4.265
323.2	240	291.70	3.428	56.59	4.912
323.2	480	479.47	3.476	52.59	5.139
323.2	600	479.47	3.476	45.32	5.516
323.2	∞	185.16	4.154	47.68	5.668

[a] Constant C from the *BET* equation corresponding to the defined time of adsorption τ.

[b] Quantity of adsorbate to cover the adsorbent with a monomolecular layer corresponding to the defined time of adsorption τ.

assumed that the difference is caused by the specific interactions between benzene and the surface of active carbon [bonding of type π]. A different course of adsorption for both adsorbates is proved also by the fact that only the benzene adsorption satisfies theoretical assumptions of the *Langmuir* model[16]. One may therefore conclude that benzene is adsorbed on carbon in a monomolecular layer while *n*-hexane builds a multilayer already in the initial stage of adsorption. An additional

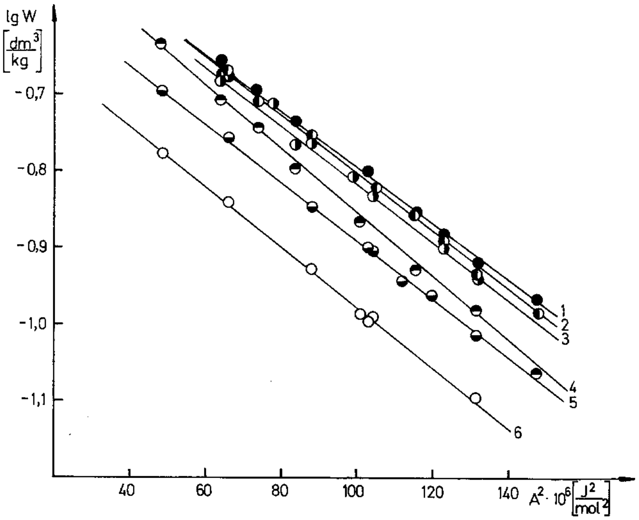

Fig. 5. Isochrones for the sorption of n-hexane in coordinates from the *Dubinin-Radushkevich* equation. *1* $\tau = \infty$; *2* $\tau = 600$s; *3* $\tau = 480$s; *4* $\tau = 240$s; *5* $\tau = 120$s; *6* $\tau = 60$s

confirmation for the differencies results from application of the *Polanyi-Dubinin* potential theory[17, 18].

The fundamental condition for the *Polanyi-Dubinin* potential theory is the temperature independence of the characteristic curve $A = f(W)$ described by equation:

$$\left(\frac{\partial A}{\partial T}\right)_W = 0 \tag{3}$$

where A is the differential molar work of adsorption; and W is the volume of adsorption space.

In the cases studied, the kinetic characteristic curves for different τ are independent on temperature only for n-hexane (Fig. 5) and they are described by the general *Dubinin-Radushkevich* equation (*DR*) in the form:

$$\Theta = \frac{W}{W_0} = \exp\left[-(A/\beta E_0)^2\right] \tag{4}$$

where Θ is the degree of filling of micropores, W_0 is the limit volume of adsorption space equal to the volume of micropores in adsorbent, E_0 is the characteristic energy of adsorption, and β is the affinity coefficient of characteristic curves.

The obtained pressure isochrones for n-hexane adsorption according to the *DR* equation are presented in Fig. 5.

Corresponding values for parameters resulting from the *DR* equation are given in Table 4.

The obtained kinetic results confirm that only *n*-hexane is adsorbed following a mechanism according to the theory of volume filling of micropores[19]. Gradual filling of the adsorption space in active carbon is proved by the values of constant W_0 (Table 4) increasing with adsorption time. It may be assumed that during the *n*-hexane adsorption process the filling of micropores occurs initially in the most easyly accessible ones and next in pores which are filled as a result of diffusion inside the porous structure of adsorbent. It is confirmed by the highest value of E_0 for the isochrones at $\tau = \infty$, corresponding to isotherms in the equilibrium state. The differencies in the adsorption mode are the result of different structure of the adsorbates (*n*-hexane is linear in contrast to benzene) and of specific interactions between benzene and the active carbon surface (π-type bonding).

Table 4. *Parameters from the D–R equation characteristic for the adsorption of n-hexane on active carbon E for proper isochrones*

τ [s]	E_0 [kJ/mol]	W_0 [dm^3/kg]
60	12.29	0.558
120	12.54	0.601
240	12.35	0.637
480	12.62	0.644
600	12.55	0.655
∞	12.84	0.675

The differencies in the mechanism of *n*-hexane and benzene adsorption are also confirmed by the differencies in the values of the effective diffusion coefficients D_e in dependence on the instantaneous degree of adsorbent filling (Figs. 6 and 7).

In the case of *n*-hexane the value D_e possesses a clear maximum (Fig. 6) independent on temperature and on the assumed shape of adsorbent. The D_e value for *n*-hexane is determined in the initial stage of adsorption by the pressure of the gas phase. After the maximum D_e is probably determined by the interaction adsorbate—adsorbent. For benzene the D_e value shows a constant decrease within the whole range studied (Fig. 7). This shows that the value of the effective diffusion coefficient depends mainly on interactions adsorbate—adsorbent (depending in turn on the texture of active carbon used). Indirect

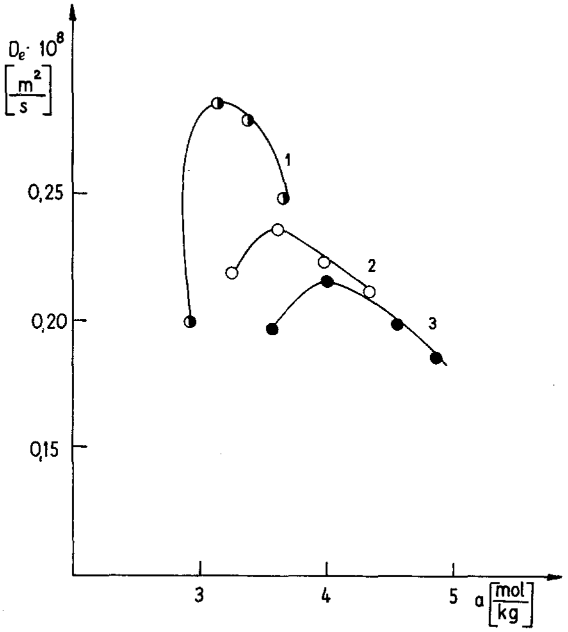

Fig. 6. Values of the effective diffusion coefficient D_e at different temperatures as a function of the *n*-hexane adsorption value. *1* $T = 323.2$ K; *2* $T = 306.2$ K; *3* $T = 298.2$ K

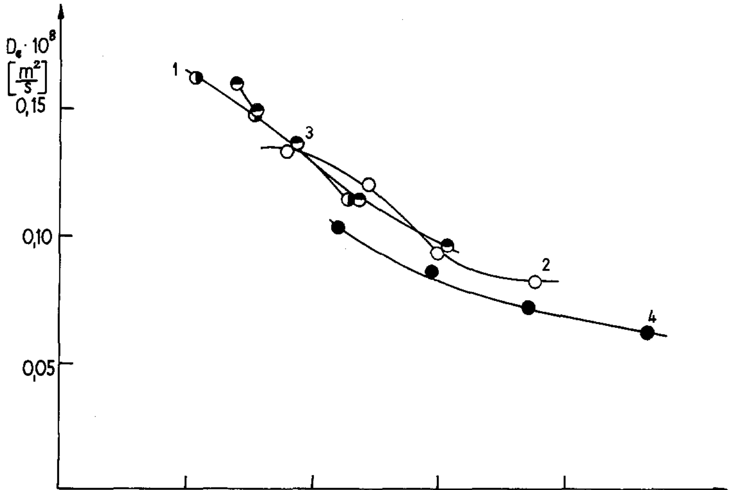

Fig. 7. Values of the effective diffusion coefficient D_e at different temperatures as a function of the benzene adsorption value. *1* $T = 323.2$ K; *2* $T = 306.2$ K; *3* $T = 314.2$ K; *4* $T = 298.2$ K

confirmation of the clear influence of the pressure on D_e for n-hexane is the constant parameter n in the formula[20]

$$\tau_{0.5} = k \cdot p^{-n} \qquad (5)$$

where k, n are constants characteristic for a given system adsorbate—adsorbent, giving the dependence between adsorption half-time and pressure at the constant mean value of adsorption. A similar dependence was observed by *Sedlacek*[20] who studied the adsorption of n-hexane on carbon of the supersorbon type.

The curves characterizing the dependence of changes of the activation energy of the diffusion—adsorption process[15] and the mean value of adsorption of adsorbates (Figs. 3 and 4) show also a different shape. During the n-hexane adsorption a constant decrease is observed (Fig. 3), while for benzene it shows a clear maximum and minimum (Fig. 4). Since the observed course is similar to changes of the isosteric adsorption heat for adsorbates[21], it may be concluded that the activation energy of the diffusion—adsorption process is connected with the heat of adsorption[22]. Changes of the activation entropy of the diffusion—adsorption process in dependence on the adsorption value are given in Tables 1 and 2. These parametres have negative values independent on the adsorbate used. Therefore, for n-hexane and benzene the adsorbate molecules can pass from one type of pores to another[22, 9]. In both cases of n-hexane (Table 1) and benzene (Table 2), the values of entropy of the diffusion—adsorption process increase with a change of the geometric shape of adsorbent samples in the direction from sphere ($L = R$) to cylinder ($L = 4R$).

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