

UNCERTAINTY OF ADSORPTION ISOTHERMS OF n-HEXANE ON ACTIVE CHARCOAL IN THE REGION OF SMALL PRESSURES AND ITS INFLUENCE ON CALCULATIONS OF HEATS OF ADSORPTION

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Adsorption isotherms of n-hexane were measured on active charcoal Supersorbon — Hrušov (SSHR) at 22°, 28°, 36°, and 44°C. From the measured values the dependence of the isosteric heat of adsorption and of the integral molar heat of adsorption on the adsorbed amount were calculated. The dependence of the isosteric heat of adsorption on the adsorbed amount exhibits two maxima. The adsorption isotherms show an "anomalous" course in the region of pressures below 10^{-3} Torr. The results indicate that this anomaly might be explained either by the presence of traces of inert gases or by a chemical instability of the adsorbate under the experimental conditions of this study.

In studying physical adsorption of gases on solid substances, the integral molar heat of adsorption is one of the basic quantities necessary for characterizing the state of the adsorbate in the adsorbed layer. The integral molar heat of adsorption was calculated from the measured adsorption isotherms by the usual method, *i.e.* first the dependence of the isosteric heats on the adsorbed amount was calculated, and from it the dependence of the integral heats of adsorption on the adsorbed amount was evaluated. However, it was found that both these dependences could be but poorly determined for low pressures (below 10^{-3} Torr): the values of the calculated heats depended on the particular pair of isotherms that were used in the calculations. The difficulties could not be accounted for by experimental errors in the measurements, as the adsorption isotherms were measured with a sufficient accuracy, and the course of the onsets of isotherms of several other adsorption systems was similarly uncertain. In the concluding discussion of this paper, two possible explanations of this uncertainty are given: the presence of traces of inert gases or a chemical instability of the adsorbate.

The integral molar heat of adsorption in an adsorption system consisting of an inert adsorbent and a single-component chemically stable adsorbate (which exhibits ideal behaviour in the gas phase) can be calculated from the following relations

$$(u_A)_a = 1/a \int_0^a q_{st}(a) da + RT, \quad (1)$$

$$q_{st} = -RT^2(\partial \ln p / \partial T)_a, \quad (2)$$

where q_{st} is the isosteric heat of adsorption, R is the gas constant, a is the adsorbed amount at a temperature T and an equilibrium pressure p . It is assumed in this calculation that the isosteric heat of adsorption is independent of temperature over the studied temperature region. The integral molar heat of adsorption can be also calculated from the relation

$$(u_\lambda)_a = q_\varphi + RT - (\Phi/a), \quad (3)$$

where

$$q_\varphi = -RT^2(\partial \ln p / \partial T)_\varphi \quad (4)$$

and the spreading pressure

$$\Phi = RT \int_0^p a(p) d \ln p. \quad (5)$$

It follows from equations (1) and (3)

$$q_\varphi = 1/a \int_0^a q_{st}(a) da + (\Phi/a). \quad (6)$$

EXPERIMENTAL

Active charcoal of the type SSHR (granulation 0.4–0.6 mm) was used as the adsorbent; thus, the sample was the same as that one in the previous study¹. The adsorbate, n-hexane, was prepared from propylbromide and sodium. The product of the reaction was rectified and the fraction of 99.95% purity (as determined by a gas chromatograph) was used in the measurements. Dissolved gases were removed from the sample of n-hexane by multiple condensation and evacuation at the liquid nitrogen temperature. The sample of n-hexane thus prepared was introduced into a reservoir of the evacuated apparatus over a thoroughly degassed molecular sieve (type 4 A). Within the adsorption apparatus, the sample of n-hexane was again several times condensed or solidified and evacuated using either a liquid nitrogen bath or a carbon dioxide-ethanol bath. The apparatus and the way the measurements were carried out were described essentially in our preceding communication¹. Only the procedure of introducing doses of the adsorbate has to be added here. The dosing of the adsorbate into the apparatus was carried out by means of a mercury float valve. Before opening the valve completely, the mercury level in the U-shaped tube of the valve was lowered to such an extent only that the level difference in both arms of the U-tube — with the valve closed — showed the adsorbate pressure difference in the reservoir and in the balance compartment. Temperature of the adsorbate in the reservoir was then adjusted to such a value that the vapour pressure of the adsorbate in the reservoir was slightly higher than the equilibrium pressure of the adsorbate in the balance compartment. Thereafter, the valve was completely opened by further lowering the mercury level. By gradually increasing the temperature of the adsorbate, its vapour pressure increased until a required value was reached. The temperature of the liquid adsorbate in the reservoir was then maintained by a thermostat at a given value for a time interval sufficient for the adsorption to proceed up to the equilibrium. Only then the mercury valve was closed. This procedure ensured that the adsorption process was conducted in an equilibrium manner.

RESULTS AND DISCUSSION

Four adsorption isotherms of n-hexane on the active charcoal SSHR at 20°, 28°, 36°, and 44°C were measured. The results are summarized in Fig. 1. The region of low pressures (between 10^{-5} and 10^{-1} Torr) was measured more in detail. In this region the dependence of the adsorption on the equilibrium pressure is very steep. Therefore, the dependence $a-\log p$ was chosen to plot these isotherms. It is evident from Fig. 2 that the course of the isotherms in the pressure region below 10^{-3} Torr is quite irregular and differs from the course of the dependence at higher pressures (which is similar for various isotherms).

The course of the dependence $a-p$ in the initial part of the adsorption isotherm has a substantial influence on the values of the integral molar heats of adsorption as calculated with the use of either equations (1) and (2) or (3) to (6). Therefore, reasons of the irregularities in the course of the isotherms in Fig. 2 were investigated more in detail. The initial parts of the isotherms (up to 10^{-2} Torr) were measured several times. The results of the repeated measurements of this part of the isotherm of n-hexane on the active charcoal SSHR at 20°C are given in Fig. 3. First, the curve A was measured. When the adsorption corresponding to the eight point of the curve was reached, the adsorption apparatus and the adsorbent sample were evacuated by a diffusion pump coupled with a liquid nitrogen cooled trap. After a minimum pressure was reached, the sample of the adsorbent was heated to 380°C and evacuated at this temperature for 20 hours to 10^{-6} Torr. Then the isotherm B was measured. By repeating the procedure described above the isotherm C was obtained. During each evacuation of the apparatus, when the minimum pressure was reached (smaller than 10^{-5} Torr), the sample of n-hexane was twice frozen and evacuated.

After the complete isotherm C was measured, the adsorption apparatus was filled with air (with the exception of the n-hexane reservoir). The apparatus was then

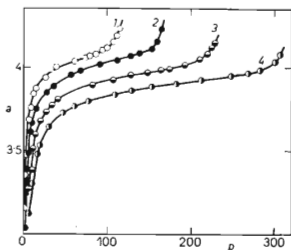


FIG. 1

Adsorption Isotherms of n-Hexane on Active Charcoal SSHR

1 20°, 2 28°, 3 36°, 4 44°C; pressure p in Torr, adsorbed amount a in mmol g^{-1} .

evacuated for 8 days. The initial part of the isotherm *D* was measured. After that, evacuation was repeated in the same way as between the measurement of the isotherms *A* and *B*. Then the isotherm *E* was measured.

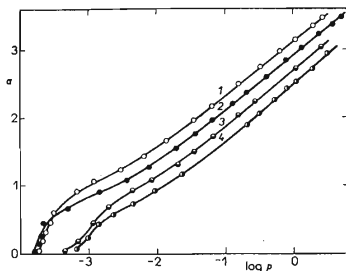


FIG. 2

Adsorption Isotherms of *n*-Hexane on Active Charcoal SSHR

1 — 20°, 2 — 28°, 3 — 36°, 4 — 44°C; pressure *p* in Torr, adsorbed amount *a* in mmol g⁻¹.

It is evident from Fig. 3 that achieving reproducibility in measuring the isotherms in the region of low pressures is difficult and that an explanation of reasons of the “anomalous” course would not be simple. The isotherms shown in Fig. 1 and Fig. 2 were measured successively at 20°, 28°, 36°, and 44°C. In each case evacuation was carried out in the same way as between the isotherms *A* and *B* in Fig. 3.

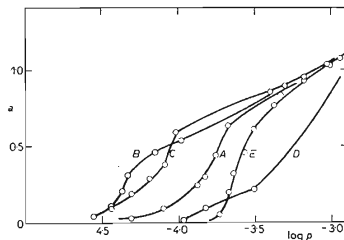


FIG. 3

Initial Parts of Adsorption Isotherms Measured at 20°C

Pressure *p* in Torr, adsorbed amount *a* in mmol g⁻¹; for meaning of symbols denoting the curves see text.

The course of the initial part of the isotherms in Fig. 3 corresponds to the stepwise isotherm as reported often in the literature. However, it follows from our experiments that those dependences that were measured later (with respect to the beginning of the whole experiment) started to rise gradually at lower and lower pressures, and that the almost vertical part of the isotherm curve became gradually lower and lower. Therefore, the reasons reported often to lead to stepwise isotherms, *i.e.* two-dimensional condensation, preferential adsorption on those homogeneous parts of the surface that are energetically more convenient, cannot be accepted in this case. The course of the initial parts of the isotherms as reported here rather indicates the presence of inert gases or a chemical instability of the adsorbate under the given experimental conditions.

In a system in which adsorption is studied, traces of inert gas are always present: it may be occluded on the walls of the apparatus, adsorbed on the adsorbent, dissolved in grease, or even dissolved in the adsorbate itself. The term "inert gas" means in this case any other adsorbate, except n-hexane, present in the adsorption apparatus.

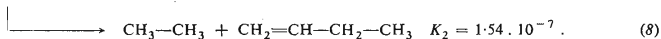
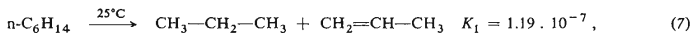
If the pressure of the adsorbate is gradually increased, this inert gas may be evolved into the gas phase and thus it may increase the total equilibrium pressure measured. It is understandable that this effect can play a role only at low pressures. Therefore, the equilibrium pressure would depend on conditions of the exchange adsorption and on the amount of inert gases present in the system. By repeated adsorption and by repeated evacuation the amount of inert gases in the system decreases and this may cause shortening of the steep part of the isotherm and its shifting towards the region of lower pressures.

The course of the adsorption isotherms *D* and *E* (Fig. 3) shows that the presence of traces of inert gases has a profound influence on the position and on the shape of the isotherms in the region of very low pressures (these isotherms were measured after air was introduced into the apparatus and over the sample of the adsorbent, and the equipment was then evacuated for a time interval as long as the sum of the time intervals of evacuation when the isotherms *A*, *B* and *C* were measured). A long-lasting evacuation itself is not sufficient to ensure obtaining of reproducible data on the adsorption isotherms.

Another possible reason of inaccuracies in the measurement of the initial parts of these isotherms is a chemical instability of the adsorbate. In case of linear paraffinic hydrocarbons, thermal decomposition takes place at 400–800°C and at the atmospheric pressure. The mechanism of this decomposition is very complex: first, longer molecules of paraffins split to form shorter molecules and olefins, and the primary products of decomposition desintegrate further. It can be said unambiguously about the thermal decomposition of n-paraffins that the changes of the mol number of decomposition reactions are positive, *i.e.* that during these processes the total pressure of the gaseous mixture increases. The mechanism of the thermal decomposition of n-hexadecane catalyzed by active charcoal at 500°C and 1 atm pressure was

described². The equations describing the decomposition show that an increase in decomposition of n-paraffins occurs both with increasing the temperature and by decreasing the pressure. If we apply the mechanism of the thermal decomposition of n-paraffins to the adsorbate n-hexane, studied by ours, at 25°C (at this temperature the apparatus was maintained when isotherms at 20°C were measured) and in the region of low pressures, the total equilibrium pressure of the gaseous mixture can be calculated as well as its composition can be determined, assuming the decomposition reactions are sufficiently catalyzed.

According to the mechanism of decomposition of n-paraffins on active charcoal², two most important decomposition reactions may be written that would split n-hexane:



The equilibrium constants were obtained from tabulated values³ of $(\Delta G_f^0)_{298,15}$. Equations (7) and (8) can be solved simultaneously as a competing chemical equilibrium assuming that the apparatus contained a constant pressure of saturated mercury vapours ($1.55 \cdot 10^{-3}$ Torr; the apparatus contained mercury at 25°C in the U-manometer, in the McLeod manometer, and in the mercury float valve). It was found that the equilibrium partial pressure of n-hexane in the equilibrium gaseous mixture is always lower, for example for the equilibrium pressure of the gaseous mixture (as measured by the McLeod manometer) 10^{-4} , 10^{-3} , 10^{-2} , 10^{-1} , the partial pressure of n-hexane in the gaseous mixture was $0.071 \cdot 10^{-4}$, $0.28 \cdot 10^{-3}$, $0.65 \cdot 10^{-2}$, $0.88 \cdot 10^{-1}$ Torr, respectively. As can be seen from these values, the chemical equilibrium indicates a possible decomposition. Kinetics of the decomposition reactions remains a question. However, as active charcoal acts as a catalyst in splitting n-paraffins², the assumption of formation of decomposition products less adsorbable than n-hexane (which then participate in increasing the total equilibrium pressure measured) is very probable.

Uncertainty in determining the isotherms in the region of pressures smaller than 10^{-2} Torr substantially influences calculated values of the integral molar heats of adsorption in the entire region of pressures studied. Fig. 5 summarizes dependences of the integral molar heat of adsorption obtained in the following way:

The dependence of the isosteric heat on the adsorbed amount was determined from the integrated form of equation (2) (Fig. 4). It can be seen from this figure that starting from the adsorbed amount about 1.6 mmol g^{-1} (equilibrium pressure about 10^{-2} Torr) the three curves shown merge together. The curve A corresponds to the dependence of the isosteric heat calculated from the isotherms measured at 28° and 36°C; the curve B denotes the dependence calculated from the isotherms measured at 20° and 36°C; the curve C was obtained from values of pressure

determined by extrapolation: the dependence $\log p = k_1 + k_2 \cdot a$ which fits the experimental data between 0.01 Torr and 1 Torr was extrapolated into the region of lower pressures.

Results obtained by calculation from the other possible combinations of pairs of isotherms are not given, as these values lie between the extreme values shown in Fig. 4. The dependence of the isosteric heat on the surface coverage was calculated from all four isotherms for coverages starting at 1.6 mmol g^{-1} .

The integral molar heat of adsorption was calculated by integrating the dependence of the isosteric heat on the surface coverage. From the curves A, B, and C in Fig. 4 the curves A, B, and C in Fig. 5, respectively, were calculated by inserting the data into equation (1). By comparing the dependences in Figs 4 and 5, one can see that the courses of various curves differ from each other, though they ought to be identical. By analyzing possible errors in the measurement of the adsorption isotherms it can be shown that the experimental arrangement is sufficiently accurate. Thus, the observed disagreement is not caused by experimental errors. The integral molar heats of adsorp-

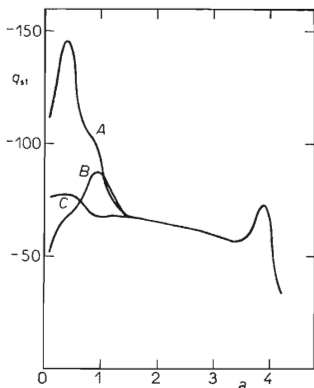


FIG. 4

Dependence of the Isosteric Heat of Adsorption q_{st} (J mmol^{-1}) on the Adsorbed Amount a (mmol g^{-1}) for the System n-Hexane and Active Charcoal SSHR.

For meaning of symbols denoting the curves see text.

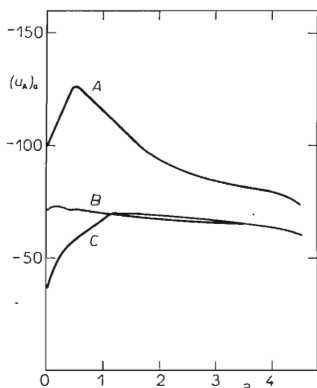


FIG. 5

Dependence of the Integral Molar Heat of Adsorption $(u_A)_a$ (J mmol^{-1}) on the Adsorbed Amount a (mmol g^{-1}) for the System n-Hexane and Active Charcoal SSHR.

tion were calculated from equation (3) to (6), too. The resulting values showed complete agreement with the values of the heats as calculated by means of (1) and (2).

The relations used in the calculations of the heats of adsorption were derived with the use of the same model of the adsorption system. Therefore, the agreement of the calculated values of the heats of adsorption is in this case a mere confirmation that the numerical methods used were suitably chosen.

In conclusion, the unusual course of the initial parts of the adsorption isotherms in the region of low pressures in experiments on adsorption of n-hexane on the active charcoal SSHR causes an entire uncertainty in calculations of the integral molar heats of adsorption. The course of the adsorption isotherm in its initial part may be explained presumably on the basis of the two hypotheses discussed above: by the presence of inert gases or by a chemical instability of the adsorbate.

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