KINETICS OF ADSORPTION. V.*

ISOTHERMAL AND ISOBARIC ISOCHRONES IN THE BINARY SYSTEM ACTIVE CARBON "SUPERSORBON"-CYCLOHEXANE

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Isothermal and isobaric isochrones were constructed from single kinetic isotherms of cyclo-hexane on active carbon "Supersorbon". The isothermal isochrone was correlated by an equation whose independent variable coordinate was numerically the same as that of the equilibrium adsorption isotherm plotted from end points of single kinetic isotherms. From the linear course of isobaric isochrones, the equilibrium isobar, and the density of liquid adsorbate on temperature and with respect to a satisfactory agreement when calculating the limiting volume both from the equilibrium isobar and from the equilibrium isotherms constructed from single kinetic isotherms, the conclusion can be drawn that the state of adsorbate in pores is close to the state of normal liquid.

Isobaric isochrone[1] expresses the dependence of adsorbed amount at a given time on temperature at constant pressure. Isothermal isochrone[2] expresses the dependence of adsorbed amount at a given time on pressure at constant temperature and it was correlated by an equation which for $\tau \to \infty$ turns into the equation for the equilibrium adsorption isotherm. In order that initial conditions might be easily reproducible the pressure was chosen for kinetic isotherms which was equal to the saturated vapour pressure of adsorbate at a temperature of 0°C. The temperatures at which kinetic isotherms were measured were maintained at a constant value by means of a thermostat with an accuracy of ±0·05°C.

The number of molecules adsorbed on a solid adsorbent is a function of temperature T, pressure P and time τ. An increase in the adsorbed amount a can be expressed by the equation

$$\mathrm{d}a = (\partial a/\partial \tau)_{\mathrm{T,P}} \, \mathrm{d}\tau + (\partial a/\partial P)_{\mathrm{T},\tau} \, \mathrm{d}P + (\partial a/\partial T)_{\mathrm{P},\tau} \, \mathrm{d}T. \tag{1}$$

If the intensive parameters, temperature and pressure, are kept constant then on carrying out the integration of Eq. (1) under the condition that the adsorbent does not contain an adsorbate

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at a time $\tau = 0$, we obtain a relation which gives the dependence of adsorbed amount on time at constant temperature and pressure (*i.e.* kinetic isotherm).

When integrating Eq. (*1*) at constant temperature and time on the condition that at the beginning of experiment is $P = 0$, $a = 0$, we get a relation which expresses the dependence of adsorbed amount on pressure at a chosen time and at a constant temperature (*i.e.* isothermal isochrone). By integrating Eq. (*1*) in case of $\tau \rightarrow \infty$ and $T =$ const., we get an expression for the equilibrium adsorption isotherm. On integrating Eq. (*1*) at constant pressure and time on the condition that the adsorbent is evacuated at the beginning of experiment, we get a relation which defines the isobaric isochrone, *i.e.* it expresses the dependence of adsorbed amount on temperature at a constant pressure and at a chosen time. By integration of Eq. (*1*) in case of $\tau \rightarrow \infty$ and $P =$ const., we obtain a relation for the equilibrium adsorption isobar.

For the most different kinds of carbonaceous adsorbents (active carbon, carbon black, and others like that), *i.e.* the adsorbents of the first structural type, the equilibrium adsorption isotherm and the equilibrium isobar can be described, on the basis of the potential theory, by a characteristic curve which may be expressed in a sufficient approximation by the equation

$$\log a_e = \log W_0 \varrho - 0.43 B T^2 \log^2 (P_0/P)/\beta^2 , \tag{2}$$

where a_e is the equilibrium adsorbed amount in grams per one gram of adsorbent, W_0 the limiting volume of adsorption space (cm^3/g), B the constant characterizing the microporosity of adsorbent, T the absolute temperature of the isotherm, P_0 the saturated vapour pressure of adsorbate at temperature T, P the equilibrium pressure in the gas phase, β the affinity coefficient, and ϱ the density of the liquid adsorbate. The temperature dependence of the density of liquid adsorbate can be expressed by the relation[3] $\varrho = \alpha + \beta t + \gamma t^2 + \ldots$, where α, β, γ are constants and t is temperature in °C. The first term, α, gives the density of the liquid adsorbate at a temperature of 0°C. At this temperature the liquid is supercooled for the melting point of cyclohexane[4] is 6·55°C.

From the end points of single kinetic isotherms measured at different temperatures and identical pressure it is possible to construct the isobar. From the equilibrium isobar we can calculate according to Eq. (*2*) the constants W_0 and B as well.

EXPERIMENTAL

Substances used. Cyclohexane was prepared at the Department of Synthetic Fuels in the laboratory of Professor Mostecký. Its purity was checked by gas chromatography. Cyclohexane was ten times distilled out of an ampoule which was placed in the bath of solid carbon dioxide and acetone into the ampoule cooled in the bath of liquid air over a molecular sieve 4 A which was degassed after each distillation at a temperature of 350°C for 4 hours at a pressure of 10^{-5} Torr. After each degassing the molecular sieve 4 A, the ampoule with this sieve was cooled in the bath of solid carbon dioxide with acetone and the adsorbate passed during the distillation through the whole bed of the molecular sieve. In the last cycle, cyclohexane was distilled into the appara-

tus. In this way the thorough degassing and dehydrating of adsorbate was attained. The measured saturated vapour pressure at 0°C was 27·15 Torr (tabulated value[4] 27·14 Torr). As an adsorbent, one grain was chosen by measuring about 100 grains of active carbon "Supersorbon". It was of the shape of an equilateral cylinder, 6 mm in diameter. The grain was placed into a vessel and heated to 350°C. Simultaneously the liberated substances were exhausted by a vacuum pump. After cooling down, the grain was wound by a platinum wire weighed in advance, weighed and suspended on a quartz spiral balance. Before each measurement, the weight of the evacuated carbon sample was determined from the elongation of spiral.

Apparatus. The kinetic isotherms of cyclohexane on active carbon were measured by the same method as in the work[5], however, a non-greased sorption apparatus with reservoirs of a total volume of 33 litres was used. This apparatus has some advantages in comparison with that which was described in the paper[5]. The sample of adsorbent does not get into contact with air neither after the first degassing nor between single measurements. The stopcocks of mercury reservoirs in the handling part are replaced by de-aerating valves[6]. The sintered glasses used enable a new construction of the mercury reservoirs. Gold threads, 0·05 mm in diameter and of 2 m² surface fixed before the tube in which the quartz spiral balance with adsorbent is located, entrap mercury vapours. The apparatus has no vacuum cocks tightened by vacuum grease.

RESULTS

The kinetic isotherm is experimentally most easily accessible and expresses the dependence of adsorbed amount on time at constant pressure and temperature. From the kinetic isotherms measured at constant temperature and different pressures, the isothermal isochrones were correlated (Fig. 1). The isothermal isochrones[2], expressing the dependence of adsorbed amount on pressure at constant temperature and time, were correlated by means of equations whose independent variable coordinate was numerically the same as that for the equilibrium adsorption isotherm constructed from end points of single kinetic isotherms. The linear form of the equation for isothermal isochrone is

$$\log a_{ij} = \log W_{0j}\varrho - 0·43 B_j T^2 \log^2 (P_0/P_i)/\beta^2 , \qquad T, \tau_j = \text{const.} \qquad (3)$$

where subscript i denotes the number of kinetic isotherms used for correlation, the second subscript the j-th isochrone, W_{0j} is the limiting volume of adsorption space for the j-th isochrone, B_j the constant characterizing the course of the j-th isochrone, P_i the equilibrium pressure in the gas phase at which the i-th kinetic isotherm was measured, a_{ij} the adsorbed amount in grams per gram of adsorbent for the i-th kinetic isotherm and time j, and the other symbols have the same meaning as in Eq. (2). For $\tau \to \infty$, the quantities a_{ij}, W_{0j}, B_j take the limiting values a_e, W_0, B which describe the equilibrium adsorption isotherm (Eq. (2)), Fig. 1.

The isobaric isochrone expressing the dependence of adsorbed amount on temperature at constant pressure and time (Fig. 2) and the equilibrium isobar can be expressed, at the pressure corresponding to the saturated vapour pressure of cyclo-

hexane at a temperature of 0°C, in a given temperature interval, by the relations

$$a_{kj} = C_j + D_j t_k, \qquad P, \tau_j = \text{const.} \qquad (4)$$

$$a_e = C + D t_k, \qquad P = \text{const.} \qquad (5)$$

where subscript k denotes the number of temperatures (kinetic isotherms) and the second subscript the j-th isochrone, a_{kj} is the adsorbed amount at a given time τ_j at a temperature t_k, C the equilibrium adsorbed amount on one gram of adsorbent at a temperature of 0°C, D the change of the equilibrium amount on one gram of adsorbent corresponding to a change of temperature by 1°C, a_e the equilibrium adsorbed amount on one gram of adsorbent at the temperature t_k. For $\tau \to \infty$, the values of constants C_j, D_j take the limiting values corresponding to the equilibrium isobar
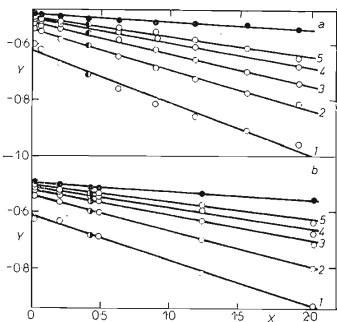

Fig. 1

Isothermal Isochrones and Equilibrium Adsorption Isotherms Constructed from Kinetic Isotherms of Cyclohexane on Active Carbon "Supersorbon"

a 20°C, b 30°C, geometrical shape of grain — equilateral cylinder 6 mm in diameter, $Y = \log a$ (for isochrones — Eq. (3)), $Y = \log a_e$ (for equilibrium data — Eq. (2)), $X = \log^2 (P_0/P)$, ○ kinetic isotherms, ◐,◑ kinetic isotherm $P = 27 \cdot 2$ Torr, ● equilibrium; numbers denote time of isochrones in minutes.

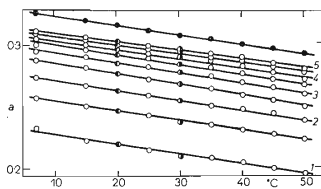Fig. 2

Isobaric Isochrones and Equilibrium Adsorption Isobar Constructed from Kinetic Isotherms of Cyclohexane on Active Carbon "Supersorbon" at the Pressure of 27·2 Torr

a is the adsorbed amount of cyclohexane in grams per gram of adsorbent, ○ kinetic isotherms, ◐,◑ (see Fig. 1), ● equilibrium from end points of kinetic isotherms (Eq. (5)); numbers denote time of isochrones in minutes.

defined by Eq. (5), Fig 2. At the temperature of 0°C, $a_e = C$ and when substituting into Eq. (2) for the density α, we get $\log C = \log (W_0 \alpha)$, for $P = P_0$ and after finding the antilogarithm, we can write $C/\alpha = W_0$. In this way it is possible to determine the limiting volume of adsorption space from the temperature dependence of end points of single kinetic isotherms measured at the constant pressure corresponding to the vapour pressure of cyclohexane at the temperature of 0°C. On the assumption of the validity of the potential theory we can calculate the characteristic curve from one isotherm and from it determine the equilibrium adsorbed amount at another temperature and corresponding pressure. The end points of kinetic isotherms measured at a temperature of 20°C were correlated by Eq. (2) and, in addition, converted point by point to the temperature of 30°C under the condition $T_1 \log (P_{01}/P_1) = T_2 \log (P_{02}/P_2)$ and simultaneously $a_1/\varrho_1 = a_2/\varrho_2$, where the subscript 1 stands for the temperature of 20°C and the subscript 2 for the temperature of 30°C and the meaning of the other symbols is the same as in Eq. (2). The obtained values of adsorbed amount and pressures were again correlated according to Eq. (2). The calculation showed the agreement both in the limiting volume W_0 and in the constant B (Table I). On the basis of this result all end points of kinetic isotherms were converted in the same way to the standard temperature of 30°C and correlated by Eq. (2). In Table I, the results of correlation by means of Eq. (2) are compared with the result obtained from the linear course of the equilibrium isobar. The values of the limiting volume determined according to Eqs (2) and (5) are in good agreement,

TABLE I

Constants W_0, B of Eq. (2) for Active Carbon "Supersorbon" Determined by Adsorption of Cyclohexane at Various Temperatures and Pressures

Data used for correlation	Calculation by means of equations	W_0	$B \cdot 10^6$
Isotherm 20°C	(2)	0·411	1·04
Isotherm 30°C	(2)	0·414	1·11
Isotherm 30°C, after discarding one point	(2)	0·413	1·04
Isotherm 30°C, conversion point by point from isotherm 20°C	(2)	0·411	1·04
Equilibrium isobar 0°C (extrapolated) — — 50°C	(2), (5)	0·415	0·96
Equilibrium isobar 7°C—50°C	(2), (5)	0·412	1·13
Isotherm 30°C, conversion point by point from all kinetic isotherms	(2)	0·412	1·06
Average values of constants		0·413	1·06

taking into account that the first term in the polynomial represents the extrapolated value of supercooled liquid adsorbate. Melting point of cyclohexane is 6·55°C. The constants $\alpha = 0.79744 \pm 0.00005$, $\beta = -0.000947 \pm 0.000001$ were calculated from the density data of liquid cyclohexane[4] for the temperature interval of $7-64°C$ with sufficient accuracy; mean deviation amounts to $\pm 0.011\%$. The first term in the polynomial is the extrapolated equilibrium adsorbed amount at 0°C for the lowest kinetic isotherm was measured at a temperature of 7°C (Table II). It is evident from the deviations presented in Table II that for the analytical expression of dependences of adsorbed amount on temperature it is sufficient, in the given temperature interval, to use the equation with two constants likewise for the temperature dependence of the density of liquid adsorbate.

TABLE II

Linear Isobaric Dependence of Adsorbed Amount of Cyclohexane on Temperature (according to Eq. (5))

$a_e = (0.3309 \pm 0.0004) - (0.00079 \pm 0.00001)t.$

°C	a_e(exp.) g/g	a_e(calc.) g/g	Dev.[a] %	°C	a_e(exp.) g/g	a_e(calc.) g/g	Dev.[a] %
7	0·3257	0·3254	0·09	25	0·3106	0·3111	−0·16
15	0·3186	0·3190	−0·13	25	0·3111	0·3111	0·00
15	0·3191	0·3190	0·03	30	0·3066	0·3072	−0·20
20	0·3142	0·3151	−0·29	35	0·3038	0·3032	0·20
20	0·3152	0·3151	0·03	35	0·3038	0·3032	0·20
20	0·3148	0·3151	−0·10	40	0·2995	0·2993	0·07
25	0·3109	0·3111	−0·06	45	0·2956	0·2953	0·10
25	0·3100	0·3111	−0·36	50	0·2909	0·2914	−0·17

[a] Mean deviation ± 0.14.

To obtain the isobaric isochrones from single kinetic isotherms it is necessary to carry out every measurement at the same pressure. The constancy of pressure during the measurement of kinetic isotherms was secured on the one hand by immersing the ampoule with adsorbate into the Dewar flask with ice and on the other hand by the large capacity of the gas phase (the reservoirs of the volume of 33 litres). In Table III, the values of the cyclohexane adsorption up to 5 minutes and the equilibrium adsorbed amount are presented for the temperatures of 15°C, 25°C, and 35°C. The measured data show a satisfactory agreement taking into consideration that the

adsorbent is in vacuum at the beginning of the experiment and during 5 minutes over ninety per cent of the equilibrium adsorbed amount is adsorbed on it.

TABLE III

Reproducibility of Kinetic Isotherms

°C	Number of measurements	Adsorbed amount (average)	% deviation min.	max.	Mean error of one measurement
		Isochrone 1st minute			
15	2	0·2207	−0·36	+0·36	±0·0011
25	4	0·2140	−0·05	+0·05	±0·0011
35	2	0·2072	−0·24	+0·24	±0·0007
		Isochrone 2nd minute			
15	2	0·2677	−0·34	+0·34	±0·0013
25	4	0·2595	−0·43	+0·58	±0·0013
35	2	0·2500	−0·52	+0·48	±0·0018
		Isochrone 3rd minute			
15	2	0·2898	−0·14	+0·14	±0·0006
25	4	0·2827	−0·34	+0·42	±0·0009
35	2	0·2736	−0·07	+0·04	±0·0002
		Isochrone 4th minute			
15	2	0·2998	−0·17	+0·13	±0·0006
25	4	0·2938	−0·07	+0·51	±0·0011
35	2	0·2861	−0·03	0·0	±0·0001
		Isochrone 5th minute			
15	2	0·3066	−0·26	+0·29	±0·0012
25	4	0·2993	−0·33	+0·43	±0·0010
35	2	0·2923	−0·10	+0·10	±0·0004
		Equilibrium			
15	2	0·3189	−0·09	+0·06	±0·0004
25	4	0·3107	−0·23	+0·13	±0·0005
35	2	0·3038	−0·0	+0·0	±0·0000

DISCUSSION

In the literature it is stated as a rule that according to Eq. (2) we can calculate from one isotherm measured the isotherm of the same vapour on the given active carbon at any other temperature $(T < T_k)$ if the respective density and saturated vapour pressure are known. Eq. (2), however, makes it possible to calculate as well the equilibrium isobar which expresses the dependence of the equilibrium adsorbed amount on temperature at constant pressure. In Table I, the results are given of the correlation of equilibrium isobar constructed from end points of single kinetic isotherms measured at pressures corresponding to the vapour pressure of cyclohexane at 0°C, *i.e.* at 27·2 Torr. The mean value of constants $W_0 = 0·414$, $B = 1·05 . 10^{-6}$ calculated according to Eqs (2) and (5) is very close to the mean value obtained from all measurements $W_0 = 0·413$, $B = 1·06 . 10^{-6}$ and also to the values obtained from single equilibrium isotherms. This agreement indicates that each kinetic isotherm representing one independent measurement was measured with sufficient accuracy. The results of the correlation of equilibrium isobar (Table II) prove this fact. Mean deviation is 0·14%. In monograph[1], the adsorption potential is defined by the relation $\varepsilon = RT \ln (P_0/P)$. Consequently it is a function of temperature and pressure and can be represented in a space diagram with coordinates ε, T, P. Whereas the projections of dependences of adsorption potentials on pressure into the first basic plane with coordinates ε, P in the space diagram are curves, the projections of adsorption potentials on temperature into the second plane with coordinates ε, T can be in a good approximation expressed by straight lines for various constant pressures. The limiting case of isothermal isochrones, Eq. (3), is Eq. (2) which expresses the relation between the equilibrium adsorbed amount and the adsorption potential and from which Eq. (5) can be derived on the basis of a linear dependence of adsorption potential on temperature. Eq. (5) is the limiting case of isobaric isochrones of Eq. (4).

The results in Table III show that the kinetic isotherms were measured with sufficient accuracy irrespective of the fact that within 5 minutes over ninety per cent of the equilibrium amount is adsorbed. Considering the considerable rate of transfer of adsorbate in the starting stage, the mean error of one measurement is acceptable. The correlation of densities for the given temperature interval by means of the equation of straight line is satisfactory, for mean deviation is 0·011%.

From the linear course of the isobaric isochrones, the equilibrium isobar (Fig. 2) and the density of liquid adsorbate on temperature with regard to the satisfactory agreement when calculating the limiting volume both from the equilibrium isobar and from the equilibrium isotherms constructed from single kinetic isotherms (Table I), the conclusion can be drawn that the state of adsorbate in pores is close to that of normal liquid. The temperature change of the equilibrium amount (Table II) in relation to the temperature change of liquid adsorbate can be expressed by the relation $da/dt \approx 0·9 \, d\varrho/dt$.

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