Non-isothermal adsorption in a fixed bed of adsorbent*

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The non-isothermal adsorption was investigated in the system benzene—
—molecular sieve Nalsit 13X using nitrogen as a carrier gas. The measure-
ments were performed at different gas velocities, concentrations of adsorbate,
and heights of the bed of sorbent. From a comparison of the break-through
curves expressed in transformed coordinates it became evident that a con-
stant-pattern sorption front was established in the system which was also
confirmed by the finding that the temperature wave preceded the concent-
ration wave. The quantitative relationships were investigated on the basis of
the correlation between the temperature change and the value dQ/dt which
was proportional to the mass-transfer rate. In the subsequent quantitative
evaluation the dependence of differential heat of adsorption upon the amount
adsorbed was considered and these correlations were plotted in a graph
representing the change in temperature as a function of the product ΔH_{diff}
dQ/dt. From these plots it is obvious that the character of graphs is different
for the ascending and descending part of the temperature curve.

Неизотермическая адсорбция исследовалась в системе бензол—молеку-
лярное сито «Nalsit 13X» с использованием азота в качестве газа — носи-
теля. Измерения были проведены при разных скоростях газа, концентра-
циях адсорбата и разных высотах слоя сорбента. Сравнением выходных
кривых графически представленных в преобразованных координатах было
найдено, что в приведенной системе имеет место режим параллельного
переноса, что было подтверждено также наблюдаемым фактом, по которому
температурная волна перегоняет концентрационную волну. Количествен-
ные зависимости исследовались используя корреляцию между изменением
температуры и величиной dQ/dt, которая пропорциональна скорости массо-
передачи. В дальнейшей качественной оценке учитывалась также зависи-
мость дифференциальной теплоты адсорбции от адсорбированного коли-
чества, и эти корреляции были графически представлены зависимостью
изменения температуры от произведения $\Delta H_{диф}$ dQ/dt. Из приведенных
графиков видно, что ход зависимости для возрастающей и понижающейся
части температурной кривой является различным.

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Non-isothermal adsorption is far more complicated than isothermal adsorption because in this phenomenon the release of adsorption heat depending on the quantity of the amount adsorbed, the conduction of heat in the particles of sorbent, the heat exchange between gas and sorbent and the heat exchange between adsorber and its surroundings is to be considered. In spite of some partial results involving these factors, the theory of the non-isothermal adsorption is not yet worked out. Some models developed up to computational processing are simplified to such an extent that they do not allow so far an application to quantitative computation of real adsorbers. According to our opinion, it is necessary to obtain a considerable amount of experimental material on the basis of which these simple models could be completed and refined.

Theoretical

Concerning the evaluation of empirical data, first the extent should be established to which some laws of the dynamics of isothermal adsorption are applicable to the dynamics of non-isothermal adsorption.

The formation of a constant-pattern sorption front [1] is characteristic of the isothermal adsorption at a convex adsorption isotherm. For a non-isothermal adsorption the formation of constant-pattern sorption front is disturbed by thermal effects and in principle there two cases may occur:

1. The temperature wave precedes the concentration wave and a constant-pattern sorption front is established.

2. The temperature wave divides the concentration wave in two parts which advance at different rates through the bed.

Leavitt [2] used the *Michaels* method [3] of transfer zone to the analysis of data from a pilot plant. He points out that due to temperature effects two transfer zones arise in a fixed bed while different conditions of the process influence the extent and the rate of the movement of these zones. These transfer zones are separated by a middle zone in which, in general, there exists a sorption equilibrium.

On the basis of the Leavitt postulate involving the existence of two transfer zones *Pan* and *Basmadjian* [4] developed a mathematical model for the adiabatic adsorption of one component from the carrier gas. In the mentioned paper an asymptotic solution of concentration and temperature profiles is given and the authors come to the conclusion that for a negligible initial bed loading the first transfer zone is always formed and this zone moves up the bed by a parallel transfer provided the isotherm is a favourable or a linear one. Moreover, they also report the conditions of the existence of a constant-pattern sorption [5].

The formation of a constant-pattern sorption front is investigated by comparing the break-through curves in transformed coordinates $Q = f(z)$ in the beds of different heights at equal rates and concentrations where z is the transformed time defined by eqn (1)

$$z = t - t^*, \qquad (1)$$

where t^* is the time required for the stoichiometric sorption front to reach to the end of the bed. On the basis of the material balance in the adsorber it is possible to prove [6] that

$$\int_0^1 (t - t^*)\,\mathrm{d}Q = \int_0^1 z\,\mathrm{d}Q = 0, \qquad (2)$$

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Fig. 1. Graphical representation of the break--through curve in transformed coordinates.
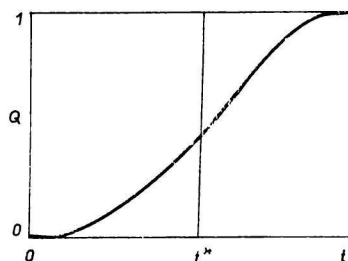
where Q is the dimensionless concentration of adsorbate in the gas leaving the bed defined by the expression

$$Q = \frac{C}{C_0}.$$

The representation of the break-through curves in transformed coordinates enables us to prove in a simple way the establishing of constant-pattern conditions. The break-through curves for the beds of a different height represented in transformed coordinates are identical if the sorption is going according to the constant-pattern conditions.

Experimental

Our study was aimed at obtaining some empirical data from which it would be possible to draw at least preliminary qualitative conclusions on the non-isothermal sorption in the system benzene—molecular sieve Nalsit 13X (fraction 2.5—2.8 mm) when using nitrogen as a carrier gas. The measurements were performed at the gas flow rate $w =$ $= 20 \pm 0.1$, 30 ± 0.1, and 40 ± 0.1 cm s^{-1} for the concentrations of adsorbate $C =$ $= 8, 10, 15, 20, 25, 30, 40$, and 50 mg l^{-1}, the accuracy in adjusting the concentrations being ± 0.1 mg l^{-1}. The height of the bed of sorbent was 16 and 20 cm.

The adsorber consisted of a ground glass column equipped with an electric heater comprising a layer of asbestous fabricate — heating element — 20 turns of canthal wire and an outside asbestous insulation. The activation of adsorbent was carried out at 400—420°C by blowing pure nitrogen. The adsorption column of 20.38 mm diameter was packed in such a way that the beds of glass balls of equal granularity as molecular sieve were situated over and below the bed of the molecular sieve. In this way a stabilization of hydrodynamic parameters in the bed of sorbent was achieved. The column was installed in a vertical position, the gas entrance being on the top.

The advance of the temperature wave was investigated by measuring the temperature in three places in the bed as well as the temperature of the gas leaving the bed by means of thermocouples installed in the column. The distance of the thermocouples (Cu-constantan) from the entrance into the column was 50, 95, and 130 mm in the bed of 16 cm and 90 mm, 135 and 170 mm in the bed of 20 cm. The fourth thermocouple (Fe-constantan) was placed 60 mm behind the bed. The temperature of the gas mixture entering the adsorption column was 20 ± 0.1°C.

Discussion

By comparing the break-through curves represented in transformed coordinates for the 16 and 20 cm beds, we found that a constant-pattern sorption front was formed already in the 16 cm bed within the whole range of concentrations and rates used (Fig. 2).
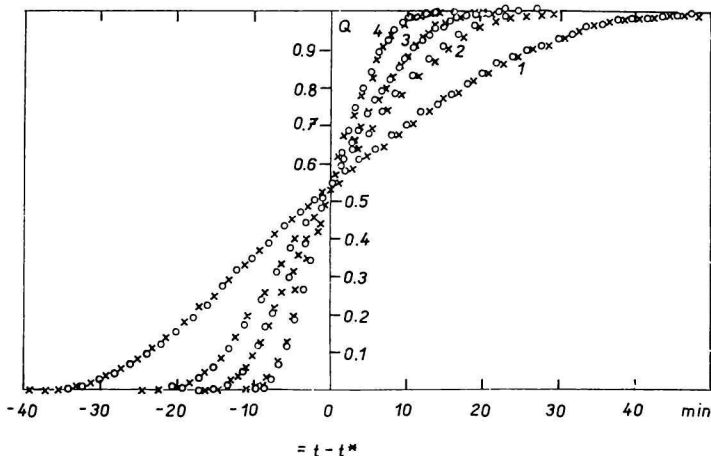

Fig. 2. Break-through curves represented in transformed coordinates.
$h_k = 16$ cm ($\bigcirc$), $h_k = 20$ cm ($\times$), $w = 40$ cm s^{-1}.
1. C $= 10$ mg l^{-1}; *2. C* $= 20$ mg l^{-1}; *3. C* $= 30$ mg l^{-1}; *4. C* $= 50$ mg l^{-1}.

By representing the temperatures waves in the $\Delta T - z$ coordinates (ΔT is the difference between the measured and the inlet temperature) we have found that the maximum of the temperature wave is in the region of the negative transformed time. The temperature wave precedes the concentration wave and therefore the conclusion has been confirmed that a constant-pattern sorption front is established provided the temperature wave precedes the concentration wave.

Since the rise in temperature in the bed of sorbent is related to the quantity of the adsorption heat released in a time unit, the increase in temperature in a given place must be closely connected with the local mass-transfer rate. By comparing the temperature curves with the differential curves (the differential curves are the relationships between dQ/dt and time) it has been found that they are very similar. For illustration, the course of the temperature curve and differential curve is shown in Fig. 3.

The first step in a deeper investigation of the quantitative relationship involving non-isothermal adsorption is the evaluation of the correlation between the change in temperature ΔT and the value of dQ/dt which is proportional to the mass-transfer rate. It ensues from this evaluation that there is a close non-linear correlation between ΔT and dQ/dt. The character of this relationship is different for the ascending and descending part of the temperature curve (Figs. 4 and 5). One of the causes
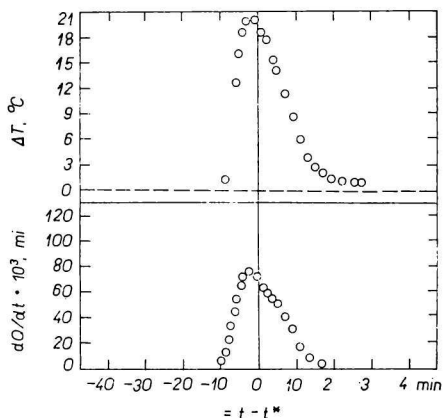
Fig. 3. Temperature curve and differential curve in transformed coordinates for the height of the bed $h_k = 16$ cm, concentration $C = 50$ mg l^{-1}, and flow rate $w = 40$ cm s^{-1}.
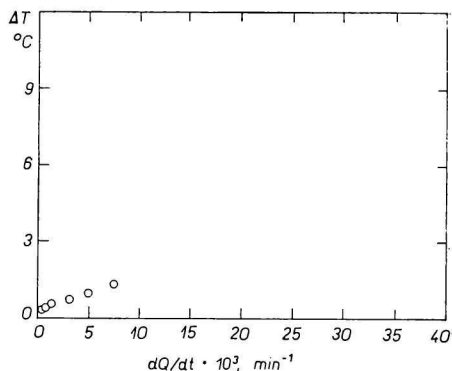
Fig. 4. Variation of ΔT with dQ/dt for $h_k = 16$ cm, $C = 20$ mg l^{-1}, and $w = 40$ cm s^{-1}.

consists in the fact that the differential heat of adsorption depends on the adsorbate concentration in adsorbent. Therefore the next step involved the construction of a correlation between ΔT and the product $\Delta H_{\text{diff}}\, dQ/dt$ which is proportional to the local rate of heat release.

The relationship between the differential heat of adsorption and the amount of substance adsorbed may be deduced from the temperature dependence of equilibrium pressure at a constant adsorbate concentration in adsorbent [7]

$$\Delta H_{\text{diff}} = RT^2 \left(\frac{\partial \ln p^*}{\partial T} \right)_a - RT. \tag{3}$$

By measuring the adsorption equilibria in a vacuum apparatus it has been found that the adsorption isotherm of the second structural type of activated carbon is valid for the system benzene—nitrogen on a molecular sieve Nalsit 13X. This adsorption isotherm may be converted to a generalized type of the Freundlich isotherm

$$p^* = \left(\frac{a}{K} \right)^{\frac{1}{n}}, \tag{4}$$

where

$$n = k\, T, \tag{5}$$

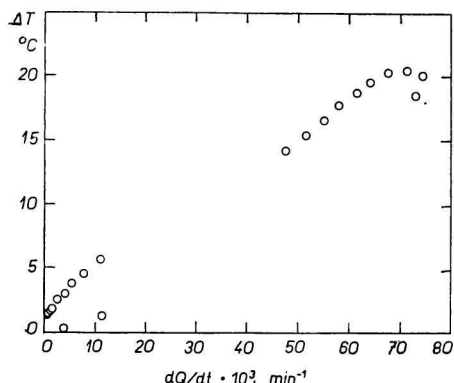$$\log K = C_1 + C_2 T, \tag{6}$$

while

$$k = \frac{A}{\beta \ln 10}. $$

Fig. 5. Variation of ΔT with dQ/dt for $h_k = 16$ cm, $C = 50$ mg l^{-1}, and $w = 40$ cm s^{-1}.
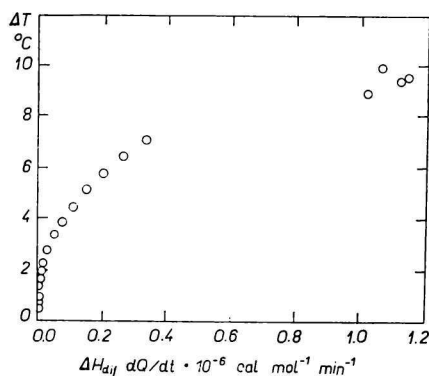
Fig. 6. Relationship between ΔT and $\Delta H_{\text{diff}} \, dQ/dt$ for $h_k = 16$ cm, $C = 20$ mg l^{-1}, and $w = 40$ cm s^{-1}.

On the basis of this equation it is then possible to calculate the temperature dependence of the equilibrium pressure of gas at a constant adsorbate concentration in adsorbent. Equation (6) is valid for a small temperature interval which is fulfilled in our case.

On the basis of the above relations we obtain the following expression for the differential heat of adsorption as a function of temperature and real adsorbate concentration in adsorbent

$$\Delta H_{\text{diff}} = - \frac{R}{k} (\ln a - C_1') - RT, \qquad (7)$$

where $C_1' = C_1 - \ln 10$.

After introducing dimensionless adsorbate concentration in adsorbent

$$q = \frac{a}{a_0^{\bullet}}, \qquad (8)$$

where $a_0^{\bullet}$ is the adsorbate concentration in adsorbent in equilibrium corresponding to the concentration C_0, it is possible to express $\ln a$ by the expression

$$\ln a = \ln a_0^{\bullet} + \ln q. \qquad (9)$$

In the stage of constant-pattern sorption and at negligible longitudinal diffusion it can be written

$$q = Q \qquad (10)$$

so that

$$\ln a = \ln a_0^{\bullet} + \ln Q \qquad (11)$$

and hence

$$\Delta H_{\text{diff}} = - \frac{R}{k} (\ln a_0^{\bullet} - C_1' + \ln Q) - RT. \qquad (12)$$

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The expression for the differential heat of adsorption may be also derived from the relationship

$$a = \frac{a_0}{p_s^n} p^n \qquad (13)$$

in the form

$$\Delta H_{\mathrm{diff}} = \frac{R}{k} \left[\ln a - \left(\ln a_0 - T \frac{d \ln a_0}{dT,} \right) \right] + \Delta H_{\mathrm{evap}} - RT. \qquad (14)$$
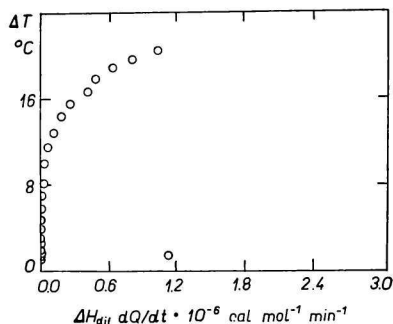

Fig. 7. Relationship between ΔT and $\Delta H_{\mathrm{diff}} \, dQ/dt$ for $h_k = 16$ cm, $C = 50$ mg l^{-1}, and $w = 40$ cm s^{-1}.

The relationship between ΔT and the product $\Delta H_{\mathrm{diff}} \, dQ/dt$ is shown in Figs. 6 and 7.

The graphical representation of these relationships shows that the character of correlation is different for the ascending and descending branch of the temperature curve and the differences increase with temperature. In the part corresponding to the approximation to equilibrium the curves are almost of a parabolic shape. This form of relationship is obviously related to the heat exchange between sorbent and gas. A deeper qualitative and quantitative analysis will necessitate a more detailed elaboration of existing experimental material and its completion with further measurements.

Symbols

a	adsorbate concentration in adsorbent
$a^{\bullet}$	adsorbate concentration in adsorbent in equilibrium
$a_0^{\bullet}$	adsorbate concentration in adsorbent in equilibrium with the concentration C_0
A	constant in the Dubinin—Radushkevich equation for the second structural type of adsorbent
C	concentration of adsorbate in gas
C_0	concentration of adsorbate in gas entering the column
C_1, C_2	parameters in eqn (6)
h_k	height of bed
ΔH_{diff}	differential heat of adsorption
ΔH_{evap}	evaporation heat of adsorbate
K	constant in the Freundlich equation of adsorption isotherm
k	parameter in eqn (5)

n	exponent in the Freundlich equation of adsorption isotherm
p	partial pressure of adsorbate
p_s	pressure of the saturated vapour of adsorbate
p^*	equilibrium partial pressure of adsorbate
Q	dimensionless concentration in gas
q	dimensionless adsorbate concentration in adsorbent
R	gas constant
t	time
t^*	time necessary for the stoichiometric sorption front to come to the end of the bed
T	absolute temperature
ΔT	temperature change in the bed
w	linear gas flow rate in the empty column
z	transformed time
β	coefficient of affinity

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