ANALYSIS OF THE TEMPERATURE CURVES IN NON-ISOTHERMAL ADSORPTION ON COMPACTED ZEOLITES

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An analytical description is presented of the temperature curves describing adsorption on thin zeolite plates. The solution, based on the model of simultaneous mass and heat transport was obtained by linearization of the kinetic equations. A method is proposed for verification of the plausibility of the model and for evaluation of the kinetic data by numerical simulation of the temperature curves.

Analytical solution of the problem of simultaneous mass and heat transport during gas adsorption in zeolites, pressed into plates was described in papers[1-3]. The described model was used for analysis of the sorption kinetics of cyclohexane on compacted zeolite NaX. The coefficients of diffusion and heat transport were estimated by fitting the experimental curves to the theoretical curves[4,5]. It has been found that it is of advantage to analyze also the temperature curves measured in the adsorption process[6,7]. In another paper, the method of statistical moments was applied to evaluation of the kinetic constants from the temperature curves of adsorption of the cyclohexane in zeolite NaX (ref.[8]) and of xenon in zeolite NaA (ref.[9]). The theoretical basis for analysis of the temperature curves by the method of moments was described in paper[11].

The present paper provides an analytical description of the temperature curves and describes a method for estimation of the kinetic parameters from the experimental temperature curves.

THEORETICAL

A thorough description of the model of simultaneous mass and heat transport during gas adsorption in zeolites which had been compacted into thin plates was given in paper[1]. At this place, we shall mention just the basic premises of this model. It is assumed that the adsorption kinetics of a single species proceeds on a thin plate with a thickness $2L$, while the remaining dimensions of the plate are much larger.

From the various possible mechanisms of mass transport, the intercrystalline diffusion is only taken into account and the mass flow density $\boldsymbol{i}$ in the transport pores is considered to be ruled by the Fick law:

$$i = -D_g \operatorname{grad} c_g\,, \tag{1}$$

where c_g is the concentration gradient of the sorbing species in the volume of the transport pores and D_g is the diffusion coefficient of the species in these pores.

The heat released during the adsorption raises partly the temperature of the plate, by $\Delta T(t)$ (the temperature curve). The impact of this effect on the magnitude of the diffusion coefficient of the species sorbing on the plate is usually regarded as negligible. On the other hand, the above temperature increase changes the adsorption equilibrium. In order to describe this effect, we have used a following linear approximation

$$\Delta c'_a = \varepsilon\,\Delta c_g - \omega\,\Delta T\,, \tag{2}$$

where c'_a is the concentration of the species sorbing in zeolite crystallites (expressed as amount of the substance in a mass unit of the crystal – mmol g^{-1}), $\Delta T = T - T_0$ (T_0 is the thermostat temperature). Quantities ε and ω are defined in the following way:

$$\varepsilon = (\partial c'_a/\partial c_g)_T > 0 \tag{3}$$

$$\omega = (\partial c'_a/\partial T)_{c_g} > 0\,. \tag{4}$$

In addition, we shall postulate that the dissipation of the released heat is limited by heat transfer from the surface of the plate, *i.e.* we take the temperature within the plate as uniform.

Based on these conditions, we can write for the heat balance in the plate the following equation:

$$-\partial(\Delta T/\partial\tau) = \alpha\,\Delta T - \delta(\partial\gamma/\partial\tau)\,, \tag{5}$$

where

$$\alpha = hL/(D_{eff}\varrho_p\varkappa_p) \tag{6}$$

$$\tau = D_{eff}t/L^2\,. \tag{7}$$

Relative saturation $\gamma(t)$ of the sorbent is described by a relation

$$\gamma(t) = \{m(t) - m(0)\}/\{m(\infty) - m(0)\}\,, \tag{8}$$

where $m(0)$, $m(t)$, $m(\infty)$ signify the amounts of the substance adsorbed at time $t = 0$, $t = t$ and $t \to \infty$. Function $\gamma(t)$ is called a kinetic curve. Other quantities have a following meaning:

$$\delta = [\Delta c_a'(\infty)]_{\text{isoth}} (-\Delta H_{\text{ad}})/\varkappa_p \,, \tag{9}$$

where $-\Delta H_{\text{ad}}$ is the change in adsorption enthalpy [J mol^{-1}], h is the coefficient of heat transfer along the gas-plate boundary [J cm^{-2} s^{-1} K^{-1}] and D_{eff} is the coefficient of intercrystalline diffusion [cm^2 s^{-1}]

$$D_{\text{eff}} = \frac{D_g}{\tau_g} \left(\frac{1 - \alpha_g}{\alpha_g} \varepsilon + 1 \right)^{-1} \tag{10}$$

$\varkappa_p$ denotes the heat capacity of the zeolite [J g^{-1} K^{-1}], ϱ_p is the density of the plate, α_g is a fraction of the intercrystalline void volume in the plate and τ_g is the tortuosity factor.

Solution of the Model

We shall introduce into equation (*5*) dimensionless temperature ϑ defined by equation (*11*)

$$\vartheta = \Delta T / \Delta T_{\text{adiab}} \tag{11}$$

where

$$\Delta T_{\text{adiab}} = \frac{[\Delta c_a'(\infty)]_{\text{adiab}} (-\Delta H_{\text{ad}})}{\varkappa_p} = \frac{[\Delta c_a'(\infty)]_{\text{isoth}} (-\Delta H_{\text{ad}})}{\varkappa_p(1 + \beta)} \tag{12}$$

$$\beta = (-\Delta H_{\text{ad}}) \, \omega / \varkappa_p \,. \tag{13}$$

In this way we obtain the equation

$$\frac{\mathrm{d}\vartheta}{\mathrm{d}\tau} + \alpha\vartheta = \varphi(\tau) \,, \tag{14}$$

where

$$\varphi(\tau) = (1 + \beta) \, \mathrm{d}\gamma/\mathrm{d}\tau \,. \tag{15}$$

We shall substitute for $\gamma(\tau)$ into equation (*14*), the expression obtained from solution of the problem of non-isothermal sorption kinetics^2

$$\gamma(\tau) = 1 - \sum_{n=1}^{\infty} A_n \exp(-q_n \tau) \,, \tag{16}$$

$$A_n = \frac{2(\operatorname{tg} q_n/q_n)^2}{(\operatorname{tg} q_n/q_n) \{q_n^2(\operatorname{tg} q_n/q_n) + 1\} + 2/\beta + 1} \tag{17}$$

and q_n are the positive roots of the equation

$$\beta q_n \operatorname{tg} q_n = \alpha - q_n^2 \; ; \quad n = 1, 2, \dots \tag{18}$$

Integrating equation (*14*) for the initial condition $\vartheta = 0$ at $\tau = 0$, we obtain the final form of equation describing the temperature curve:

$$\vartheta = (1 + \beta) \sum_{n=1}^{\infty} \{A_n q_n^2 [\exp(-\alpha\tau) - \exp(-q_n^2\tau)]\} / (q_n^2 - \alpha) \, . \tag{19}$$

For the adiabatic case with $\alpha = 0$, we get

$$\vartheta = \sum_{n=1}^{\infty} \{2(1 + \beta)^2 \, [(1 - \exp(-q_n^2\tau)]\} / (q_n^2 + \beta^2 + \beta) \, . \tag{20}$$

RESULTS AND DISCUSSION

From the physical point of view it is evident that the temperature curve must pass through a maximum. An analogous conclusion is obtained also from equation (*19*): the function $\vartheta(\tau)$ is evidently continuous within the interval $(0, \infty)$ and for $\tau \rightarrow 0$ and $\tau \rightarrow \infty$ it converges to zero. Furthermore it is clear that function $\vartheta(\tau)$ fulfils in the range $(0, \infty)$ a condition $\vartheta > 0$, so that:

$$\lim_{q_n^2 \to \alpha} [\exp(-\alpha\tau) - \exp(-q_n^2\tau)] / (q_n^2 - \alpha) = \alpha \exp(-\alpha\tau) > 0 \tag{21}$$

and the numerator and denominator of the fraction have for $q_n^2 < \alpha$ and $q_n^2 > \alpha$ identical signs.

One can see that the temperature curve can be interpreted as a probability distribution of a random quantity and the statistical moments of the temperature curves can be therefore calculated (with respect to the origin of coordinates) according to the formula

$$m_n = \int_0^{\infty} \tau^n \vartheta \, d\tau \, , \quad \text{where} \quad n = 0, 1, 2, \dots \tag{22}$$

Integration of equation (*14*) with respect to τ, within the limits from zero to infinity yields

$$m_0 = (1 + \beta)/\alpha \, . \tag{23}$$

Considering equations (*7*) and (*12*), we can see that relation (*23*) is in full accordance with the expression for μ_0 derived in the previous paper[10]:

$$\mu_0 = \int_0^{\infty} (T - T_0)\,\mathrm{d}t = (-\Delta H_{\mathrm{ad}})\, L[\Delta c'_{\mathrm{a}}(\infty)]_{\mathrm{isoth}}\, \varrho_{\mathrm{p}}/h\,. \tag{24}$$

In the same paper we have derived the expression for μ'_1

$$\mu'_1 = \mu_0(\lambda_1 + \tau_{\mathrm{q}})\,, \tag{25}$$

which can be evaluated from the temperature curves using the formula

$$\mu'_1 = \int_0^{\infty} t(T - T_0)\,\mathrm{d}t\,, \tag{26}$$

where λ_1 is the first statistical moment of the kinetic curve in coordinates $\gamma - t^1$

$$\lambda_1 = \frac{L^2}{D_{\mathrm{eff}}}\left(\frac{1}{3} + \frac{\beta}{\alpha}\right), \tag{27}$$

τ_{q} is the characteristic time for the rate of heat transfer through the surface of the plate[10]

$$\tau_{\mathrm{q}} = (\varkappa_{\mathrm{p}}\varrho_{\mathrm{p}}L)/h\,. \tag{28}$$

On basis of the above equations we have derived the formula for m_1

$$m_1 = m_0\left\{\frac{1}{3} + \frac{\beta + 1}{\alpha}\right\}. \tag{29}$$

The expression for the maximum of the temperature curve can be obtained from equation (*14*)

$$\vartheta_{\max} = \frac{1 + \beta}{\alpha}\left(\frac{\mathrm{d}\gamma}{\mathrm{d}\tau}\right)_{\tau = \tau_{\max}} \tag{30}$$

and it expresses a relation between the maximum temperature value and the rate of adsorption at time $\tau_{\max}$ corresponding to the maximum at the temperature curve.

At very small α ($\alpha < 0{\cdot}1$), we are dealing with a "two-stage" process[2]. The first stage is a "quasi-adiabatic" process during which the temperature of the adsorbent quickly approaches its maximum, appearing close to the temperature corresponding

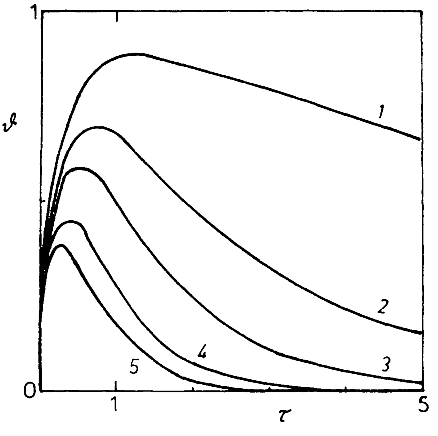

FIG. 1

Theoretical temperature curves $\vartheta - \tau$, for $\beta = 0{\cdot}2$, in dependence on parameter α: *1* $\alpha = 0{\cdot}1$; *2* $\alpha = 0{\cdot}5$; *3* $\alpha = 1{\cdot}0$; *4* $\alpha = 2{\cdot}0$; *5* $\alpha = 3{\cdot}0$

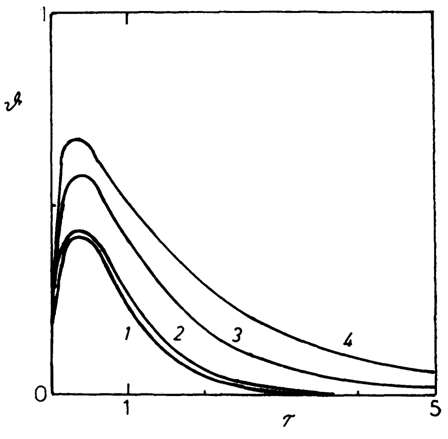

FIG. 2

Theoretical temperature curves $\vartheta - \tau$, for $\alpha = 2$, in depence on parameter β: *1* $\beta = 0{\cdot}01$; *2* $\beta = 0{\cdot}1$; *3* $\beta = 1{\cdot}0$; *4* $\beta = 2{\cdot}0$

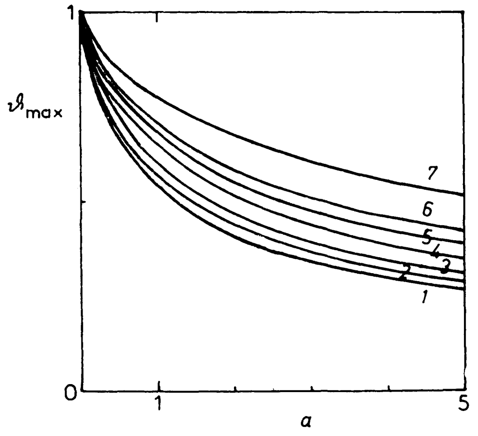

FIG. 3

Dependence of the calculated values ϑ_{max} on α and β: *1* $\beta = 0{\cdot}01$; *2* $\beta = 0{\cdot}1$; *3* $\beta = 0{\cdot}25$; *4* $\beta = 0{\cdot}5$; *5* $\beta = 0{\cdot}8$; *6* $\beta = 1{\cdot}0$; *7* $\beta = 2{\cdot}0$

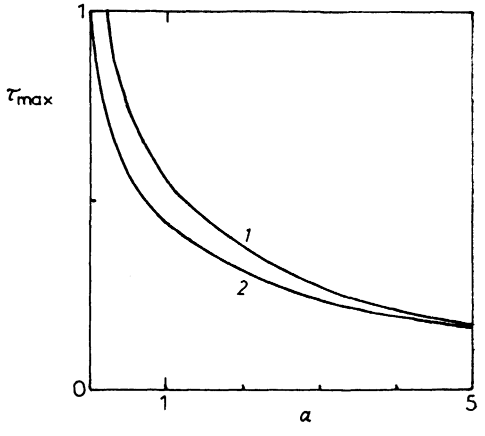

FIG. 4

Dependence of the calculated values τ_{max} on α and β: *1* $\beta = 0{\cdot}01$; *2* $\beta = 2{\cdot}0$

to the adiabatic process. The second stage is given by a relatively slow cooling from the maximum value, to $\Delta T = 0$.Substituting equation (*31*) into (*14*), we obtain an expression describing the dependence of ϑ on time. The kinetic curve for the two stage process can be written as

$$\gamma(\tau) = \frac{\beta}{1+\beta}\left[1 - \exp\left(-\frac{\alpha\tau}{1+\beta}\right)\right] + \frac{1}{1+\beta}\left[1 - 2\sum_{n=1}^{\infty}\frac{(1+\beta)}{\beta+\beta^2+q_n^2}\exp\left(-q_n^2\tau\right)\right]. \qquad (31)$$

The solution for the initial condition $\vartheta = 0$ has a form:

$$\vartheta = \exp\left(-\frac{\alpha}{1+\beta}\tau\right) - 2\sum_{n=1}^{\infty}\frac{(1+\beta)}{q_n^2+\beta+\beta^2}\exp\left(-q_n^2\tau\right). \qquad (32)$$

Examples of the calculated temperature curves are presented in Fig. 1 and 2. Fig. 1 shows the effect of parameter α at constant β. Fig. 2 gives, on contrary, the effect of parameter β at the constant value of α. The dependence of the maxima values of the temperature curves on the parameters α and β is plotted in Fig. 3, while the dependence of the quantity $\tau_{\max}$ (position of the maxima) on the same parameters α and β is presented in Fig. 4.

The theoretical temperature curves $\vartheta - \tau$ can be applied for the evaluation of the experimental data. It is possible to use for this purpose, the above mentioned method of the moments. This method was fundamental in the analysis of the adsorption of cyclohexane in NaX zeolites (ref.[8]) and of xenon in NaA zeolites (ref.[9]). One can also use the method of fitting of the experimental and theoretical kinetic curves, respectively a combination of both these methods.

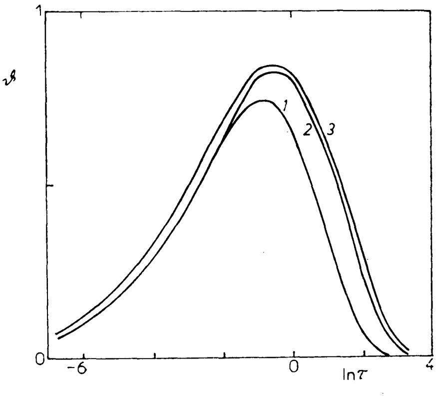

FIG. 5

Calculated temperature curves $\vartheta - \ln\tau$ in dependence on α and β: 1 $\alpha = 1$; $\beta = 1{\cdot}5$; 2 $\alpha = 0{\cdot}5$; $\beta = 1{\cdot}5$; 3 $\alpha = 0{\cdot}5$; $\beta = 2{\cdot}0$

For evaluation of the kinetic parameters by comparison of the theoretical and experimental temperature curves, it is profitable to determine the value of parameter β as well as, the value of the adiabatic temperature increase ΔT_{ad}, from independent equilibrium measurements in each experiment (*i.e.*, it is necessary to find the value of the isothermal adsorption heat and the corresponding slope of the adsorption isobars). A relatively rough, yet fast estimation of the kinetic parameters was based on determination of the size of the temperature curve maxima ϑ_{max}. For a known value of β, it is possible (using a plot of the dependence ϑ_{max} on α and β (Fig. 3)) to find the range within which the quantity α can be found. In the case that the coefficient of heat transfer is evaluated from equation (*24*), it is possible to estimate the value of the diffusion coefficient D_{eff} by means of equation (*6*).

The following method seems to be most reliable for obtaining the kinetic data. The experimental kinetic curves in ϑ – ln t coordinates are compared with a set of theoretical curves (Fig. 5) plotted in the ϑ – ln τ coordinates. The curves are selected for the independently determined parameter β and for a set of values of parameter β and for a set of values of parameter α. The seeked value α is found on basis of the agreement between the experimental temperature curve and one curve from the family of the theoretical curves; for this purpose, the experimental curve is displaced along the axis ln τ. It is obvious from equation (7) that in the above described way one can evaluate the value of ln D_{eff}/L^2, for any arbitrary quantity ϑ according to the following relation:

$$\ln D_{eff}/L^2 = \ln \tau_\vartheta - \ln t_\vartheta\,, \qquad (33)$$

where h is determined (based on α and D_{eff}) from equation (*6*).

It is evident that the above described method can be used not only for verification of the model of simultaneous mass and heat transport but also for determination of the kinetic parameters.

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