

MOLECULAR TRANSPORT IN A TWO-DIMENSIONAL LATTICE OF SORPTION SITES

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It is known from experimental study of the sorption of some aromatic compounds (such as *p*-xylene) in zeolites with the MFI lattice that the adsorption kinetics in such systems exhibits appreciable deviations from the 2nd Fick law. To account for those deviations, whose origin lies in the crystal bulk, the existence of two phases which are not in local chemical equilibrium is postulated: a mobile phase is assumed to occur in the straight zeolite channels whereas an immobile phase is assumed in the zig-zag channels. A microkinetic model is proposed assuming localization of the sorbed molecules on two kinds of centres arranged in a regular two-dimensional lattice, along which migration takes place in agreement with the Langmuir kinetics of exchange of molecules between the occupied and unoccupied centres. For an exact description of the time evolution of the considered physical system the model results in a set of ordinary differential equations which are transformed into a system of two partial differential equations providing a spatially continuous description of the physical system. This approach enables the phenomenological kinetic parameters to be interpreted in terms of the jump frequency of molecules between the various kinds of adsorption centres. For small perturbations in the concentration of the sorbing substance the mathematical model is linearized, and the behaviour of the system is illustrated using the numerical solution of the model equations. In dependence on changes in the model parameters, the transition from the case of pure diffusion along a one-dimensional lattice in the mobile phase, with the zig-zag channels inaccessible, via the case of a slowly establishing local equilibrium between the two sub-lattices, to the limiting case of instantaneously establishing local equilibrium between the sub-lattices is discussed.

Appreciable deviations from the kinetics obeying the 2nd Fick law have been observed in the sorption of some benzene derivatives in zeolites with the MFI structure¹⁻⁴. The anomalies are strongly dependent on the zeolite synthesis and its previous treatment. Deviations of such kind, where additional resistance to the transport of the sorbing substance in the zeolite surface layer (suggested, e.g., in ref.⁴) does not play a major role, can be accounted for in terms of the hypothesis that in the crystal there exist groupings of spatially close centres of several types between which a local equilibrium is not established instantaneously. Thus, the intracrystalline space of the zeolite acts as a two-phase space.

The anomalous sorption kinetics of this kind cannot be treated without an adequate microkinetic model. The model conception concerning the disturbance of the local equilibrium in the crystal must lean on available facts regarding the shape of the channels in the MFI-structure and the packing of the sorbing molecules in them. The necessary facts are summarized below.

The arrangement of channels in zeolites of the MFI structure is schematically shown in Fig. 1: the void space of the zeolite contains two kinds of intersecting channels, i.e. straight channels, which are parallel to the crystallographic b axis, and zig-zag channels, which are parallel to the a axis. The channel dimensions given in Fig. 1 caption refer to silicalite 1 and were taken from ref.⁵, whereas ref.⁶ reports somewhat different dimensions. Other details concerning the structure of MFI zeolites, the shape and dimensions of the oxygen windows which are responsible for the channel permeability, as well as data on the location of molecules of aromatics (p -xylene, benzene) in the MFI zeolite lattice are summarized in refs⁷⁻²¹. No such data pertaining to the location of p -ethyltoluene in the MFI lattice, which is the object of our interest, have been published.

The present knowledge of this matter can be summarized as follows:

- Channels of both types can host molecules of benzene and p -xylene.
- The straight channels are better accessible for adsorption and diffusion than the zig-zag channels.
- Sorption of the molecules mentioned has a localized character with one centre in the straight channels in the space of the channel intersection (segment III in Fig. 1) and one centre in the zig-zag channels (segment I).

With some circumspection, statements *a*) through *c*) can be extrapolated to p -ethyltoluene. In the assessment of the accessibility of the zig-zag channels we lean on our

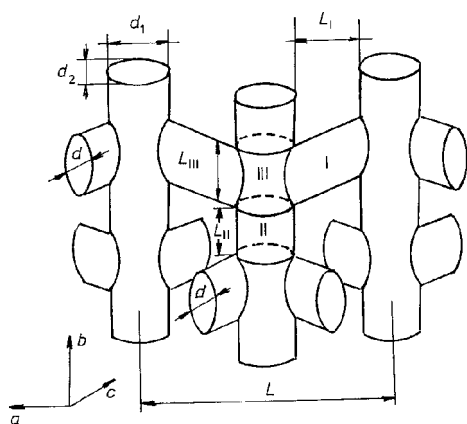


FIG. 1

Layout of channels in the MFI structure. The following length parameters (in nm) are assumed for silicalite 1: d 0.54, d_1 0.51, d_2 0.57, L_1 0.665, L_{II} 0.45, L_{III} ($= d$) 0.54, L 2.006. One-quarter of the elementary cell is represented by the union of spaces I, II, III

own measurements where 5.62 molecules of *p*-ethyltoluene were adsorbed per unit cell²². This sorbed amount – which is certainly not the limiting one – exceeds by 1.62 molecules the assumed sorption capacity of the straight channels for benzene and *p*-xylene.

Based on these premises, we confine ourselves to a model of localized sorption on a two-dimensional lattice of sorption centres. The simplest conception which is consistent with the observed deviations from the 2nd Fick law is that the molecules of the sorbing substance move freely through the straight channels in the one-dimensional sorption site sub-lattice. We will refer to this fraction of sorbate molecules as the “mobile phase”. Furthermore, we assume that the process of slow filling of the zig-zag channels is responsible for the disturbance of the local equilibrium. The sorption sites in the zig-zag channels thus form another sub-lattice for localized sorption (henceforth referred to as the “immobile phase”). The term “mobile phase” should not be interpreted as non-localized adsorption.

THEORETICAL

Sorption Kinetics and Migration in the Two-Dimensional Lattice of Sorption Sites

To simulate the deviations from the 2nd Fick law we will use the lattice shown in Fig. 2. There are two types of centres in the lattice. Centres denoted by the sign X, in which the molecules are mobile, and centres denoted by boxes, in which the molecules

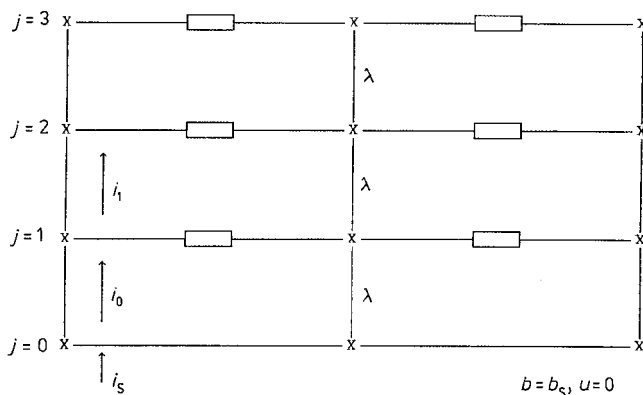


FIG. 2

Two-dimensional lattice of sorption sites in the MFI structure; the symbols X represent sorption sites in the mobile phase, the boxes represent sorption sites in the immobile phase

are immobile. The adsorption centre planes through which the mass flow of the sorbing substance is regarded are oriented perpendicularly to the drawing plane and are labelled by number j starting with $j = 0$ at the crystal surface. The spacing of the planes is λ . In the formulation of the kinetic equations describing the rate of occupation of the lattice layers starting from the crystal surface it is convenient to express the concentration of the molecules via the amount of substance per unit area in the plane perpendicular to the transport direction (i.e., in mol m^{-2}). In this representation, all terms expressing the contributions to the rate of concentration increase of the mobile or immobilized components in the given plane will have the meaning of mass fluxes. Denote the concentration of the X type centres b_∞ and the concentration of the "box" type centres u_∞ . The concentrations of the mobile and immobilized molecules will be b and u , respectively. In the case chosen we have $b_\infty = u_\infty$. No immobilization centres are assumed on the crystal surface, i.e. in the plane with $j = 0$. The concentration of the mobile molecules on the crystal surface is denoted b_S , hence $b_0 = b_S$.

We assume that the Langmuir model holds true for the occupation of all kinds of centres. The concentration of vacant sites, or the probability of their occurrence in a given site of the sorption space, plays a major role in that model. Thus, we write the following equations for the rate of population of occupied centres of the two kinds:

$$db_S/dt = k_a b_\infty \theta_S p - k_d b_S - i_0 = i_S - i_0 \quad (1)$$

$$db_j/dt = i_{j-1} - i_j - k_{bu} u_\infty b_j \eta_j + k_{ub} b_\infty u_j \theta_j \quad (2)$$

$$du_j/dt = k_{bu} u_\infty b_j \eta_j - k_{ub} b_\infty u_j \theta_j \quad (3)$$

$$(j = 1, \dots, j_{\max}).$$

Here k_a and k_d are the adsorption and desorption rate constants, respectively, on the crystal surface, k_{bu} and k_{ub} are the immobilization and mobilization rate constants, respectively, p is pressure, t is the time coordinate, and θ_j and η_j are the fractions of unoccupied centres in the j -th plane in the mobile and immobile phases, respectively,

$$\theta_j = (b_\infty - b_j)/b_\infty \quad (4)$$

$$\eta_j = (u_\infty - u_j)/u_\infty. \quad (5)$$

These quantities have the meaning of probabilities that the jumping molecule finds the site unoccupied. The quantities i_0 , i_{j-1} and i_j in Eqs (1) – (3) are the mass flow densities in the mobile phase in the direction perpendicular to the j -th plane; i_j is the mass flux in the space between the planes labelled j and $j + 1$ and it is a vector whose direction is towards the higher subscript. The quantity i_s is the density of the mass flux from the gas phase into the crystal.

The flux terms are written, in agreement with the Langmuir kinetics, in the form

$$i_{j-1} = k_{bb}b_{\infty}b_{j-1}\theta_j - k_{bb}b_{\infty}b_j\theta_{j-1} \quad (6)$$

$$i_j = k_{bb}b_{\infty}b_j\theta_{j+1} - k_{bb}b_{\infty}b_{j+1}\theta_j, \quad (7)$$

where k_{bb} is the rate constant of the quasichemical reaction for the exchange of the sorbed molecule at the given adsorption site with a vacancy at the neighbouring site. Equations (6) and (7) involve the implicit assumption that such exchange can only take place between nearest neighbour sites. This assumption is warranted in view of the profound analogy between the zeolite systems considered and solid phases containing bulky impurity or interstitial atoms.

Now, let us consider Eq. (2) for a moment without the source terms. By substituting from Eqs (6) and (7) into Eq. (2) we obtain Eq. (8) for the rate of accumulation of mobile molecules in the j -th layer:

$$db_j/dt = \Gamma_{j-1,j}b_{j-1} - \Gamma_{j,j+1}b_j - \Gamma_{j,j-1}b_j + \Gamma_{j+1,j}b_{j+1}. \quad (8)$$

Thus, we obtain a relation known from the transport of atoms or ions in the solid phase (cf., e.g., ref.²²), which contains the jumping frequency $\Gamma_{j-1,j}$. This is the number of completed jumps (failed attempts are excluded) per time unit for a molecule from a given centre in the plane labelled $j - 1$ to the neighbouring centre in the plane labelled j . We have

$$\begin{aligned} \Gamma_{j-1,j} &= k_{bb}b_{\infty}\theta_j; & \Gamma_{j,j+1} &= k_{bb}b_{\infty}\theta_{j+1}; \\ \Gamma_{j,j-1} &= k_{bb}b_{\infty}\theta_{j-1}; & \Gamma_{j+1,j} &= k_{bb}b_{\infty}\theta_j. \end{aligned} \quad (9)$$

The system considered, obeying the Langmuir model for a quasichemical reaction of molecule exchange between the sites in mobile phase, has the following remarkable

property. Taking into account the fact that by definition of the fraction of vacant sites in the mobile phase (Eq. (4)) we have for any j :

$$b_{\infty}\theta_j + b_j = b_{\infty} \quad , \quad (10)$$

we can write Eq. (8) in the form

$$db_j/dt = \Gamma_0(b_{j-1} - 2b_j + b_{j+1}) \quad , \quad (11)$$

where $\Gamma_0 = k_{bb}b_{\infty}$ is the jump frequency of a molecule to a chosen neighbouring site in the case of zero filling of the sorption space, i.e. for the situation where $\theta_j \rightarrow 0$. However, the jump frequency Γ_0 , which is independent of the degree of coverage, rules the microdynamics across the entire concentration region $b \in \langle 0, b_{\infty} \rangle$. This property has already been reported in the literature for single phase systems²³. By completing Eq. (11) with the source terms and combining the definitions (4) and (5) and Eqs (2) and (3) we obtain kinetic equations describing the time dependence of population of the occupied sites in the two sub-lattices:

$$db_j/dt = \Gamma_0(b_{j-1} - 2b_j + b_{j+1}) - k_{bu}b_j(u_{\infty} - u_j) + k_{ub}u_j(b_{\infty} - b_j) \quad (12)$$

$$du_j/dt = k_{bu}b_j(u_{\infty} - u_j) - k_{ub}u_j(b_{\infty} - b_j) \quad (j = 1, \dots, j_{\max}) \quad . \quad (13)$$

This system of equations provides an exact description of the sorption kinetics if additional conditions characterizing (i) the interaction of the system with its environment and (ii) the state of the system at the beginning of the experiment are included.

Examine the situation at a constant concentration of the mobile phase on the crystal surface, i.e.

$$b_j = b^0 \text{ for } j = 0, t \leq 0, \quad b_j = b_S \text{ for } j = 0, t > 0 \quad (14)$$

and with a homogeneous starting spatial distribution of the substance in the two phases, i.e.

$$\begin{aligned} b_j &= b^0 \text{ for } j = 0, \dots, j_{\max}, t = 0 \\ u_j &= u^0 \text{ for } j = 1, \dots, j_{\max}, t = 0 . \end{aligned} \quad (15)$$

Equations (14) and (15) must be complemented with a condition relating to the surroundings of the plane labelled j_{\max} , which is the crystal symmetry plane. This condition is

$$b_{j_{\max}-1} = b_{j_{\max}} \quad (16)$$

The use of discontinuous models is applicable in some cases, and analytical solutions have been obtained for a number of problems of this kind (see, e.g., ref.²⁴). However, in the case of the system of Eqs (12) – (16), which include concentration-dependent source terms, we decided to seek to this dynamic model with a high dimension a corresponding continuous model, consistent with the Langmuir sorption kinetics in a two-phase system (model of ideally localized sorption).

Continuous Model of Sorption Kinetics in the Two-Phase System

Model of ideally localized sorption. The fact has to be borne in mind that if a dynamic model with an infinite dimension is attributed to a model with a finite – although high – dimension, the former exhibits some type of asymptotic behaviour in time of the latter. This has been demonstrated, e.g., by Kelly²⁵ for the case of diffusion into a plate, where the effect of the source terms was ignored. Therefore, we do not require a full equivalence of the two models; we only require that the validity of the discontinuous model derived in the present paper, i.e. Eqs (12) – (16), shall follow from the continuous model to be designed.

Since the term

$$(b_{j-1} - 2b_j + b_{j+1})/\lambda^2$$

is a difference approximation to the partial derivative $(\partial^2 b/\partial y^2)_{t,y_j}$ of the function $b(t,y)$ which is continuous in time as well as in the spatial coordinate y oriented parallel to the crystallographic b axis ($y_j = j\lambda$), we shall regard the function $b(t,y)$ as an approximation to the solution of the system of Eqs (12) – (16) provided that it satisfies the system of partial differential equations

$$\partial b/\partial t = D_b(\partial^2 b/\partial y^2) - \partial u/\partial t \quad (17)$$

$$\partial u/\partial t = k_{bu}b(u_\infty - u) - k_{ub}u(b_\infty - b) \quad (18)$$

for $t > 0$, $0 \leq y \leq L_b \equiv j_{\max}\lambda$.

The conditions (14) – (16) transform into

$$b = b^0 \text{ for } y = 0, t \leq 0$$

$$b = b_s \text{ for } y = 0, t > 0 \quad (19)$$

$$b = b^0 \text{ for } 0 < y < L_b, t = 0$$

$$u = u^0 \text{ for } 0 < y < L_b, t = 0 \quad (20)$$

$$\partial b / \partial y = 0 \text{ for } y = L_b, t \geq 0 \quad (21)$$

It is evident that the application of the straight lines method (see, e.g., ref.²⁶) to this system of equations, when discretizing the spatial coordinate y with a step of λ and using the above difference approximation for the 2nd partial derivative term in Eq. (17), transforms the problem represented by Eqs (17) – (21) into that represented by differential-difference equations (12) – (16). Hence, validity of the continuous model implies validity of the discontinuous model, whereas the reverse is not true.

The function $u(t,y)$ is a continuous function of the coordinates t and y in Eqs (17) and (18) and replaces the system of functions u_j from Eqs (12) and (13). The corresponding time derivatives of the functions b_j and u_j are replaced by the corresponding partial derivatives in Eqs (17) and (18). The term L_b is the distance of the crystal symmetry plane from its surface (hence the crystal half width), and D_b is the diffusion coefficient in the mobile phase, for which

$$D_b = \Gamma_0 \lambda^2. \quad (22)$$

This expression has been obtained by introducing the second partial derivative with respect to y in Eq. (12) after extending the term $b_{j-1} - 2b_j + b_{j+1}$ with λ^2 . When treating the diffusion of atoms in a solid, an alternative expression is used for the diffusion coefficient in terms of the total jump frequency ν and the coordination number z , which represents the number of nearest-neighbour sites to the adsorption centre considered (in the phase in question), to which the sorbate molecule can jump. The term ν_0 is the total number of completed jumps in a time unit to some of the nearest-neighbour sites in the mobile phase. Since we have $\nu_0 = \Gamma_0 z$ and, in our case, $z = 2$, we can write the diffusion coefficient D_b as

$$D_b = (\nu_0/2)\lambda^2. \quad (23)$$

Transition from the concentrations b and u , per unit area, to the concentrations b' and u' per unit crystal volume is a straightforward step in the continuous model. We have

$$b = \lambda b' , u = \lambda u' , b_{\infty} = \lambda b_{\infty}' , u_{\infty} = \lambda u_{\infty}' . \quad (24)$$

By inserting from Eq. (24) in Eqs (17) – (21) we obtain the primed quantities in place of the unprimed, and the rate constants k_{bu} and k_{ub} are replaced by the constants γ and μ which are

$$\gamma = \lambda k_{bu} , \mu = \lambda k_{ub} . \quad (25)$$

Introducing those new constants in Eq. (18) we can omit the primes for the sake of simplicity, the concentrations, however, will have a new dimension, e.g. mol m⁻³.

The model derived exhibits a similarity to the immobilization models designed to describe the process of textile fibre dyeing (e.g. ref.²⁷). There is, however, a substantial difference: in the latter case the mobile phase is constituted by a virtually free liquid in the porous fibre structure, so that the mobilization process resembles desorption into a gas, with no participation of vacant sites in the mobile phase. This fact is mirrored, among other things, by the equilibrium properties of the system, which we are not going to analyze because they are the subject of a separate study. We shall only touch the problem briefly in relation to the generalization of the above kinetic model.

Generalized Model of Sorption Kinetics in the Two-Phase System

The first straightforward step in generalizing the model consists in abandoning the assumption of ideally localized sorption. This step will manifest itself immediately in a different form of the dependence of the boundary condition for Eq. (17) on the sorbate pressure.

The above model, which satisfies conditions of the Langmuir sorption kinetics, can be characterized by the following condition for the mobile phase:

$$b(t,y) = b_s = (b_{\infty} B_1 p) / (1 + B_1 p) \quad \text{at } t \rightarrow \infty , 0 \leq y \leq L_b , \quad (26)$$

where

$$B_1 = k_a / k_d . \quad (27)$$

We shall use the Bragg–Williams model²⁸ as a model of localized sorption with intermolecular interactions which also involves phase transitions in the sorption layer. Consistent with the formalism of this paper, the adsorption isotherm equation is expressed as a dependence of the equilibrium pressure on the vacant site fraction θ :

$$p = [(1 - \theta)/(B_1\theta)] \exp [(zw/RT)(1 - \theta)] . \quad (28)$$

Unless the molecules of the sorbing substance in the mobile phase interact with molecules in the immobile phase, the quantity B_1 has the same meaning as in Eq. (26). The quantity z is the number of neighbouring sites in the mobile phase, hence $z = 2$. The quantity w is the energy of pair interaction between two molecules in the mobile phase per unit amount of substance of molecules in the mobile phase; we have $w < 0$ for attractive interaction. The terms R and T are the universal gas constant and absolute temperature, respectively.

Although the surface concentration b_s as a function of pressure p of the sorbing component cannot be expressed explicitly from Eq. (28), this equation specifies uniquely the new boundary condition for the equation of mass balance in the mobile phase (see Eq. (19)), replacing thus the specification of the previous boundary problem which was given by Eq. (26).

A next thing which has to be re-examined is the concentration independence of the diffusion coefficient D_b . As it seems, this independence can be interpreted as a consequence of compensation of two counteracting effects. In the analysis we shall use the relation between the diffusion coefficient D_A of the component in a binary solution and the so-called corrected diffusion coefficient D_{Ac} , deduced using the thermodynamics of irreversible processes for liquid and solid solutions to correct the diffusion coefficient measured in given conditions to the conditions of the thermodynamically ideal solution²⁹:

$$D_A = D_{Ac} \, d \ln p_A / d \ln C_A , \quad (29)$$

where C_A is the concentration of component A in solution and p_A is the local equilibrium pressure of component A corresponding to concentration C_A . Equation (29) is applicable to our problem provided that the condition of local equilibrium within the mobile phase is satisfied. This fundamental assumption can also be made in the absence of a local equilibrium between the phases. In our case, however, this assumption is only a working hypothesis which has to be verified within further study. Adopting now this hypothesis, we can replace the values D_A , D_{Ac} , p_A and C_A in Eq. (29) by D_b , D_{bc} , p and b , respectively, regarding the corresponding zeolite centres as the other component of the binary solution. Now, if the fraction θ in Eq. (4) is defined in terms of the vacant sites in the mobile phase (and the corresponding function which is continuous in the spatial coordinate y is employed in that equation), and the local equilibrium in the mobile phase is described by means of Eq. (26), the correction factor ($d \ln p / d \ln b$) attains the value

$$(d \ln p) / (d \ln b) = 1/\theta. \quad (30)$$

When passing from the discontinuous model to the continuous model, the coefficient D_b was found concentration-independent. In view of the relation (30), however, this concentration independence is only possible if the corrected diffusion coefficient D_{bc} obeys the relation

$$D_{bc} = D_{b0c} \theta, \quad (31)$$

where D_{b0c} is the corrected diffusion coefficient value at zero coverage of the sorbent. By characterizing the mobility of the molecule on the unloaded sorbent, this quantity is of similar importance for the zeolitic diffusion as the Henry constant for equilibrium sorption. An equation for the mobility of the molecules of the component in the condensed phase where – as in Eq. (31) – the mobility is proportional to the fraction of vacant sites, has been derived by Barrer and Jost³⁰.

The compensating effect, however, cannot be expected if the Bragg–Williams model with lateral interactions is regarded instead of the model of ideally localized sorption. In this case the factor to determine the corrected diffusion coefficient is

$$(\ln p)/(\ln b) = 1/\theta + (2 w/RT)(1 - \theta) \quad (32)$$

and the dependence for D_{bc} can be expected in the form

$$D_{bc} = (v_0/2) \lambda^2 \theta \exp [(2 w/RT)(1 - \theta)] = (v/2) \lambda^2 \theta, \quad (33)$$

where v is the total jumping frequency respecting the increase in the self-diffusion activation energy by a value corresponding to the pair interaction between the adsorbed molecules according to Bragg and Williams. The quantity v_0 is also assumed to obey the Arrhenius dependence on temperature, which is given by the temperature dependence of the constant B_1 . By inserting from Eqs (32) and (33) in Eq. (29) we obtain the diffusion coefficient D_b in the form

$$D_b = (v/2) \lambda^2 [1 + (2 w/RT)\theta(1 - \theta)]. \quad (34)$$

Since $w < 0$ for attractive interaction, the diffusion coefficient in the Bragg–Williams model with attractive interactions between the molecules at $\theta < 1$ is lower than in the case of ideally localized sorption. Equation (34) meets the conditions of transition to the model of ideally localized sorption because D_b becomes concentration-independent at $w = 0$.

The above relations indicate that independence of the diffusion coefficient D_b of the degree of sorbent coverage can be expected for the Henry and Langmuir adsorption isotherms only. In other cases the equation for the mass balance in the mobile phase (cf. Eq. (17)) must be transformed so that the diffusion coefficient D_b stands after the $\partial/\partial y$ operator, hence the diffusion flux divergence term have the form $\partial[D_b(\partial b/\partial y)]/\partial y$.

Linearization of the Models

The two models treated are nonlinear and so they can only be solved by numerical methods. However, kinetic experiments are usually performed in such a manner that small stepwise perturbations in the surface concentration of sorbate are imposed on the system which has been brought in equilibrium. Such measurements enable the concentration dependence of the kinetic parameters to be obtained by means of the following linearized model.

Consider a zeolite crystal in equilibrium with the sorbing substance having an equilibrium pressure p^* so that

$$b = b^*, \quad u = u^* \quad \text{for } 0 \leq y \leq L_b . \quad (35)$$

The actual concentrations of the sorbing substance in the two phases can be expressed as

$$b = b^* + \Delta b, \quad u = u^* + \Delta u . \quad (36)$$

Taking into account the facts that (i) b^* and u^* are independent of the time and spatial coordinates, (ii) $D_b(b^* + \Delta b) \approx D_b(b^*) \equiv D_b^*$, and (iii) the quantities b^* and u^* are interrelated by

$$\gamma b^*(u_\infty - u^*) = \mu u^*(b_\infty - b^*) \quad (37)$$

due to the equilibrium between the phases, we obtain, after substituting from Eqs (36) and (37) in Eqs (17) – (21) including the definitions (25), a system of linear equations describing the boundary problem for functions Δb and Δu

$$\partial \Delta b / \partial t = D_b^* \partial^2 \Delta b / \partial y^2 - \partial \Delta u / \partial t \quad (38)$$

$$\partial \Delta u / \partial t = \gamma^* \Delta b - \mu^* \Delta u , \quad (39)$$

where

$$\gamma^* = \gamma(u_\infty - u^*) + \mu u^*, \quad \mu^* = \mu(b_\infty - b^*) + \gamma b^* .$$

Furthermore,

$$\begin{aligned} \Delta b &= 0 \quad \text{for } y = 0, \quad t \leq 0 \\ \Delta b &= \Delta b_S \quad \text{for } y = 0, \quad t > 0 , \end{aligned} \quad (40)$$

where $\Delta b_s = b_s - b^*$.

The initial conditions (20) are transformed into

$$\begin{aligned}\Delta b &= 0 \quad \text{for } 0 < y < L_b, \quad t = 0 \\ \Delta u &= 0 \quad \text{for } 0 < y < L_b, \quad t = 0.\end{aligned}\quad (41)$$

The symmetry condition (21) takes the form

$$\partial \Delta b / \partial y = 0 \quad \text{for } y = L_b, \quad t \geq 0. \quad (42)$$

The problem described by Eqs (38) – (42) can be solved analytically, the solution is given, e.g., in monograph³¹; an alternative solution is suggested in ref.³².

The amount of substance accumulated in the sorbent from the beginning of the experiment to the time t is an experimentally observable quantity. This amount normalized by the amount of substance sorbed to the equilibrium is referred to as the relative sorbent saturation $f(t)$. Based on the solution of the problem (38) – (42), the function $f(t)$ can be expressed as follows:

$$f(t) = g f_b(t) + (1 - g) f_u(t) \quad (43)$$

$$f_b(t) = [\Delta \bar{b}(t) / \Delta b(\infty)] \quad (44)$$

$$f_u(t) = [\Delta \bar{u}(t) / \Delta u(\infty)] \quad (45)$$

$$g = \Delta b_\infty / [\Delta b(\infty) + \Delta u(\infty)] = \mu^* / (\mu^* + \gamma^*) = 1 / (1 + K_{ub}^*) \quad (46)$$

$$\Delta \bar{b}(t) = \frac{1}{L_b} \int_0^{L_b} \Delta b(y, t) dy \quad (47)$$

$$\Delta \bar{u}(t) = \frac{1}{L_b} \int_0^{L_b} \Delta u(y, t) dy. \quad (48)$$

The quantity K_{ub}^* in Eq.(46) is the effective equilibrium constant expressed in terms of the $\Delta u(\infty) / \Delta b(\infty)$ ratio.

Figure 3 shows simulated kinetic curves f vs $t^{1/2}$ obtained by means of the ZEUS simulator³³ (ZEolite Uptake Simulator) by Mücke. Constant values of $D_b^* = 1.5 \cdot 10^{-14} \text{ m}^2 \text{ s}^{-1}$, $2 L_b = 5 \cdot 10^{-6} \text{ m}$ and $\gamma^* / \mu^* = 1$ were used. The mobilization rate constant μ^* , which varies across six orders of magnitude, is the curve system parameter. In the region of low μ^* values the immobile phase space appears to be virtually inaccessible to mole-

cules occurring in the mobile phase space. The sorption kinetics is controlled by the rate of jumps of molecules along the one-dimensional lattice and in the continuous model is exactly described by the solution of the 2nd Fick law. If all kinetic curves in Fig. 3, including this limiting case, are normalized in accordance with Eq. (43), we obtain for this particular case the relation

$$\lim_{t \rightarrow \infty} f = g . \quad (49)$$

The situation where the equilibrium establishes instantaneously is the other limiting case. This is a case where $\mu^* \rightarrow \infty$. Also in this case, the sorption kinetics is exactly described by the solution of the 2nd Fick law, the effective coefficient D_{eff} , however, must be applied in the form

$$D_{\text{eff}} = D_b^* g = D_b^* (1 + K_{\text{ub}}^*) . \quad (50)$$

There is a continuous transition between the two limiting cases, where the area bounded by the kinetic curve, the $t = 0$ straight line, and the $f = 1$ straight line decreases with increasing value of the mobilization constant μ^* . This area is numerically equal to the first statistical moment of the kinetic curve and characterizes the time constant M_Σ of the kinetic process,

$$M_\Sigma = \int_0^1 t \, df . \quad (51)$$

For the model discussed we derived the expression

$$M_\Sigma = L_b^2 (1 + K_{\text{ub}}^*) / 3 D_b + [K_{\text{ub}}^* / (1 + K_{\text{ub}}^*)] (1 / \mu^*) . \quad (52)$$

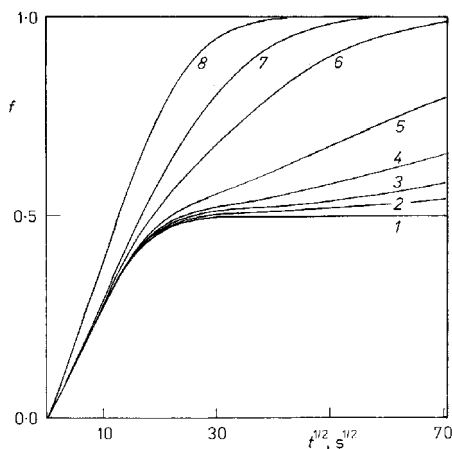


FIG. 3
Simulated f vs $t^{1/2}$ dependences for $D_b = 1.5 \cdot 10^{-14} \text{ m}^2 \text{ s}^{-1}$, $L_b = 5 \cdot 10^{-6} \text{ m}$, $\gamma^* = \mu^*$; μ^* (s^{-1}):
1 $1 \cdot 10^{-6}$, 2 $2 \cdot 10^{-5}$, 3 $4 \cdot 10^{-5}$, 4 $8 \cdot 10^{-5}$, 5 $2 \cdot 10^{-4}$, 6 $8 \cdot 10^{-4}$, 7 $2 \cdot 10^{-3}$, 8 $1 \cdot 10^0$

Two consistency tests complement the above properties of the linearized model in the case of localized sorption:

- 1) D_b^* is independent of b^* , u^* across the entire region of sorption space loading, and
- 2) $\gamma^* \mu^* = (\gamma \mu) u_\infty b_\infty$, which is also independent of u^* , b^* across the entire region of sorption space loading.

CONCLUSIONS

The theoretical analysis gave evidence that the microdynamic description of sorption and transport of molecules within the regular lattice of the two kinds of sorption sites is consistent with the patterns of sorption kinetics of light aromatics (benzene, *p*-xylene, *p*-ethyltoluene) in ZSM-5 zeolites.

The linearized immobilization model derived, including the diffusion in the straight channels of MFI zeolites and the subsequent immobilization process, appears adequate for the processing of kinetic curves of light aromatics in zeolites of these types.

The assumption of local equilibrium within the mobile phase was adopted as a working hypothesis. This enabled the mobility of the sorbed molecules in the straight channels to be expressed by means of diffusion coefficients obtained from the linearized immobilization model.

SYMBOLS

b_∞	concentration of X type centres (Fig. 1)
b	concentration of mobile molecules per unit area in the crystal plane perpendicular to the space coordinate y , mol m ⁻²
b_S	concentration b in the crystal surface layer, mol m ⁻²
B_1	constant in the Langmuir adsorption isotherm defined by Eq. (27), Pa ⁻¹
C	molar concentration of component in solution, mol m ⁻³
D_b	diffusion coefficient of sorbing component in the mobile phase, m ² s ⁻¹
D_{eff}	effective diffusion coefficient defined by Eq. (50), m ² s ⁻¹
f	normalized concentration, or relative sorbent saturation
g	statistical weight of molecules sorbed in the mobile phase, defined by Eq. (46)
i_j	mass flux density between planes labelled j and $j + 1$, mol m ⁻² s ⁻¹
i_S	mass flux density from the gas phase to the crystal, mol m ⁻² s ⁻¹
k_a	adsorption rate constant, s ⁻¹ Pa ⁻¹
k_d	desorption rate constant, s ⁻¹
k_{bb}	quasichemical reaction rate constant, m ² mol ⁻¹ s ⁻¹
k_{bu}	immobilization rate constant, m ² mol ⁻¹ s ⁻¹
k_{ub}	mobilization rate constant, m ² mol ⁻¹ s ⁻¹
K_{ub}^*	effective equilibrium constant
L_b	distance of the crystal symmetry plane from the surface, i.e. crystal half width, m
M_Σ	total time constant of sorption kinetics, s
p	pressure, Pa
p_A	local equilibrium pressure of component A corresponding to concentration C_A , Pa
R	gas constant, J mol ⁻¹ K ⁻¹

T	temperature, K
t	time, s
u	concentration of immobile molecules per unit area in the crystal plane perpendicular to the space coordinate y , mol m ⁻²
u_{∞}	concentration of "box" type centres (Fig. 1), mol m ⁻²
w	energy of pair interaction of two sorbed molecules, J mol ⁻¹
y	space coordinate along the straight channels, m
z	number of neighbouring sites nearest to the given adsorption site in the mobile phase
$\Gamma_{j-1,j}$	frequency of jumps from a centre in the plane labelled $j-1$ to a centre labelled j , s ⁻¹
Γ_0	frequency of jumps of a molecule to a chosen neighbouring site for the case of zero filling of the sorption space, s ⁻¹
γ	immobilization rate constant, m ³ s ⁻¹ mol ⁻¹
γ^*	effective immobilization rate, s ⁻¹
Δ	deviation of a quantity from its equilibrium value
η	unoccupied sites fraction in the immobile phase
λ	distance of two lattice points (Fig. 2) in the y coordinate direction, m
μ	mobilization rate constant, m ³ s ⁻¹ mol ⁻¹
μ^*	effective mobilization constant, s ⁻¹
v	total number of jumps in unit time from a given sorption site to some of the neighbouring sites in the mobile phase, s ⁻¹
v_0	v value for zero loading of the sorption space, s ⁻¹
θ	unoccupied sites fraction in the mobile phase
Superscripts	
0	initial state, i.e. value at time $t = 0$
*	equilibrium state
'	relative to unit crystal volume
Subscripts	
A	pertaining to component A in solution
b	pertaining to the mobile phase
c	corrected to the conditions of a thermodynamically ideal solution
j	labelling of layers in the crystallographic b axis (space coordinate y) direction
j_{\max}	crystal symmetry plane labelling
u	pertaining to the immobile phase
S	pertaining to the surface layer ($j = 0$)

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