THE ROLE OF INERT MATERIAL IN AN ADSORPTION BED

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An influence of the presence of inert material in an adsorption bed is studied, with special regard to the width of breakthrough curves, the breakthrough time and the efficiency and dynamic capacity of an adsorption bed. The positive influence of the inert component is due to the decrease of the effective distribution constant. This influence is reflected in the terms characterizing the axial dispersion in a bed.

The chromatographic determination of Henry constants in the gas/solid phase system is widely applied. It has been developed especially in the laboratory of A. V. Kiselev, who devoted to the applications of gas chromatography in adsorption studies already several monographies[1,2].

In this paper we shall examine one theoretical way how to satisfy the empirical requirement for narrow chromatographic curves, to be met in the determination of Henry constants. Preferentially we shall be concerned with the applications investigating properties of the crystalline zeolites.

The fine-grain size of crystallites in zeolites (in a range of μm) makes it very difficult to ensure reasonable hydrodynamic conditions for the carrier-gas flow along a bed. For this reason, the „pelletized" zeolites — in which crystallites are hold together in the granules by a binder, are used in the practical catalytic and adsorption applications.

In the laboratory-scale studies of zeolite properties it is often useful to work with pure crystallites. The crystallites are, therefore, usually pressed together and then crushed again and sieved. A selected fraction of crystalline agglomerates (roughly 0·5 mm in diameter) is used for the experiments. From private communication[3,4] we have learned about other attempts to ensure the proper arrangement of the crystalline zeolites in an adsorption bed. Successful attempts to deposit zeolitic crystallites on a wide-pore inert support were carried out in the Laboratory of A. V. Kiselev; Lechert deposited the zeolites on a non-porous inert material.

A technique is also described in literature by which porous sorbents and ion-exchangers are deposited on inert cores. These are known as „PLB materials" (porous layer beads)[5].

A question arises, what is the role of the inert material in an adsorption bed. First of all, one is interested in the influence of inert material on the width of breakthrough curves and on the efficiency of a bed — for various kinetic factors. A solution of this problem can find applications also in other fields[6−8].

As a starting point in investigation of the influence of the kinetic effects on a form of breakthrough curves we shall apply the method of separation of the overall adsorption kinetics from the effects of convection and axial dispersion[9,10].

Mathematical Model of the Processes in an Adsorption Column Filled with Adsorbent Diluted by Inert Material

Let us consider an adsorption bed containing particles, which, for simplicity, are all identical in shape and size. A fraction of these particles will stay inert in the sorption process while the remainder will be able to sorb molecules of the given compound from the stream of non-sorbable carrier gas. There will be no other limitations on mutual positions of the inert and sorbing particles and on their relative abundance but that the packing of a bed must represent a quasi-homogeneous medium.

We shall, in the first step, consider the packing of the adsorber as a black box and we shall formulate the mass balance equations for a volume element, making no difference between individual types of particles in the packing.

Under the assumptions summarized in a previous paper[10] we obtain:

$$\partial C(z, t)/\partial t + u\, \partial C(z, t)/\partial z + [(1 - \alpha)/\alpha]\, K_L\, \partial A(z, t)/\partial t =$$
$$= D_z\, \partial^2 C(z, t)/\partial z^2 , \qquad (1)$$

where $C(z, t) = \Delta c(z, t)/\Delta c_\infty$, $\Delta c(z, t) = c(z, t) - c(z, 0)$ is the sorbate concentration change in the mobile phase, expressed as the amount of sorbate in intergranular volume per a unit intergranular volume; $\Delta c_\infty = c(0, t) - c(z, 0)$ is the sorbate concentration change in the mobile phase at the inlet of an adsorber, $A_L(z, t) = \Delta \bar{a}_L(z, t)/\Delta \bar{a}_{L\infty}$ is the instantaneous value of relative saturation of the adsorbent at a given point of a column. $\Delta a_L(z, t) = \bar{a}_L(z, t) - \bar{a}_L(z, 0)$ is the change of the amount of sorbate in a bed packing per a unit volume of the particles in a packing (without distinguishing their quality), $\Delta \bar{a}_{L\infty} = \lim\limits_{t \to \infty} \Delta \bar{a}_L(z, t)$, $K_L \equiv \Delta \bar{a}_{L\infty}/\Delta c_\infty$ is the sorbate effective distribution constant between the volume of column packing and the intergranular space volume, D_z is the coefficient of axial dispersion, u is the linear flow-velocity $u = v/\alpha q$ (where v denotes the volume flow-velocity, q the total cross-section of an adsorber and α the fraction of the intergranular space in a bed).

In the next step, we shall take into account the structure of the bed filling. Let us assume that N_G is the number of sorbent particles and N_i is the number of inert particles. We do not take into account the internal structure of granules of the adsorbent. This structure was considered in a previous paper[6].

Let us introduce the concentration $\bar{a}_G(z, t)$, expressed as the amount of sorbate in the solid phase per the volume of particles of the sorbent; then

$$K_L = \Delta\bar{a}_{L\infty}/\Delta c_\infty = (\Delta m_a/\Delta c_\infty)\,(V_G + V_i)]^{-1} =$$

$$= \frac{\Delta m_a/V_G}{\Delta c_\infty}\,[V/(V_G + V_i)] = (\Delta\bar{a}_G/\Delta c_\infty)\,[N_G/(N_G + N_i)] = K_G\varphi_G\,, \qquad (2)$$

where Δm_a is the overall amount of sorbate in the solid phase in the bed at equilibrium and V_G and V_i are the volumes of the sorbent and inert particles in a bed, respectively.

$\varphi_G = N_G/(N_G + N_i) = V_G/(V_G + V_i)$ is the volume fraction representing the adsorbent.

We can therefore substitute into equation (1):

$$K_L = K_G\varphi_G \qquad (3)$$

and

$$A_G(z, t) \equiv A_L(z, t)\,. \qquad (4)$$

Since K_G represents the true distribution constant of the sorbate between the sorbent volume and intergranular volume, we can interpret this result (which can be expected by intuition) as a decrease of the effective partition constant K_L due to dilution of the sorbent by inert material.

It is evident that, in this way, a problem of the adsorption dynamics in the adsorption bed diluted by inert material is transformed into the problem formulated in a previous paper[10] — assuming that the distribution constant K is replaced by the effective distribution constant $K_L = K_G\varphi_G$. In order to investigate the effect of dilution on a form of the breakthrough curve we shall modify the previously derived expressions[9,10]. It is postulated that the overall adsorption kinetics is not influenced by this type of dilution.

The Characteristics of a Breakthrough Curve

The first normal statistical moment μ'_1 is given by equation

$$\mu'_1 = (\mu'_1)^v + (\mu'_1)^a = (z/u)\,[1 + K_L(1 - \alpha)/\alpha]\,, \qquad (5)$$

where $(\mu'_1)^v$ is the average residence time of a molecule in the intergranular volume and $(\mu'_1)^a$ is the average residence time of a molecule in the adsorbent.

The second central moment μ_2 of the breakthrough curve can be expressed as

$$\mu_2 = \mu_1'(\tau_D + 2\lambda_1 f_a) . \tag{6}$$

The third central moment μ_3 is given by the equation

$$\mu_3 = 3\mu_1'\{(\tau_D)^2 + 2\lambda_1\tau_D f_a + \lambda_2 f_a\} , \tag{7}$$

where

$$\tau_D = 2(D_z/u^2) K_L(1 - \alpha)/\alpha \tag{8}$$

is the time parameter characterizing axial dispersion[10].

$$f_a = (\mu_1')^a/\mu_1' \tag{9}$$

λ_n is the nth normal moment of the kinetic curve, measured for the sample of the adsorption column packing[9,10]. The number of theoretical plates N characterizes the efficiency of an adsorption column. It is given by the relation

$$N = (\mu_1')^2/\mu_2 . \tag{10}$$

The Effect of Dilution of an Adsorption Bed on a Form of Breakthrough Curves

We shall investigate two types of dilution. In a bed of a given length L, containing only particles of a sorbent $(\varphi_G = 1)$, we shall replace definite amount of the sorbent by particles of the inert material so that the required value $\varphi_G < 1$ is reached. b) To a bed of a given length L, containing only particles of a sorbent, we shall add definite amount of the inert material so that the same value φ_G as in case (a) is reached.

The length of the bed will be therefore $L' > L$. Because, according to the assumption in (b):

$$(V_G + V_i)_L = (V_G)_{L'} , \tag{11}$$

we get

$$L'/L = (V_G)_{L'}/(V_G)_L = (V_G + V_i)_L/(V_G)_L = 1/\varphi_G . \tag{12}$$

The corresponding relations for a bed with the inert component — for the case of dilution of the adsorption layer according to (a) — we obtain after substituting in equations $(5)-(10)$ for K_L, $K_L = K_G\varphi_G$.

For the first normal statistical moment of the breakthrough curve we get

$$(\mu_1')_\varphi = \frac{L}{u}[1 + K_G\varphi_G(1 - \alpha)/\alpha] . \tag{13}$$

We shall restrict our discussion at the frequent case $K_G \varphi_G (1 - \alpha)/\alpha \gg 1$, in which the accumulation of a sorbate in the intergranular space is neglected. One can therefore write:

$$(\mu_1')_\varphi \approx (\mu_1')_1 \varphi_G , \qquad (14)$$

where $(\mu_1')_1$ corresponds to the case $\varphi_G = 1$. From equation (8) we get

$$(\tau_D)_\varphi \approx (\tau_D)_1 \varphi_G . \qquad (15)$$

For the second central moment of the chromatographic curve we obtain, using equations (6), (14) and (15)

$$(\mu_2)_\varphi \approx (\mu_2)_1 \varphi_G \vartheta_\varphi/\vartheta_1 , \qquad (16)$$

where

$$\vartheta_1 = (\tau_D)_1 + 2\lambda_1 \qquad (17)$$

and

$$\vartheta_\varphi = (\tau_D)_1 \varphi_G + 2\lambda_1 . \qquad (18)$$

For the efficiency of the column with the inert component we get the expression

$$N_\varphi \approx N_1 \varphi_G \vartheta_1/\vartheta_\varphi . \qquad (19)$$

The function expressed by equation (19) increases monotonously with φ_G. Depending on the extent of participation of the overall adsorption kinetics, the following limiting cases can occur:

$$(\tau_D)_1 \ll 2\lambda_1 \quad \text{and} \quad 2\lambda_1 \ll (\tau_D)_1 \varphi_G .$$

In all cases must be $N_\varphi \leqq N_1$. $\qquad (20)$

We can therefore conclude that — for this way of dilution — the static adsorption capacity of a bed decreases proportionally to $(\mu_1')_\varphi$ and the efficiency of a column deteriorates or, in the best case, it remains unchanged.

For the dilution of the adsorption layer according to (b) we must find at the outlet $(z = L')$ — in agreement with equations (12) and (14) — again:

$$(\mu_1')_\varphi' \approx (\mu_1')_1 . \qquad (21)$$

The primes behind brackets signify that the symbols correspond to the dilution according to (b). For the second central moment of the breakthrough curve it is pos-

sible to derive

$$(\mu_2)' \approx (\mu_2)_1 \, \vartheta_\varphi / \vartheta_1 \tag{22}$$

and the efficiency of an adsorption bed, for this way of dilution, is

$$N' = N_\varphi / \varphi_G \approx N_1 \vartheta_1 / \vartheta_\varphi . \tag{23}$$

From this relation and from equations (17) and (18), an important result is obtained

$$N'_\varphi \geqq N_1 . \tag{24}$$

The equality holds for the case where the effect of axial dispersion is absent. The higher efficiency of a diluted bed is due to the fact that the obtained chromatographic curves are narrower with the diluted beds (see equation (22)).

Grubner and Underhill[11] derived, based on a solution by means of the moments, a simple expression for determination of the breakthrough time t_C — for the given concentration C and frontal arrangement of the experiment:

$$t_C \approx \mu'_1 \left\{ 1 + \frac{\sqrt{\mu_2}}{\mu'_1} T_C + \frac{0 \cdot 166 \mu_3}{\mu_2 \mu'_1} (T_C^2 - 1) \right\} . \tag{25}$$

(In the original paper[11] — instead of the coefficient $0 \cdot 166$, an evidently incorrect value $0 \cdot 208$ was used.) μ_3 is the third central moment of the breakthrough curve and T_C is the argument of the function

$$\frac{1}{\sqrt{(2\pi)}} \int_{-\infty}^{T_C} e^{-x^2/2} \, dx = C , \tag{26}$$

T is the reduced time, defined by equation

$$T = (t - \mu'_1) / \sqrt{\mu_2} . \tag{27}$$

From a practical point of view, of interest are in the first place the low breakthrough concentrations C, for which $T_C < 0$.

We shall investigate now the effect of the dilution according to (b) on the breakthrough time t_C — under conditions at which on the basis of previous considerations, one can expect the maximum effect of the dilution (i.e. for $\lambda_1, \lambda_2 \to 0$). This is the case where only the axial dispersion is effective. From equation (25) we obtain the expressions

$$(t_C)_1 \approx (\mu'_1) \{ 1 - N_1^{-1/2} |T_C| + 0 \cdot 498 N_1^{-1} (T_C^2 - 1) \} , \tag{28}$$

$$(t_C)'_\varphi \approx (\mu'_1)_1 \{1 - N_1^{-1/2}|T_C| \varphi_G^{1/2} + 0.498 N_1^{-1}(T_C^2 - 1) \varphi_G\} \qquad (29)$$

$$N_1 = (\mu'_1)/(\tau_D)_1 \qquad (30)$$

gives the number of plates in the original bed with a pure adsorbent.

Combining equation (28) and (29) one can express the relative increase δ of break-through time due to the dilution according to (b).

$$\delta = 100[(t_C)' - (t_C)_1]/(t_C)_1 =$$

$$= 100 \frac{(1 - \varphi_G^{1/2}) \{|T_C| N_1^{1/2} - 0.498(T_C^2 - 1)(1 + \varphi_G^{1/2})\}}{N_1 - |T_C| N_1^{1/2} + 0.498(T_C^2 - 1)} \qquad (31)$$

Fig. 1 presents the results of calculation of the expression for δ, for a series of values φ_G (with $C = 0.01$, where $T_C = 2.3264$ and $(T_C^2 - 1) = 4.4121$). As expected, the highest increase of efficiency takes place in the low-value region of N_1. Although the validity of equations (25), (28), (29) and (31) for the region of low N_1 ($N_1 < 10$) is limited, it is possible to use relation (31) for the estimation of breakthrough time
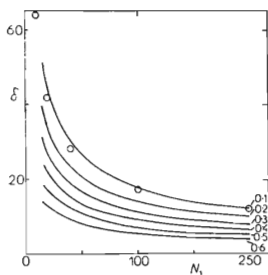

FIG. 1

Dependence of $\delta(\%)$ on N_1; for $C = 0.01$. Solid curves were calculated from equation (31); numbers attached to the curves signify values of parameter φ_G; $\circ$ points were determined by means of exact solution of equation (32), for $\varphi = 0.1$
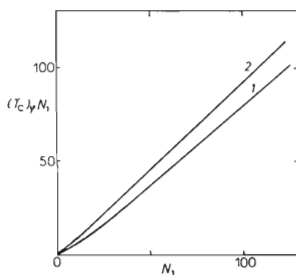

FIG. 2

Dependence of $\tau_C N_1$ on N_1; for $C = 0.01$; based on exact solution of equation (32); 1 $\varphi_G = 1$; 2 $\varphi_G = 0.1$

in a wide range of N_1; in this way, the effect of dilution on the breakthrough time and dynamic capacity can be simulated.

Individual points along the curve $\varphi_G = 0.1$ were obtained from the exact solution of a problem of the adsorption dynamics with axial dispersion[12].

$$C = 1 - 0.5\{\Psi[N/2]^{1/2}(\tau_C^{-1/2} + \tau_C^{1/2})] + \Psi[(N/2)^{1/2}(\tau_C^{-1/2} - \tau_C^{1/2})]\}, \quad (32)$$

$$\psi(\tau) = (2/\sqrt{\pi})\int_0^\tau e^{-\xi^2}\,d\xi, \quad (33)$$

$$\tau_C = t_C/\mu_1'. \quad (34)$$

For the case of a non-diluted bed is $N = N_1$ and $\tau_C = (\tau_C)_1$. For diluted beds we substitute in equation (32) the values $N = N_1/\varphi_G$ and $\tau_C = (\tau_C)_\varphi$.

For δ we get

$$\delta = 100[(\tau_C)_\varphi - (\tau_C)_1]/(\tau_C)_1. \quad (35)$$

The effect of dilution on dynamic capacity F_A of a bed, for different amounts of the adsorbent, is evident from Fig. 2. Based on a numerical solution of equation (32) (which we have carried out for $C = 0.01$ and for a range of parameters N_1), the dependence of $\tau_C N_1$ on N_1 was constructed for a non-diluted ($\varphi_G = 1$) and diluted ($\varphi_G = 0.1$) bed. Let us write:

$$\tau_C N_1 = B_F F_a \quad (36)$$

and

$$N_1 = B_g g, \quad (37)$$

where g is the weight of adsorption packing related to a unit cross-section of a bed. The quantities

$$B_F = [\Delta c_\infty q u(\tau_D)_1]^{-1} \quad (38)$$

and

$$B_g = K_G[u\varrho_G(\tau_D)_1]^{-1} \quad (39)$$

represent constants for the given conditions of the experiment, i.e. for given values Δc_∞, u and the given sorbate and sorbent. ϱ_G denotes the density of particles in the adsorption packing.

One can conclude that the addition of an inert material to the packing of an adsorber effects positively the width both of the frontal and outlet elution curves, as well as, the efficiency of the adsorption bed. In principle, this effect can be used for improvement of the conditions in chromatographic determination of Henry constants of the

compounds sorbed on zeolite catalysts and adsorbents. It is shown that the effect is due to a decrease of the value of the effective distribution constant K_L. This effect is reflected in the terms characterizing axial dispersion in a bed. The overall adsorption-kinetics within the particles of a sorbent is, however, not affected by the application of a given type of dilution.

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Translated by Z. Dolejšek.