Sorption–Diffusion in Molecular Sieves

I. Evaluation of Thermodynamic and Kinetic Parameters by the Gas Chromatographic Pulse Method

Lucio Forni,[1] Carlo F. Viscardi, and Cesare Oliva

Dipartimento di Chimica Fisica ed Elettrochimica, Università di Milano, Via Golgi 19, 20133 Milan, Italy

The gas chromatographic pulse method has been applied to the problem of the evaluation of thermodynamic and kinetic parameters relating to the sorption–diffusion of aromatic hydrocarbons in zeolites at relatively high temperature (613–713 K). Equations derived from the theory of moments and the procedure for collection of data and for their treatment have been adapted to the present case by proper adjustment and simplification, aiming at the separation of the effects of the various sorption–diffusion phenomena involved. The reliability of the parameters thereby evaluated, the probable errors involved, and the limits and advantages of the method are discussed. © 1986 Academic Press, Inc.

INTRODUCTION

When applied to the study of the sorption–diffusion of relatively bulky molecules in zeolites, the gas chromatographic (GC) pulse method may present difficulties connected with the fact that many different phenomena may contribute in determining the shape of the elution peak at the column exit. As a consequence, a great number of alternative methods, under either static or dynamic conditions (*1–9*), have been suggested for these studies and some good reviews, covering various aspects of the problem (see, e.g., Ref. (*10*)), may be found in the recent literature. The principal advantages of the GC pulse method lie in the very simple apparatus required and in the rapidity of data collection, mainly if the signal from the GC detector is processed directly by a computer.

The present paper reports on the application of the method based on the theory of moments of Kubín (*11*) and Kučera (*12*), subsequently adopted by other authors (*13–16*), to the evaluation of thermodynamic

---

and kinetic parameters relating to the sorption–diffusion of aromatics in porous pellets made from zeolitic crystalline powder ("cake").

METHOD

The most useful equations obtained by means of the theory of Kubín and Kučera are those correlating thermodynamic, kinetic, and geometric parameters of the GC system with the first absolute (μ_1') and second central (μ_2) moments of the GC peak. The moments μ_1' and μ_2 may be calculated by numerical integration or may be estimated from the geometric shape parameters of the peak. Other equations may be obtained from the theory (*13–15*), correlating higher-order moments μ_n with physical parameters of the GC column. However, the experimental evaluation of higher-order moments rapidly becomes extremely unreliable with increasing order n of the moment. Therefore, the practical interest for the latter relations drops very quickly.

As reported by Smith and co-workers (*13, 14*) and by Ma and Mancel (*15*), the relations correlating μ_1' and μ_2 with thermodynamic and kinetic parameters of the sor-

[1] To whom correspondence should be addressed.

bent–sorbate system and with geometric parameters, relative to the solid phase and to the GC column, may be derived from the mass balance equations of the sorbate pulse within the column. For a column packed with spherical or pseudospherical pellets of radius R_p (cm), made from zeolitic crystals of radius R_c (cm), the mass transfer process from the gaseous phase to the stationary phase involves three steps: (i) diffusion through the gas film surrounding the pellet, (ii) diffusion through the intercrystalline macropores of the pellet, and (iii) intracrystalline "diffusion" within the micropores of the zeolite crystals.

By assuming (a) the absence of any chemical reaction, (b) a linear adsorption isotherm (i.e., adsorption equilibrium limited to the Henry law region), and (c) an instantaneous injection pulse for a nonisobaric GC column (16) the previously mentioned relations may be written as

$$\mu_1' = f_1(P_r) \frac{\varepsilon L}{u_s^\circ} (1 + \delta_0) \tag{1}$$

$$\mu_2 = \frac{2L\varepsilon}{u_s^\circ} \left[f_2(P_r) \frac{E_A(1 + \delta_0)^2 \varepsilon^2}{(u_s^\circ)^2} + \delta_1 \right] \tag{2}$$

where

$$\delta_0 = \frac{1 - \varepsilon}{\varepsilon} \theta \left[1 + \frac{K}{\theta} \right] \tag{3}$$

$$\delta_1 = \frac{1 - \varepsilon}{\varepsilon} \theta \left[f_1(P_r) \frac{K}{\theta} \delta_{int} + f_1(P_r)\delta_K \right. $$
$$\left. + f_2(P_r)\delta_b \right] \tag{4}$$

$$\delta_b = \frac{R_p^2 \theta}{15} \left(1 + \frac{K}{\theta} \right)^2 \left(\frac{\tau}{\theta} \frac{1}{D_{AB}} + \frac{5}{k_f R_p} \right) \tag{5}$$

$$\delta_k = \frac{R_p^2 \theta}{15} \left(1 + \frac{K}{\theta} \right)^2 \frac{\tau}{\theta} \frac{1}{D_k} \tag{6}$$

$$f_j(P_r) = \frac{2}{j + 2} \frac{P_r^{j+2} - 1}{P_r^2 - 1} \qquad j = 1, 2. \tag{7}$$

In these equations, $f_j(P_r)$ are the correction factors for pressure drop along the column; $P_r = (P_i/P_o)$ is the relative pressure at the column inlet (subscripts i and o indicate inlet and outlet, respectively, and $f_j(P_r)$

= 1 for the isobaric column); E_A (cm² s⁻¹) is the effective axial dispersion coefficient measured at the exit pressure; ε and θ are the external and internal void fractions, referred to the bed of particles and to the pellet, respectively; L (cm) is the column length; u_s° (cm s⁻¹) is the superficial flow rate of the gas at the column exit; $K = (c_i/c_a)_{equil}$ is the thermodynamic parameter (equilibrium constant) for the adsorption process, c_i and c_a (g cm⁻³) being the concentrations of the sorbate in the zeolite crystals and in the gas phase filling the intercrystalline macropores, respectively; k_f (cm s⁻¹) is the mass-transfer coefficient relative to the gas film surrounding the pellet; D_{AB} and D_k (cm² s⁻¹) are the bulk and Knudsen diffusion coefficients, respectively, measured at the exit pressure; and τ is the tortuosity factor for diffusion in the macropores of the pellets. The latter three parameters are related to the effective diffusivity D_c (cm² s⁻¹) within the macropores by the well-known equation (17)

$$\frac{1}{D_c} = \frac{\tau}{\theta} \left(\frac{1}{D_{AB}} + \frac{1}{D_k} \right). \tag{8}$$

As for the δ parameters, δ_0 is connected only with the thermodynamic parameter K; δ_b (s) represents the sum of two contributions of bulk diffusion to mass-transfer resistance, the first contribution being related to the gas film surrounding the particle, and the second to the gas within the macropores; δ_k (s) represents the contribution relative to Knudsen diffusion in macropores; δ_{int} (s) is connected with the time constants relative to the intracrystalline kinetic process. For the latter, three cases may be distinguished:

Case 1. If the rate-determining process is the Fickian diffusion within the micropores,

$$\delta_{int} = \frac{1}{15} \frac{R_c^2}{D_i}. \tag{9}$$

Case 2. If the resistance to mass transfer is localized at the external surface of the

crystal, as suggested in some instances (2, 18),

$$\delta_{int} = \frac{R_c}{3} \frac{K}{k_s} = \frac{R_c}{3} \frac{1}{k_{-s}}. \quad (10)$$

Case 3. If the rate-determining step is the adsorption–desorption process,

$$\delta_{int} = \frac{K}{k_{ads}} = \frac{1}{k_{des}}. \quad (11)$$

In Eqs. (9)–(11) D_i (cm^2 s^{-1}) is the effective diffusion coefficient of the sorbate in micropores; k_s and k_{-s} (both in cm s^{-1}) are the rate constants for the direct and reverse interphase-crossing process, defined by

$$r_{ic} = k_s c_a - k_{-s} c_i, \quad (12)$$

r_{ic} (mol s^{-1} cm^{-2}) being the rate of such a process, whereas k_{ads} (s^{-1}) and k_{des} (s^{-1}) are the rate constants for direct and reverse adsorption, defined by

$$r_{ads} = k_{ads} c_a - k_{des} c_i, \quad (13)$$

r_{ads} (mol s^{-1} cm^{-3}) being the rate of the process.

Of course, in both cases 2 and 3, rate constants are connected with each other by the equilibrium constant K.

The effective axial dispersion coefficient E_A is usually written as the sum of two terms, connected with molecular diffusion and eddy dispersion, respectively,

$$E_A = \frac{D_{AB}}{\tau_l} + \kappa R_p u_s^\circ \quad (14)$$

where κ is a numerical coefficient and τ_l is the external tortuosity factor for the bed of particles.

From a measure of the first absolute moment μ_1' the value of the thermodynamic parameter K may be calculated; from this value and from a measure of the second central moment μ_2 information on the kinetic parameters k_f, D_c, k_s, k_{ads}, and D_i can be obtained. For this purpose, the correlation between the height equivalent to a theoretical plate (HETP) and the moments is employed:

$$HETP = L \frac{\mu_2}{(\mu_1')^2}. \quad (15)$$

The parameter HETP was first introduced by van Deemter *et al.* (*19*) for a Gaussian-shaped peak.

From Eqs. (1)–(11), (14), and (15) is derived the equation

$$HETP = g_2(P_r)A + g_2(P_r) \frac{B\varepsilon}{u_s^\circ}$$
$$+ g_2(P_r) \frac{C_b}{\varepsilon} u_s^\circ + g_1(P_r) \frac{C_{i+k}}{\varepsilon} u_s^\circ \quad (16)$$

in which

$$A = 2\kappa R_p = \kappa d_p \quad (17)$$

$$B = 2D_{AB}/\tau_l \quad 1 \leq \tau_l \leq 2 \quad (18)$$

A (cm) and B (cm^2 s^{-1}) represent the contributions to peak spreading due to eddy and molecular diffusion, respectively; d_p (cm) is the pellet diameter, C_b (s) represents the contribution to the van Deemter parameter C, connected with molecular diffusivity D_{AB},

$$C_b = \frac{d_p^2}{30(1 - \varepsilon)} \left(\frac{\tau}{\theta} \frac{1}{D_{AB}} + \frac{5}{k_f R_p} \right), \quad (19)$$

and C_{i+k} (s) is the sum of contributions to C connected with intracrystalline "diffusion" and Knudsen diffusion in macropores, respectively. For adsorption of relatively bulky molecules in zeolites, as in the present work, $K \gg 1$, so that, from Eqs. (1)–(4), (6), and (7),

$$C_{i+k} = C_i + C_k$$
$$= \frac{2\varepsilon}{1 - \varepsilon} \frac{\delta_{int}}{K} + \frac{d_p^2 \varepsilon}{30(1 - \varepsilon)} \frac{\tau}{\theta} \frac{1}{D_k}. \quad (20)$$

Returning to Eq. (16), $g_j(P_r)$ are the correction factors for pressure drop along the column, given by

$$g_j(P_r) = \frac{f_j(P_r)}{[f_1(P_r)]^2} \quad j = 1,2. \quad (21)$$

The variable P_r may be conveniently eliminated by introducing the relation $P_r = P_r(u_s^\circ)$. For laminar flow, the well-known Blake–Kozeny equation holds (*20*), so that

$$P_r = \sqrt{\frac{300 G_{BK} \eta u_s^\circ L}{P_o} + 1} \qquad (22)$$

where

$$G_{BK} = \frac{(1 - \varepsilon)^2}{\varepsilon^3 d_p^2} \qquad (23)$$

is a constant depending on the geometric parameters of column packing, and η (g cm^{-1} s^{-1}) is the viscosity coefficient of the carrier gas.

The mass-transfer coefficient k_f relative to the gas film surrounding the particles is generally obtained through well-known correlations among the Sherwood (Sh), Reynolds (Re), and Schmidt (Sc) numbers. For laminar flow, a simplified formula may be used, i.e., Sh $\cong 2/G_f$, in which G_f represents the thickness of the gas film, expressed in terms of pellet radius (20). For an isolated sphere $G_f = 1$, so that $k_f R_p = D_{AB}$. Some authors (13, 15) assume this formula to hold also for a bed of particles. We prefer to put $G_f \leqq 1$ and to leave D_{AB}/G_f for $k_f R_p$ in Eq. (19), i.e., to write

$$C_b = \frac{d_p^2}{30(1 - \varepsilon)} G_B \frac{1}{D_{AB}} \qquad (24)$$

where

$$G_b = \frac{\tau}{\theta} + 5G_f. \qquad (25)$$

EXPERIMENTAL

Apparatus. The apparatus employed for the collection of data is shown in Fig. 1. It consists of a U-shaped Pyrex-glass column, ca. 30 cm long and 3 mm i.d., through which a carefully pretreated flow of ultrapure He is led. The outcoming gas enters a flame ionization detector (FID), the electrical output of which is digitalized and fed directly to an EPSON HX20 portable computer. The temperature of the column is controlled within ±0.5 K by means of a proportional-integrative-derivative (PID) temperature recorder–controller, through an electric furnace, heating the 316 AISI S.S. metal block, tightly jacketing the
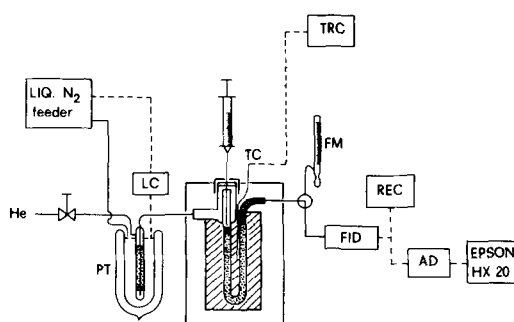

Fig. 1. Sketch of the experimental apparatus employed. PT = helium purging trap (precalcined molecular sieves cooled in liquid N₂), LC = level control, TC = thermocouple, FM = soap-bubble flowmeter, FID = flame ionization detector, TRC = proportional-integral-derivative (PID) temperature recorder–controller, AD = analog-to-digital converter, REC = recorder.

column. Particular care was given to reducing to a minimum any dead volume between the end of column packing and the flame tip of the FID. Furthermore, the adsorbate (strictly speaking, the adsorptive) was injected just within the small flock of quartz wool (1–2 mm long) preceding the packing.

Check of the validity of assumptions. The assumptions on which the method is based need to be checked before the collection of data. This may be done easily. The absence of chemical reactions is verified if the form of the elution peak is close to Gaussian and if no shoulders or "twin" peaks are present. The linearity of the adsorption isotherm is verified if the values of K obtained are independent of peak area m_0 (mV s), i.e., of adsorbate concentration. The instantaneousness of the GC pulse is verified if the duration of adsorbate injection is some orders of magnitude lower than the elution time. The assumption $K \gg 1$ (Eq. (20)) may be easily verified from the results.

Data collection. For each adsorbate pulse, the digitalized signal corresponding to the elution peak was immediately processed by the computer, previously fed with the geometrical parameters of both column and packing and with the value of the Blake–Kozeny constant G_{BK}. G_{BK} and

ε were evaluated, for each column, by means of Eqs. (22) and (23), by conducting some preliminary experiments at different u_s^o and monitoring the pressure P_i of carrier gas at the column inlet. The computer printed the values of peak moments μ_1' and μ_2, of peak area m_0, and of HETP, together with the superficial gas rate u_s^o at the column exit.

For each column, typically a set of 10 to 30 pulses of the same adsorbate were injected at each temperature, by varying u_s^o.

RESULTS

Evaluation of Thermodynamic and Kinetic Parameters

The data relative to the same set of pulses were processed on another computer (HP 9825A) to obtain the values of the thermodynamic parameter K and of the van Deemter constants A, B, C_b and C_{i+k}, by means of Eqs. (1)–(7) and (16)–(21).

Thermodynamic parameter. The calculation of K was done by simply averaging the 10 to 30 values corresponding to the data of the same set. An example is given in Fig. 2. It may be noted that when the column is assumed as isobaric (upper set of data in the figure) the value of K strongly depends on u_s^o, while, by introducing the correction
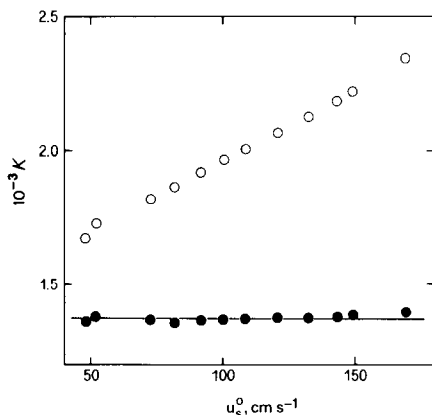

FIG. 2. Effect of correction for pressure drop along the column. Value of K calculated by Eq. (1) (○) by assuming $f_j(P_r) = 1$ (Eq. (7)), and (●) by taking into account the correction ($f_j(P_r) \neq 1$). System: benzene on NaZSM-5 at 633 K.

for the nonisobaric column (Eqs. (1), (3), (7), and lower set of data) K becomes independent of u_s^o, as expected.

Evaluation of the parameters of the van Deemter equation. Although in principle the constants A, B, C_b, and C_{i+k} can be obtained simultaneously by nonlinear regression, a safer procedure was preferred: precalculating two of the constants independently as follows. The second term of Eq. (16) becomes very small and could be neglected by collecting the data at relatively high values of u_s^o. However, we preferred to calculate B from Eq. (18) by putting $\tau_1 = 1$ (19) and by introducing for D_{AB} a value calculated by well-known methods (17). Furthermore, Eq. (24), correlating C_b with the geometric parameters of the GC column, shows that C_b depends essentially on the nature of the carrier gas. The value of C_b was then determined by performing experiments with two different carriers, namely, He and N_2, and by employing the formula

$$\left(\frac{\mathrm{HETP}}{g_2} - \frac{B\varepsilon}{u_s^o}\right)_{N_2} - \left(\frac{\mathrm{HETP}}{g_2} - \frac{B\varepsilon}{u_s^o}\right)_{He}$$
$$= (A_{N_2} - A_{He}) + \frac{1}{\varepsilon}[(C_b)_{N_2} - (C_b)_{He}]u_s^o.$$

$$(26)$$

Remembering Eq. (24) one obtains:

$$\left(\frac{\mathrm{HETP}}{g_2} - \frac{B\varepsilon}{u_s^o}\right)_{N_2} - \left(\frac{\mathrm{HETP}}{g_2} - \frac{B\varepsilon}{u_s^o}\right)_{He}$$
$$= (A_{N_2} - A_{He}) + \frac{1}{\varepsilon}(C_b)_{He}\left(\frac{D_{a.N_2}}{D_{a.He}} - 1\right)u_s^o$$

$$(27)$$

By plotting the first term of Eq. (27) vs u_s^o, the value of $(C_b)_{He}$ may be calculated from the slope of the straight line so obtained, D_{a,N_2} and $D_{a,He}$ representing the bulk diffusion coefficient of the adsorbate (a) in the two different carriers, evaluated as mentioned (17). An additional advantage of this procedure is that, from the so-determined value of C_b and by means of Eq. (24), the value of the geometric constant G_b may also be calculated. The latter, in turn, permits

one to calculate C_b by the same equation, (24), from new values of d_p, ε, and D_{AB}. In addition, if the particles packing the GC column are made by the same procedure, e.g., by pressing the zeolite cake under similar conditions, as a first approximation the same value of G_b may be used for different zeolites. In fact, Eq. (25) shows that the value of G_b corresponds to the sum of two terms. One of them $(5G_f)$ is rigorously constant, since it depends only on the geometric parameters of the column; the other (τ/θ) is constant, provided the zeolite microcrystals are geometrically similar. An example of the evaluation of the constant G_b is shown in Fig. 3, with respect to NaY zeolite. The adsorbate (benzene) was eluted at 633 K. The average diameters of particles and of crystals were $d_p = 0.04$ cm and $d_c = 1$ μm, respectively. Under such conditions was obtained $C_b \cong 0.1C_{i+k}$.

Returning to Eq. (16), once B and C_b were known, the remaining parameters A and C_{i+k} were obtained by nonlinear regression from the experimental values of HETP, u_s° and P_r. Some examples of fitting between experimental data and the curve (solid line) calculated by means of Eq. (16)

FIG. 4. Effect of correction for pressure drop along the column. Curves fitted by Eq. (16). Dashed line fitted by assuming $f_j(P_r) = 1$; solid line, by taking into account the effect of pressure drop $(f_j(P_r) \neq 1)$. System: benzene on NaY at 641 K.

are shown in Figs. 4–7. The parameters B and C_b have been calculated by the procedure described. The same value of G_b has been employed for all the adsorbates and zeolites of the examples. Such a value was obtained by repeating at three different temperatures (673, 653, and 633 K), the procedure used for the example shown in Fig. 3. The three results, differing by ca. 10%, were then averaged. For comparison, in Figs. 4–7 are also reported, as dashed lines, the curves calculated for the isobaric column, i.e., by putting $f_j(P_r) = 1$. It may be observed that, by taking into account the
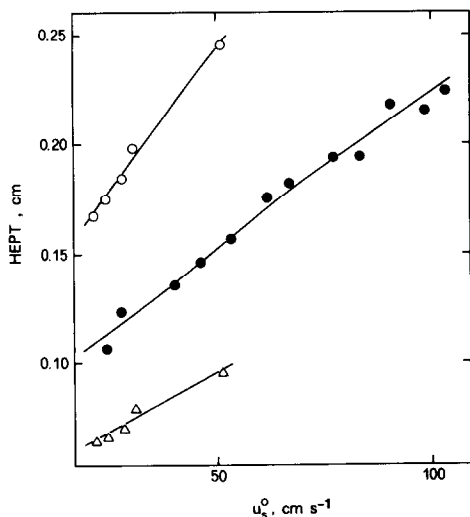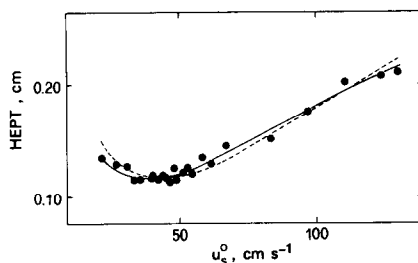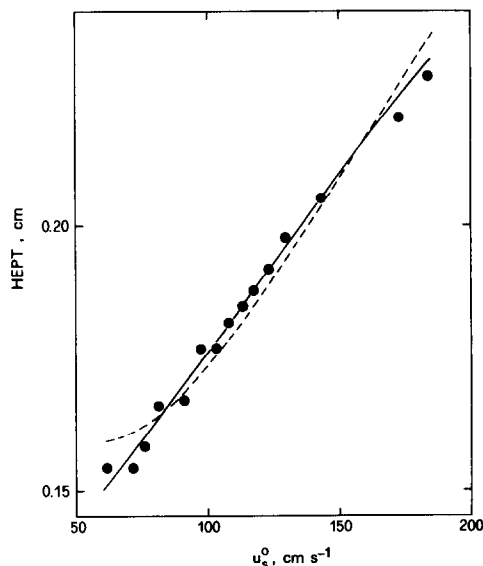

FIG. 3. Example of evaluation of parameters C_b and G_b (system: benzene on NaY at 633 K): (●) carrier gas He, (○) carrier gas N_2 (curve fitted by Eq. (16) in both cases), (△) "difference" straight line (Eq. (27)).

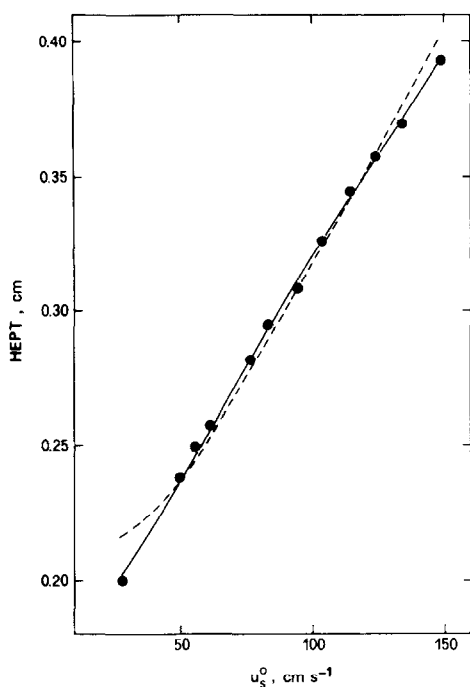FIG. 5. As for Fig. 4. System: p-xylene on NaY at 648 K.

FIG. 6. As for Fig. 4. System: benzene on NaZSM-5 at 653 K.

pressure drop along the column, a much better fit is obtained.

Parameter A. This constant represents the contribution to peak spreading due to axial eddy diffusion (Eqs. (14) and (17)) and it is of minor importance when kinetic parameters have to be calculated, i.e., when only the higher-u_s^o portion of the HETP vs u_s^o curve is considered, as in the present case.

Parameter C_{i+k}. C_{i+k} is the constant which permits one to obtain information on kinetic parameters relative to the mass-transfer process within the stationary phase. However, it contains the contribution of both intracrystalline mass-transfer resistance and Knudsen-type intercrystalline diffusion resistance. The separation of such two contributions may be obtained as follows. By introducing in Eq. (20) the well-known (*17*) equation

$$D_k = 9700 r_p \sqrt{\frac{T}{M}} \quad (28)$$

where r_p (cm) is the average radius of intercrystalline macropores, and M (g mol^{-1}) is the molecular weight of the adsorbate. The contribution C_k to the parameter C_{i+k}, due to Knudsen diffusion, is expressed by

$$C_k = \frac{\varepsilon}{1 - \varepsilon} d_p^2 \sqrt{\frac{M}{T}} 3.44 \times 10^{-6} G_k \quad (29)$$

where

$$G_k = \frac{\tau}{\theta r_p}. \quad (30)$$

As a consequence, Eq. (20) becomes

$$C_{i+k} = C_i + \frac{\varepsilon d_p^2}{1 - \varepsilon} \sqrt{\frac{M}{T}} 3.44 \times 10^{-6} G_k \quad (31)$$

and it may be employed for evaluating both C_i and G_k by conducting some experiments on columns made from particles of different diameter d_p. An example is given in Figs. 8 and 9. From Eq. (31), by plotting

$$y = \frac{(1 - \varepsilon) \sqrt{(T/M)} C_{i+k}}{3.44 \times 10^{-6} \varepsilon d_p^2}$$

vs

$$x = \frac{2 \sqrt{(T/M)}}{3.44 \times 10^{-6} d_p^2}$$

a straight line should be obtained, the intercept and slope of which give directly the values of G_k and δ_{int}/K (connected with C_i through Eq. (20)), respectively. In Fig. 8
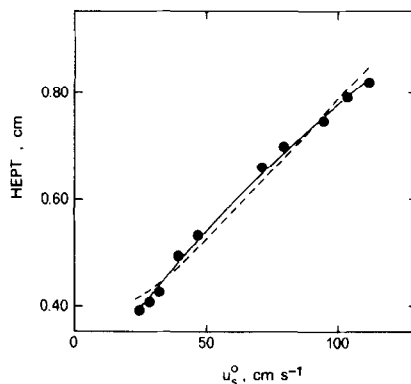

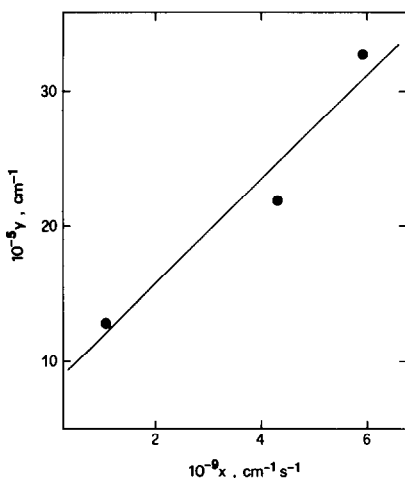FIG. 7. As for Fig. 4. System: toluene on NaZSM-5 at 673 K.

FIG. 8. Example of evaluation of G_k and C_i (see text). System: benzene on NaY at 673 K.
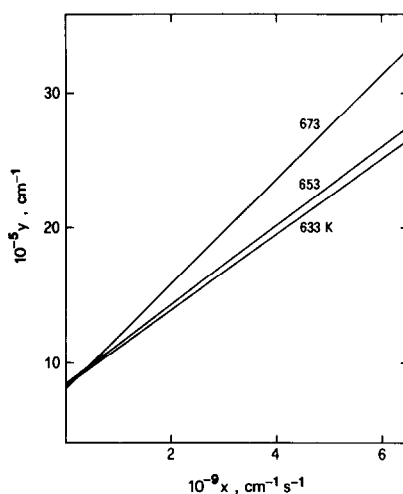

FIG. 9. Example of convergence of straight lines, obtained (see text) at three different temperatures, to the same intercept, i.e., to the same value of constant G_k. System: benzene on NaY.

the fitting between experimental points and the straight line (least-squares method) is shown for benzene on NaY at 673 K. The particle diameter d_p ranged from 0.017 to 0.04 cm. Figure 9 shows that the value of G_k is independent of temperature, as expected. As additional information, for the system in the present example it was observed that the influence of Knudsen diffusion becomes appreciable for $d_p > 0.02$ cm, while for $d_p = 0.04$ cm intracrystalline process and intercrystalline Knudsen diffusion each contribute ca. 50% to C_{i+k}.

As pointed out for constants G_b and C_b, in a similar way the value of G_k permits one to calculate C_k by means of Eq. (29), from new values of d_p, ε, and M. In addition, for crystals of two zeolites, 1 and 2, of similar geometric characteristics, from Eq. (30)

$$G_{k,1}d_{c,1} = G_{k,2}d_{c,2}. \qquad (32)$$

Parameter C_i and kinetic parameters for the intracrystalline process. Once C_b and C_k are known, the contribution C_i to the van Deemter parameter C may be calculated. Then, from Eq. (20),

$$C_i = \frac{2\varepsilon}{1 - \varepsilon} \frac{\delta_{int}}{K} \qquad (33)$$

so that the knowledge of C_i and K permits one to obtain δ_{int}, which is correlated with

the kinetic parameters of the process by means of Eqs. (9)–(11).

By performing experiments with zeolitic crystals of different diameter, one may determine which of the three equations, (9)–(11), better fits the experimental data. Information can thereby be obtained on which is the most probable rate-determining step of the intracrystalline process.

An example is given in Fig. 10, which refers to the system benzene on NaZSM-5 at 653 K. In this example the experimental data are well fitted by a straight line δ_{int} vs
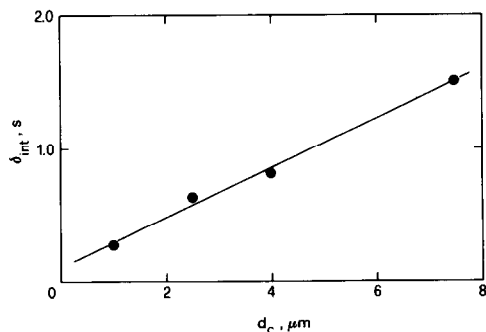

FIG. 10. Dependence of parameter δ_{int} (Eqs. (9)–(11)) on zeolite crystal diameter d_c. System: benzene on NaZSM-5 at 653 K.

d_c. This excludes a Fickian-type intracrystalline diffusion process as the rate-determining step (Eq. (9)), the latter forecasting a linear dependence of δ_{int} on R_c^2.

The resistance to the mass-transfer process seems to be localized at the external surface of the zeolite crystal (Eqs. (10) and (12)). However, since the straight line does not go through the origin, at least a partial contribution of adsorption–desorption process (Eqs. (11) and (13)) should be taken into account.

Reliability of Parameter Values

Casual deviations of experimental data with respect to the various calculated curves have been observed in every case in the present work (see, e.g., Figs. 2–7). This ensures a good reliability of the equations employed. As a consequence, the error affecting the values of the parameters so determined may be estimated from the dispersion of the experimental data with respect to the calculated curves. The standard deviations relative to the most important parameters, i.e., K, C_{i+k} (or C_i), and δ_{int}, have been calculated as ≤ 2, ≤ 5, and $\leq 10\%$, respectively. The increase in the error affecting kinetic parameters C_{i+k} and δ_{int} is clearly connected with the complex procedure to be followed, with respect to that for K. The dispersion of K values is connected with casual errors in estimation of both μ_1' and u_s^o. The value of the standard deviation for K may also be raised by incorrect evaluation of the constant G_{BK} (Blake–Kozeny) leading to imperfect correction for carrier gas pressure drop along the column. This would introduce a noncasual dependence of K on u_s^o.

The experimental error in the evaluation of HETP tends to increase either at very low elution times (less than 1 min), i.e., high gas flow rates and/or high column temperature, or at very high elution times, i.e., low flow rates and/or low temperature (very asymmetric and long-tailing peaks).

Systematic errors can be introduced by imperfect evaluation of column length L, Blake–Kozeny constant G_{BK}, and bed void fraction ε.

Other systematic errors are connected to imperfect evaluation of peak moments. In the present work it has been confirmed that the error relative to μ_1' is usually quite low (1–2%), while that relative to μ_2 is much higher (probably ca. 10%).

The evaluation of μ_2 is in any case the most critical point of the method. We observed that reliable data were obtained only when the shape of the elution peak was close to Gaussian and when tailing was practically absent. This is the most important source of error in the evaluation of kinetic parameters C_{i+k} and δ_{int}. However, it seems probable that systematic errors affecting the moments μ_1' and μ_2 are practically constant, so that the values of kinetic parameters obtained under different experimental conditions should be perfectly comparable.

The value of the Blake–Kozeny constant G_{BK} was obtained, as mentioned, from measurements of the carrier gas pressure P_i at the column inlet. This error affects the determination of correction factors for the nonisobaric column, thereby affecting evaluation of the whole set of parameters K, C_i, and δ_{int}. From the present results, we calculated that the error connected to imperfect evaluation of G_{BK} should affect K, C_i, and δ_{int} by no more than a few percent. The error connected to imperfect evaluation of the geometric parameters L and ε affects directly the value of the thermodynamic constant K (by no more than a few percent) and, to a lesser extent, that of δ_{int}. The influence on the latter is directly proportional to the relative importance of C_k and C_i. Since usually $C_k \ll C_i$, the error on δ_{int} was generally negligible.

To summarize, systematic errors on the whole should affect the value of parameters K and δ_{int} by no more than ca. 10%. Energy parameters, such as enthalpy of adsorption and apparent activation energy of the process, should be unaffected by systematic errors.

CONCLUSION

The procedure followed and the adjustments introduced in the present work have allowed us to illustrate the major advantages and disadvantages connected with the application of the GC method for the evaluation of thermodynamic and kinetic parameters involved in the sorption–diffusion processes of relatively cumbersome molecules in zeolites.

The principal disadvantage is connected to the relatively restricted limits within which the operative parameters are confined. Such limits are due to the numerous hypotheses to be verified, such as absence of chemical reactions and the assumption of a linear equilibrium isotherm for adsorption. The latter imposes a very low concentration of adsorbate in both gaseous and stationary phases. As a consequence, the method can give information practically only on higher-strength sorption centers. When a large spectrum of different-strength centers were present, as in the case of decationated (protonated) zeolites, we were unable to collect significant information either at the lowest detectable concentration of adsorbate in the gas phase, due to nonlinear equilibrium isotherm.

Another disadvantage is connected with the difficult evaluation of higher-order moments. As a consequence, thermodynamic parameters can be evaluated in a relatively simple and safe way from the first-order moment μ_1', while kinetic information must be deduced from the second-order moment μ_2 only. The employment of higher-order moments is not recommended, due to the practically unreliable determination of such values. Therefore, since the value of μ_2 is connected to a relatively large number of different phenomena, kinetic information may be obtained only through a complex procedure, after separation of the various contributions by means of experiments under different conditions. Furthermore, it must be observed that the method does not permit a direct evaluation of the dependence of the mass-transfer rate on concentration, as the form of the kinetic equations is directly involved in the hypotheses on which the method is based. Once the form of such equations is stated, the method allows one only to determine the values of the parameters involved. This is essentially due to the nature of any of the GC methods, in which the form of the elution peak is determined by the whole set of adsorbate concentrations, in both gaseous and stationary phases, ranging from zero to that of the adsorbate pulse.

In spite of such limitations, the method adopted in this work presents some important positive characteristics. As previously mentioned, the most important are the simple apparatus involved and the rapidity of data collection. The method also provided reproducible data, the dispersity of which in any case was quite low.

In our opinion, the method is not recommended if very detailed kinetic information is needed and quantitative absolute data are to be collected. However, it is very useful when a comparison is to be made of the behavior of different zeolite samples under the same experimental conditions and when the effect of different variables on thermodynamic and kinetic parameters is to be evaluated.

conclusion is perfectly in line with that of the present work.

REFERENCES

1. Hattori, T., Murakami, Y., Akizuki, I., and Kamogava, K., in "Proceedings, 5th International Conference on Zeolites" (L. V. C. Rees, Ed.), p. 449. Heyden, London, 1980.
2. Bülow, M., Struve, P., Finger, G., Redszus, Ch., Ehrhardt, K., and Schirmer, W., *J. Chem. Soc. Faraday Trans. 1* **76,** 597 (1980).
3. Eberly, P. E., in "Zeolite Chemistry and Catalysis" (J. A. Rabo, Ed.), ACS Monogr. 171, p. 392. Amer. Chem. Soc., Washington, D.C., 1976.
4. Ruthven, D. M., Graham, A. M., and Vavlitis, A., in "Proceedings, 5th International Conference on Zeolites" (L.V.C. Rees, Ed.), p. 535. Heyden, London, 1980.
5. Kärger, J., and Caro, J., *J. Chem. Soc. Faraday Trans. 1* **73,** 1373 (1977).
6. Gibilaro, L. G., and Waldram, S. P., *J. Catal.* **67,** 392 (1981).
7. Wu, P., Debebe, A., and Ma, Y. H., *Zeolites,* **3,** 118 (1983).
8. Nagy, J. B., Derouane, E. G., Resing, H. A., and Miller, G. R., *J. Phys. Chem.* **87,** 833 (1983).
9. Doelle, H.-J., and Riekert, L., *Angew. Chem. Int. Ed. Engl.* **18,** 266 (1979).
10. Ruthven, D. M., *Amer. Chem. Soc. Symp. Ser.* **40,** 320 (1977).
11. Kubín, M., *Coll. Czech. Chem. Commun.* **30,** 1104, 2900 (1965).
12. Kučera, E., *J. Chromatogr.* **19,** 237 (1965).
13. Schneider, P., and Smith, J. M., *AIChE J.* **14,** 762 (1968).
14. Suzuki, M., and Smith, J. M., *Chem. Eng. Sci.* **26,** 221 (1971).
15. Ma, Y. H., and Mancel, C., *Adv. Chem. Ser.* **121,** 392 (1973).
16. Padzerník, O., and Schneider, P., *J. Chromatogr.* **207,** 181 (1981).
17. Satterfield, C. N., "Mass Transfer in Heterogeneous Catalysis." MIT Press, Cambridge, Mass., 1970.
18. Kärger, J., Heink, W., Pfeifer, H., and Rauscher, M., *Zeolites* **2,** 275 (1982).
19. van Deemter, J. J., Zuiderweg, F. J., and Klinkenberg, A., *Chem. Eng. Sci.* **5,** 271 (1956).
20. Bird, R. B., Stewart, W. E., and Lightfoot, E. N., "Transport Phenomena." Wiley, New York, 1960.