



Letter to the editor

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Abbreviations

- D_c : Intracrystalline diffusivity ($\text{m}^2 \text{s}^{-1}$)
 D_p : Macropore diffusivity ($\text{m}^2 \text{s}^{-1}$)
 K : Dimensionless Henry law constant (-)
 r_c : Radius of microporous (crystal radius) (m)
 R_p : Particle radius (pellets/beads radius) (m)

The authors of the open access article focus in section 3.2—“What can be measured and what can go Wrong” on the work of [1] to explain that a nonlinear ZLC under equilibrium control is very similar to a normal ZLC response in kinetic control and care must be taken in analyzing ZLC data.

In such work Silva and Rodrigues [1] reported a series of ZLC experiments showing perfect coincidence of concentration responses for beads with different size; Brandani and Mangano [2] say that Silva and Rodrigues [1] took that result as *prima facie* evidence of micropore diffusion control and proceed to determine the diffusivity of CO_2 in crystals of zeolite 13X without checking for linearity of the system, taking wrong conclusions. This is not true, since Silva and Rodrigues [1] used also ZLC experiments at different

temperatures, to calculate the activation energy of the diffusional process ($\approx 27 \text{ kJ/mol}$), very different from the one that should be observed if a macropore diffusional or equilibrium regime was the dominant one in the system. It is well known, that in such regime the activation energy for the apparent reciprocal time constants ($D_p/R_p^2(1+K)$) or for the equilibrium regime (directly related through the adsorption equilibrium parameter K) should be in the order of the heat of sorption, which in the work of Silva and Rodrigues was around 43.1 kJ/mol . Moreover, Silva and Rodrigues [1] showed that for the system $\text{CH}_4/13\text{X}$ indeed such equilibrium regime is observed. Accordingly, the conclusions taken by Silva and Rodrigues [1] for the system $\text{CO}_2/13\text{X}$ were reached from the simultaneous: (1) effect of differently sized beads ZLC experiments showing perfect coincidence of concentration vs time responses and (2) the effect of temperature on ZLC desorption curves, that give rise to the calculation of an activation energy of diffusion far away from the value of the heat of sorption.

Brandani et al. [3] replicated ZLC experiments for the same system ($\text{CO}_2/13\text{X}$) in commercial beads of a different batch, at a fixed temperature of $38 \text{ }^\circ\text{C}$, and concluded that the system was dominated by macropore diffusion control regime. However, strangely they forgot to study the influence of temperature in ZLC as it should be, to show clearly that the apparent reciprocal time constants of diffusion ($D_p/R_p^2(1+K)$) measured follow indeed a van't Hoff temperature dependence related with the value of K (linked to the adsorption equilibrium isotherm), and therefore justify clearly their conclusions. This study was clearly shown in the work of Silva and Rodrigues [4] performed in pellets of 5A with n-pentane as the sorbate (that the authors Brandani et al. [3] forget to refer in Table 2), where a macropore controlled regime was observed. In such work three types of studies were shown: (1) the effect of zeolite crystal size in pellets of the same size using ZLC technique; (2) the effect of temperature on the respective ZLC desorption curves, and (3) the effect of temperature on time constants of diffusion measured from independent uptake rate experiments with a gravimetric technique. The two studies in the ZLC together with the use of an independent technique (if possible), are

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the main proof to clarify with no doubts, which is the controlling regime being measured in binder adsorbent materials. At the same time the adsorption equilibrium isotherm should be measured preferably by an independent technique such as the gravimetric or piezometric [1, 4]) and the parameters shown in the published work.

Concerning section 4-Recommendations the authors forget to recommend to the readers that in all ZLC adsorption studies it is of fundamental importance to study the effect of temperature, in order to calculate the respective activation energy of the reciprocal diffusional time constants. This is important, especially in kinetic studies performed in pellets/beads of commercial adsorbents, to clarify which of the diffusional mechanisms (micropore or macropore) govern the system. Again, we remark that the activation energy for micropore diffusion, is generally very different (much lower) from the one that govern the macropore controlled diffusional regime, which is generally linked to the heat of sorption (through parameter K) according to the Van't Hoff relation, measured from independent experiments (gravimetric/volumetric-piezometric/chromatographic, etc.).

We agree with the authors Brandani and Mangano [2] that reported crystal diffusivities measured by Silva and Rodrigues [1] are 6 orders of magnitude lower than the self-diffusivities measured by PFG-NMR [5]. However, it is very well known from literature that diffusivities measured by PFG-NMR (microscopic technique) are very different from the ones measured from macroscopic techniques [6], especially in small crystal size pelletized/bead samples, where the results seem to agree only when macroscopic studies (ZLC, gravimetric, piezometric, etc.) are performed in pure large crystals (above 30 μm). Ruthven [6] clearly show that the crystal diffusivity measured in different batch samples made in different laboratories and also studies in completely pure different crystal sizes, can vary by orders of magnitude.

Concerning the system CO_2/NaX , we take this opportunity to highlight an important reference concerning the work of Bullow [7], who revealed from piezometric studies of CO_2 in very large crystals of NaX ($\approx 100 \mu\text{m}$), that the sorption kinetics can be a complex sorption process in sorbate uptake and release during experiments of adsorption/desorption, comprised of a slow, hitherto unknown rate mechanism superimposed on a very fast intracrystalline diffusion. The instability of sorption complexes in synthetic faujasites was also observed by Riekert [8] for the system CO_2/HY , where it was shown that the amount of sorbate in the solid decreases spontaneously under certain conditions, although the pressure of the gas increases. This instability appears to be of general interest because it indicates that the uptake of the sorbate can induce changes in the structure of the solid. It was also shown [8], that the approach to this “metastable” equilibrium, where the amount of sorbate in the solid decreases spontaneously is much slower than the approach

to the other equilibrium states, where it follows typically the normal pattern. Moreover, several issues/problems can arise in the manufacture of commercial binder adsorbents related with the shaping processes and selection of the binder, that can have a great influence in the kinetic properties of adsorbents due to pore-closure effects related to cation redistribution, skin barriers, unknown rate mechanisms, etc. [9].

Concerning ZLC systems with a bi-porous material refereed in section 3.11, the authors say that an analytical solution for the ZLC with a biporous material is available [10], that has double infinite summations and it can be computationally easier and faster to invert numerically the solution in the Laplace domain using the approach of Duncan and Möller [11] for the model with a distribution of particle sizes. Once more they forget to refer that Silva and Rodrigues [12] developed a similar solution in a complete different form and give several recipes on how to apply and analyze ZLC data in bi-porous adsorbents.

Concerning sub-section 3.4 about heat effects in ZLC a criterion is given (based on a numerical solution using trial and error) by calculating the value of a dimensionless group (Eq. 14) being the condition for near isothermal responses to be lower than 1. Silva et al. [13] developed the same criterion from a much elegant analytical solution of the ZLC system with heat effects, indicating that for an isothermal system the same dimensionless group should be lower than 0.1. Following these two works Brandani [14] commented on the paper of Silva and Rodrigues [13] explaining that the analytical solution is not proper for the ZLC system because the linearization of the adsorption equilibrium system of equations is not applicable over the required range. Silva and Rodrigues rebuttal [15] states that an approximation is always an approximation but that doesn't invalidate the fact that the dimensionless group of importance to analyse heat effects in ZLC, came from a nice analytical solution instead of repeated numerical simulations.

The ZLC technique was built to be a simple technique to measure the crystal diffusivity using a macroscopic technique by eliminating the effect of axial dispersion in chromatographic studies, but if it is necessary to write a review paper of around 30 pages to give lessons on how to use it and about what can be wrong, using examples from works of experienced researchers in the field, it means that the method is tricky and can lead to a lot of pitfalls and misunderstandings. In such case, we would prefer to look at the first paper shown by Eic and Ruthven [16], and apply the simple diffusion equations reported in the fundamental book to get kinetic information of the adsorbents in pellet/beads form as they will be used in commercial applications: “The Mathematics of Diffusion” by J. Crank [17]. These procedures can be used to calculate in a simple way the kinetics of sorption in binder adsorbents, and were of a fundamental importance for the engineering of adsorption processes in the last

50 years. The title of this letter could have been “50 years of experience with shallow bed technique” as learned by one of us and reviewed by Hahn et al. [18] before Eic and Ruthven [16] popularized ZLC name.

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Yours Truly,

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