diffusion-fundamentals

The Open-Access Journal for the Basic Principles of Diffusion Theory, Experiment and Application

Towards Observation of Single-File Diffusion Using TZLC

Abduljelil Iliyas[1], *Mladen Eić*[1*], *M. Hassan Zahedi-Niaki*[2] *and Sergey Vasenkov*[3]

[1]Dept. of Chemical Engineering, University of New Brunswick, Fredericton, Canada
[2]Department of Chemical Engineering, Laval University, Québec, Canada
[3]Chemical Engineering Dept., University of Florida, Gainesville, USA

[*]Corresponding author: meic@unb.ca

1. Introduction

The growing interest in the application of one-dimensional (1D) molecular sieves both as solid catalysts and selective adsorbents has stimulated considerable attention in the study of diffusive transport of guest molecules in the 1D pores. It has been established that normal Fickian diffusion is not necessarily applicable to describe the diffusion mechanism of guest-host interaction in 1D microporous solids, particularly when the diameter of the diffusion molecule is greater than channel radius [1]. For these systems, single-file diffusion mechanism has been employed to interpret the data from experimental studies using techniques such as PFG NMR [1] and QENS [2] to reasonable degree of correlation.

Recently, we have compared the tracer exchange curves obtained with 3-D toluene/β-zeolite with those of 1-D toluene/ZSM-12 system under similar conditions [3]. A non-linear behavior was obtained for the long-time asymptote in the 1-D system. This behavior can be explained by the existence of a distribution over the channel lengths in spherical particles of ZSM-12. The objective of this study is to provide evidence of the suitability of tracer ZLC technique in observing molecular transport under conditions of anomalous, single-file diffusion. More specifically, we aim to observe the center-of-gravity diffusion mechanism, which is expected for sufficiently large diffusion times in single-file systems of finite length [4, 5]. In relation to this, the tracer exchange profiles of large probe molecules, i.e., toluene having kinetic diameter of 0.61nm in a host circular channeled SAPO-5 (0.73nm dia.) and elliptical channeled ZSM-12 (0.56 x 0.6 nm dia.) is compared to the corresponding tracer exchange profiles of smaller guest molecules, e.g., water ($D \approx 0.26$nm) and/or acetylene ($D \approx 0.33$nm).

2. Experimental

The detailed synthesis procedure for ZSM-12 and SAPO-5 samples used in this study is described elsewhere [6]. Textural and morphological characterizations were performed using BET, SEM and XRD methods. The tracer exchange profiles of acetylene, water and toluene were carried out using TZLC technique [7] and continuously monitored with a quadrupole mass spectrometer (Dycor Dymaxion Quadrupole MS).

3. Results and Discussion.

The SEM, XRD and N_2-adsorption results confirmed that the as-synthesized samples are of very good quality with high crystallinity. Toluene molecules in SAPO-5 and ZSM-

12 exhibit a significant deviation in the shape of the measured tracer exchange curves from monoexponential behaviour (Fig.1). The monoexponential behaviour is expected in the limit of large times for normal, i.e. Fickian diffusion in channel systems with one and the same channel length. The results in Fig.1 are in agreement with the expectation of the existence of the distribution over the channel lengths in sorbent particles. For the case of the center-of-gravity diffusion, which we expect for toluene, the influence of the distribution over the channel lengths on the measured curves should be further enhanced in comparison to the normal diffusion. Such an enhancement is expected because the center-of-gravity diffusivity is inversely proportional to the channel length. Hence, the distribution over the channel lengths should lead to a larger gap between the rates of tracer exchange in channels with different lengths for the case of the center-of-gravity (single file) diffusion than for the case of normal diffusion.

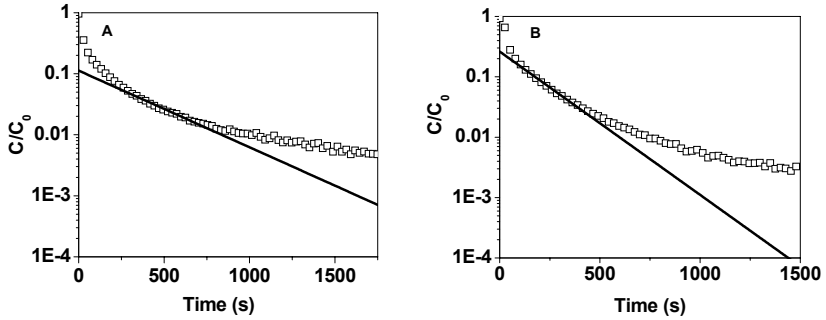

Fig 1. Experimental tracer ZLC exchange profiles of toluene at P = 0.34 torr and 30°C showing deviation from Fickian diffusion (i.e., solid lines). (A) ZSM-12; (B) SAPO-5.

To verify the existence of such additional distribution over diffusivities leading to an enhancement of deviations of the tracer exchange curves in Fig.1 from the monoexponential behaviour, tracer exchange profiles will be measured with much smaller molecules. In particular, we plan to study acetylene/SAPO-5, water/SAPO-5 and water/ZSM-12 systems, which are expected to follow the well-established Fickian-type diffusion because the kinetic diameters of both sorbates are smaller than the radius of host channels.

4. Conclusion

This study aims to provide first-time TZLC evidence of the occurrence of anomalous, single-file diffusion in microporous sorbents.

5. References

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