

# COMMENTS

## Comment on “Computer Simulation of Incommensurate Diffusion in Zeolites: Understanding Window Effects”

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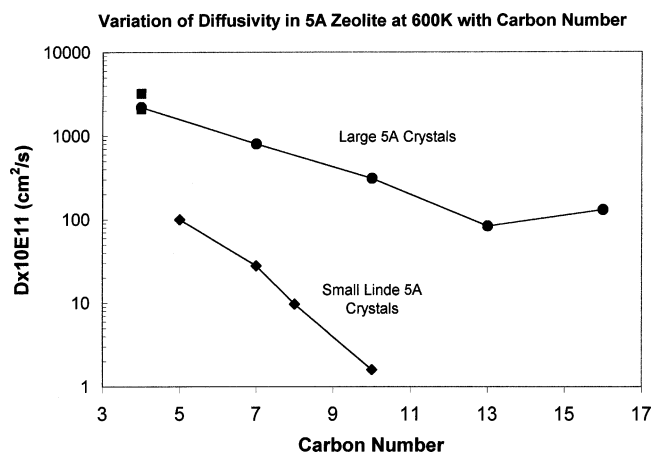
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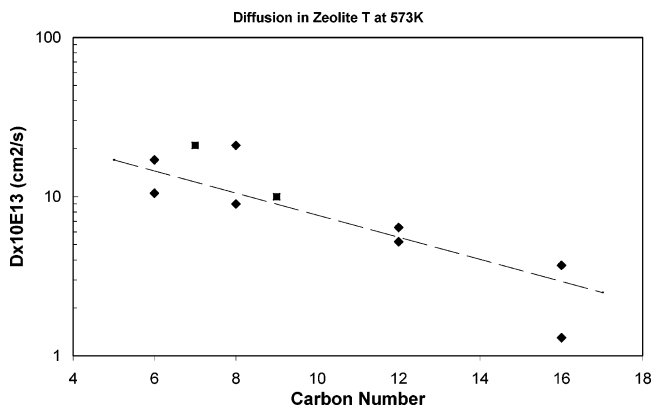
This paper<sup>1</sup> presents an interesting example of the power of molecular simulations to predict the diffusivities of sorbate molecules in zeolite adsorbents under sterically restricted conditions. There are, however, two major points which should not be allowed to pass without comment.

(1) **Diffusivities for Linear Alkanes in 5A Zeolites.** Figure 11b, which purports to show the experimental data of Eic and Ruthven<sup>2</sup> extrapolated to 600 K, indicates a clear maximum in the plot of diffusivity vs carbon number at C<sub>10</sub>. This is in accordance with the molecular simulation results which also suggest a maximum at C<sub>10</sub>, leading the authors to state: “The agreement between simulated data on a cation-free LTA type sieve and the experimental data on a cation-loaded LTA type zeolite is remarkable.” In fact the experimental data of Eic and Ruthven, which are reproduced in Figure 1, show a monotonic decline in diffusivity with carbon number. There is no evidence of a maximum in the diffusivity at C<sub>10</sub>. It should be noted that the ZLC measurements reported by Eic and Ruthven were made using several different samples of relatively large (7.3–55  $\mu$ m) laboratory synthesized crystals of 5A zeolite. Earlier gravimetric data for small (3–4  $\mu$ m) commercial Linde 5A crystals obtained by Loughlin, Derrah, Doetsch, and Vavlitis<sup>3–5</sup> were included for comparison. As may be seen from Figure 1, the two data sets are quite distinct with the reported diffusivities for the commercial material being substantially smaller and showing a steeper decrease with carbon number. We now suspect that the low diffusivity values observed for the commercial material reflect a surface resistance resulting from the severe conditions used in the initial dehydration step, as suggested by Kondis and Dranoff many years ago.<sup>6</sup> However, neither data set shows any evidence of a maximum in diffusivity at C<sub>10</sub>. The plot shown in Figure 11b of the paper by Dubbeldam and Smit is misleading and could only have been obtained by a judicious selection of data points from the two different data sets.

(2) **The “Window Effect” in Zeolite T.** The 1973 paper by Gorring<sup>7</sup> in which the idea of a “window effect” was first introduced is probably one of the most frequently cited references in zeolite science. Unfortunately, because the reported effect appears novel and interesting the validity of Gorring’s experimental data has often been accepted without critical reexamination. He used very large (5 gm) samples of small (micron sized) zeolite crystals and made integral gravimetric measurements between zero loading and one atmosphere of sorbate pressure. Only adsorption measurements were made and neither the mass of the sample nor the pressure step was changed to check for system linearity. Anyone with practical experience of this kind of measurement would realize that it would be



**Figure 1.** Variation of corrected diffusivity ( $D_0$ ) with carbon number for linear alkanes in 5A zeolites at 600K. ■,▲; gravimetric data of Yucel obtained with 3 different samples of large 5A crystals.<sup>10</sup> ●, ZLC data of Eic and Ruthven<sup>2</sup> for large laboratory synthesized 5A crystals. ◆, gravimetric data of Doetsch<sup>3</sup> and Vavlitis<sup>5</sup> for small (3–4  $\mu$ m) commercial 5A crystals.



**Figure 2.** Variation of diffusivity with carbon number for linear alkanes in Zeolite T at 573K. ■, Data of Magalhaes et al.;<sup>9</sup> ◆, data of Cavalcante et al.<sup>8</sup> ( $D_0$ ).

virtually impossible to obtain reliable intracrystalline diffusivity data from such experiments. The results would almost certainly have been impacted by nonlinearity, extracrystalline diffusion and heat transfer effects. Such considerations led two independent research groups to attempt to reproduce these measurements using more modern experimental techniques.<sup>8,9</sup> This is not straightforward since zeolite T is a poorly defined material being an intergrowth of erionite and offretite. Cavalcante et al.<sup>8</sup> therefore used two different materials containing different proportions of offretite and erionite. Their results are shown, together with the data of Magalhaes et al.<sup>9</sup> in Figure 2. Although the data show considerable scatter the two data sets are remarkably consistent and suggest a monotonic decline in diffusivity with carbon number. There is no evidence to suggest that the minimum and maximum reported by Gorring (at C<sub>8</sub> and C<sub>12</sub> respectively) are genuine.

Although, on the basis of this evidence, it would be presumptuous to state that the “window effect” does not exist,

I believe that it is reasonable to assert that there are, as yet, no *reliable* macroscopic measurements that show the existence of such an effect.

### References and Notes

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