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Diffusion of alkane mixtures in MFI zeolite

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The proper description of mixture diffusion in zeolites is important in several separation and reaction applications [1,2]. In recent years molecular dynamics (MD) simulations have been used to investigate diffusion of mixtures of molecules in a variety of zeolite topologies such as AFI, FER, MFI, BEA, ISV, FAU, LTA, CHA, MOR, and DDR [3–8]. These studies show that the zeolite structure, topology and connectivity have a strong influence on the mixture diffusion characteristics. For zeolites with intersecting channel structures, such as MFI, ISV and BEA the more mobile species is slowed down and the more tardy species is speeded up. The speeding up and slowing down phenomena also manifests for diffusion of mixtures in zeolites such as AFI, MOR and FER in which the transport is predominantly one dimensional in character. For cage type zeolites with narrow windows connecting cages, such as CHA, DDR and LTA diffusion of components occur practically independently on one another. There is also experimental evidence to support the broad picture on mixture diffusion characteristics arising from MD simulation studies [2,9–13].

It is in the context of the above mentioned studies that the MD simulation results of Hussain and Titiloye [14] for mixtures containing alkanes (methane (C1), ethane (C2), and propane (C3)) in all-silica MFI zeolite deserve comment and critical analysis. We have summarized their data on self-diffusivities in Fig. 1 for equimolar binary mixtures of (a) C1–C2, (b) C1–C3, and (c) C2–C3 at 300 K as a function of the total loading in the mixtures; their data on pure component diffusivities are also plotted for comparison with mixture diffusivity. Consider their C1–C2 data; see Fig. 1a. While the self-diffusivity of pure C1 is consistently higher than that of pure C2, the self-diffusivities in the equimolar C1–C2 mixture shows an unexpected diffusivity reversal for loadings of 6 and 8 molecules per unit cell. Another curious observation is that at loadings of 2 and 6 molecules per unit cell, *both* C1 and C2 are slowed down in the mixture. Consider their C1–C3 data; see Fig. 1b. The diffusivity of C1 in the mixture is higher than that of C3 for all loadings; there is no diffusivity reversal as experienced for C1–C2 mixture. At the lowest loading of 2 molecules per unit cell the more mobile C1 is speeded up and the tardier C3 is slowed down; this is unexpected behaviour. The most intriguing results are those reported by Hussain and Titiloye [14] for C2–C3 mixture; see Fig. 1c. The diffusivity of C2 is consistently lower than that of C3 in the mixture for all loadings, while the pure component diffusivity data indicates that C2 is the more mobile species.

Krishna and van Baten [5] have also published MD simulation simulations for self-diffusivities of C1, C2 and C3 in MFI zeolite at 300 K, for pure components and in equimolar binary mixtures; their results are presented for in Fig. 2a–c. While the pure component self-diffusivity data of Hussain and Titiloye [14] for C1, C2 and C3 at 300 K are in reasonable qualitative agreement with the MD simulation results reported by Krishna and van Baten [5], there is a significant difference in the mixture diffusion characteristics reported in the two publications. For all three binary mixtures the data in Fig. 2 shows the more mobile species is slowed down in the mixtures while the tardier species is speeded up. There is no diffusivity reversal as reported by Hussain and Titiloye [14].

Fig. 3 presents the self-diffusivity in an equimolar C1–C2–C3 mixture as reported by Krishna and van Baten [5]. In the mixture C1 is slowed down, C3 is speeded up, while the diffusivity of C2 is hardly affected. The ternary mixture data as presented in Fig. 1 of Hussain and Titiloye [14] shows that the self-diffusivities of C1, C2 and C3 are

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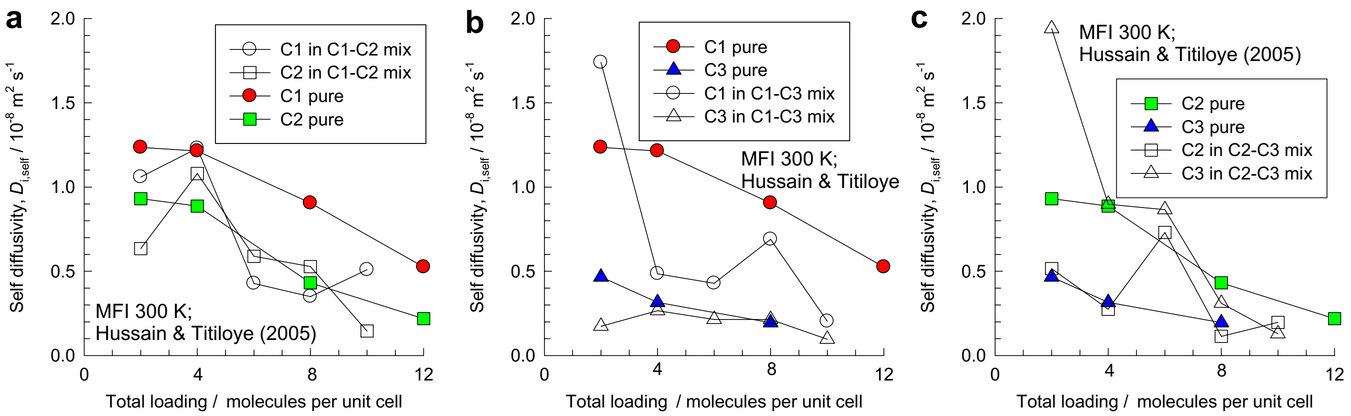

Fig. 1. Self-diffusivities of pure components and in equimolar binary mixtures of (a) C1–C2, (b) C1–C3, and (c) C2–C3 in MFI zeolite (all-silica) at 300 K as a function of the total loading. MD data of Hussain and Titiloye [14] as presented in Figs. 1,3,7,11 and Table 2 of their publication.

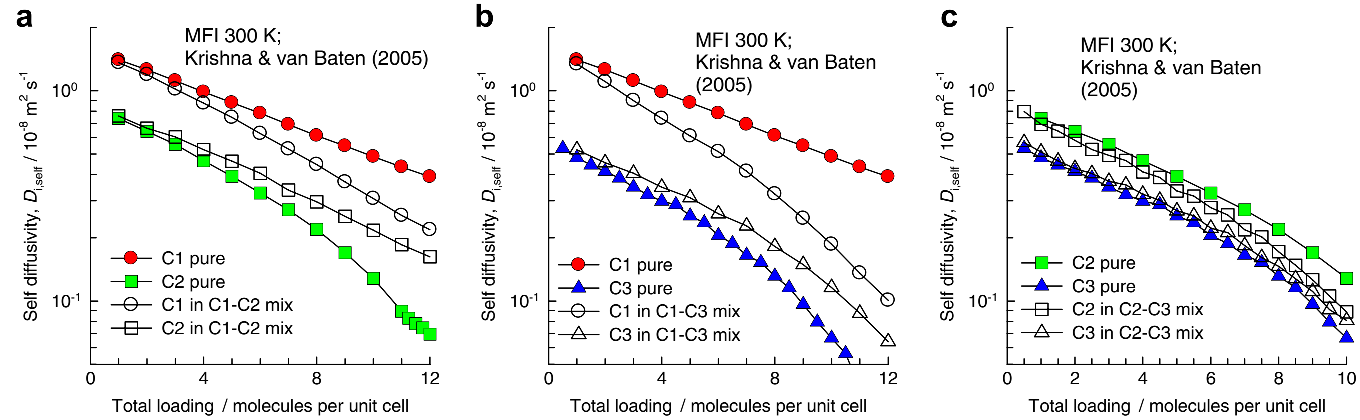

Fig. 2. Self-diffusivities of pure components and in equimolar binary mixtures of (a) C1–C2, (b) C1–C3, and (c) C2–C3 in MFI zeolite (all-silica) at 300 K as a function of the total loading. MD data of Krishna and van Baten [5] as presented in the Supplementary Information accompanying their publication.

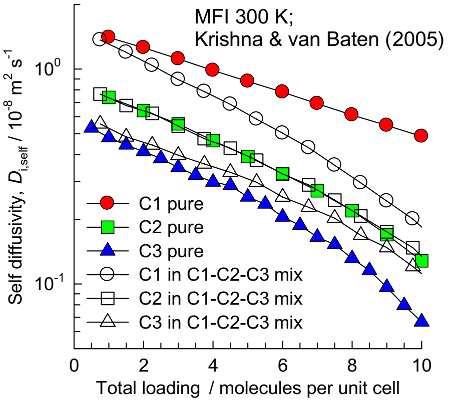

Fig. 3. Self-diffusivities of pure components and in equimolar ternary mixture of C1–C2–C3 in MFI zeolite (all-silica) at 300 K as a function of the total loading. MD data of Krishna and van Baten [5] as presented in the Supplementary Information accompanying their publication.

practically identical to one another at a total loading of 3 molecules per unit cell; this is sharp disagreement with the results of Krishna and van Baten [5] that shows large differences in the component diffusivity values.

We believe that the mixture diffusion data of Hussain and Titiloye [14], especially the phenomenon of diffusivity reversal are open to serious doubt as their results are not consistent with widely accepted picture of mixture diffusion.

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