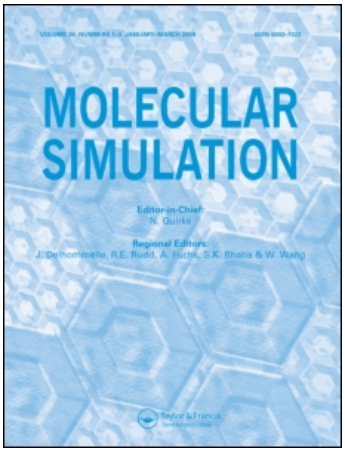

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A molecular simulation study of commensurate-incommensurate adsorption of *n*-alkanes in cobalt formate frameworks

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A molecular simulation study of commensurate–incommensurate adsorption of *n*-alkanes in cobalt formate frameworks

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The channels of the cobalt formate frameworks consist of one-dimensional channels that have a zig-zag configuration. Propane (C3) has a length that commensurates with the channel segment length; longer *n*-alkanes such as *n*-butane (*n*C4), *n*-pentane (*n*C5) and *n*-hexane (*n*C6) have conformations that straddle two channel segments. Configurational-bias Monte Carlo (CBMC) simulations show that the adsorption strength of C3 is higher than that of *n*-butane (*n*C4) and *n*-pentane (*n*C5); this unusual hierarchy is a direct consequence of the commensurate–incommensurate adsorption. CBMC simulations also reveal the possibility of separating C3–*n*C6, C3–*n*C4, *n*C4–*n*C6 and *n*C4–*n*C5 *liquid* mixtures for which the adsorbed phase contains predominantly the *shorter* alkane. Molecular dynamics simulations show that the hierarchy of self-diffusivities is non-monotonic and is the mirror image of the hierarchy of adsorption strengths.

Keywords: diffusivity; adsorption; molecular dynamics; configurational-bias Monte Carlo; linear alkanes; metal-organic frameworks; cobalt formate; manganese formate; commensurate; non-monotonous

1. Introduction

In recent years, there has been a remarkable upsurge in research activity on metal-organic frameworks (MOFs), in view of several potential applications in the field of storage [1–4], and also separation of a variety of mixtures [5–21]. Due to the wide variety of pore sizes and pore geometries, several interesting separation possibilities are possible with MOFs. For example, Finsy et al. [11] have reported a significantly higher adsorption capacity for xylene isomers in MIL-47, than for its isomers, *n*-octane (*n*C8) and ethyl benzene (EtBz). The higher capacity for xylene isomers is due to their improved 'stacking efficiency' within the channels of MIL-47, as illustrated in the snapshots in Figure 1(a), (b) for *p*-xylene and *n*C8, respectively; see also the pure-component isotherms in Figure 2. Bárcia et al. [7] report the results of an experimental study to show the feasibility of separating alkane isomers by adsorption within the framework of Zn(bdc)dabco (see the structure in Figure 3). In a subsequent study, Dubbeldam et al. [21] have used molecular simulations, which shown that the principle behind alkane isomers separation using Zn(bdc)dabco framework is based on the differences in 'efficiency' with which the isomer molecules can interact with the dabco linker atoms.

The current investigation focuses on another unusual separation potential of MOFs and has its genesis in the recent work by Li et al. [22], which reported adsorption isotherms for *n*-alcohols in cobalt formate (Co-FA) framework structure. The metal network exhibits diamondoid connectivity, and the overall framework gives rise to zigzag channels along the *b*-axis, where guest dimethylformamide molecules reside. The effective pore size of these one-dimensional channels is 5–6 Å. The unit cell and pore landscape of Co-FA is depicted in Figure 4; one unit cell of Co-FA comprises a total of four distinct channel 'segments'; each channel segment forms part of the repeat zigzag structure. The experimental adsorption data of Li et al. [22] for propanol and *n*-butanol in Co-FA are particularly intriguing (see Figure 5). We note that the adsorption strength of propanol is higher than that of *n*-butanol over the entire range of experimental pressures. The first major objective of the present communication is to show, with the help of molecular simulations, that this unusual hierarchy in adsorption strength is caused by commensurate–incommensurate molecular lengths of linear molecules within the one-dimensional channels of Co-FA. For this purpose, we have carried out a set of Configurational-bias Monte Carlo (CBMC) simulations to determine the adsorption isotherms of linear alkanes: methane (C1), ethane (C2), propane (C3), *n*-butane (*n*C4), *n*-pentane (*n*C5), *n*-hexane (*n*C6) and *n*-heptane (*n*C7) in Co-FA. The second objective is to demonstrate the exploitation of commensurate–incommensurate molecular lengths to adsorb a *shorter* linear alkane preferentially from a liquid mixture with a longer linear alkane. The third objective, using molecular dynamics (MD) diffusion of *n*-alkanes in Co-FA, is to show that the non-monotonous hierarchy of adsorption strengths is accompanied by a non-monotonous hierarchy in diffusivities.

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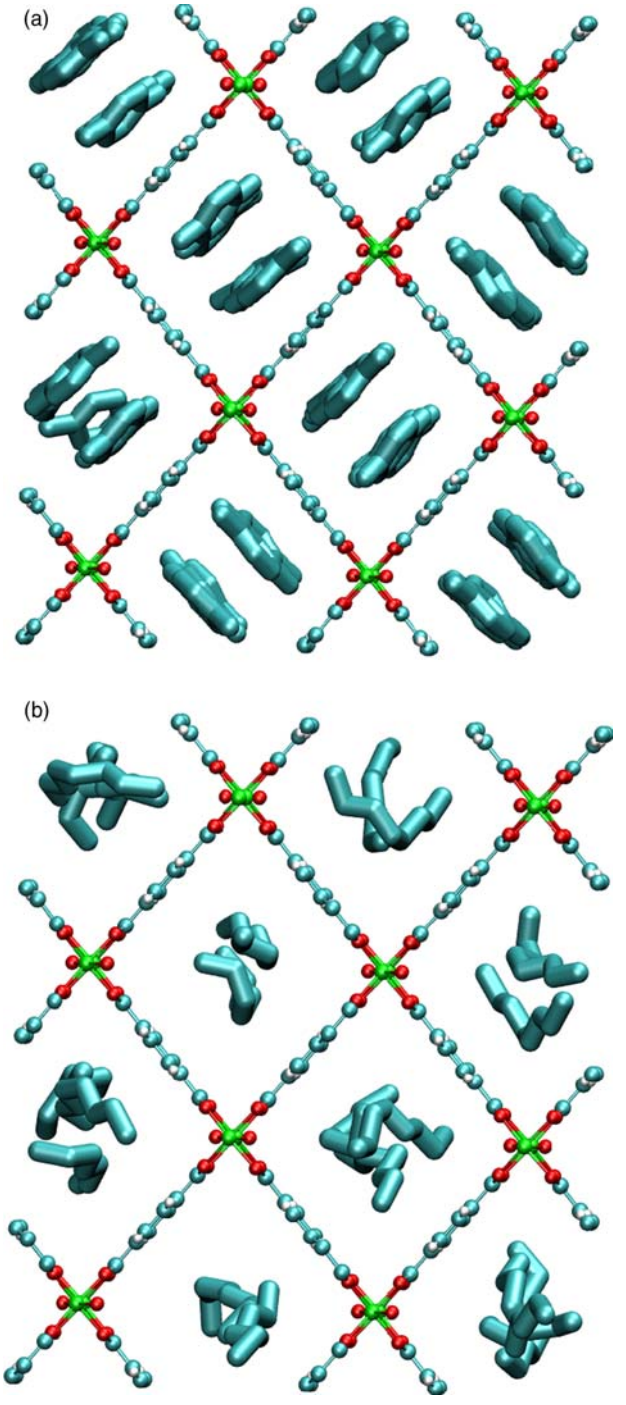

Figure 1. Snapshots showing the location and conformations of (a) *p*-xylene and (b) *n*C8 within the pores of MIL-47. The structural and simulation details are available in the supplementary material accompanying this publication.

2. Simulation details

The structural information for Co-FA is from Li et al. [22]. The adsorption isotherms were computed using CBMC simulations in the grand canonical ensemble. The united-atom force field for alkanes, developed by Dubbeldam et al. [23], is used to describe alkane–alkane, Lennard-Jones, interactions. For alkane–alkane interactions, the tabulated force fields are available in Dubbeldam et al. [23]; the potential for the *n*-alkanes includes bond stretching, bending and torsion. The framework was assumed to be rigid in the simulations.

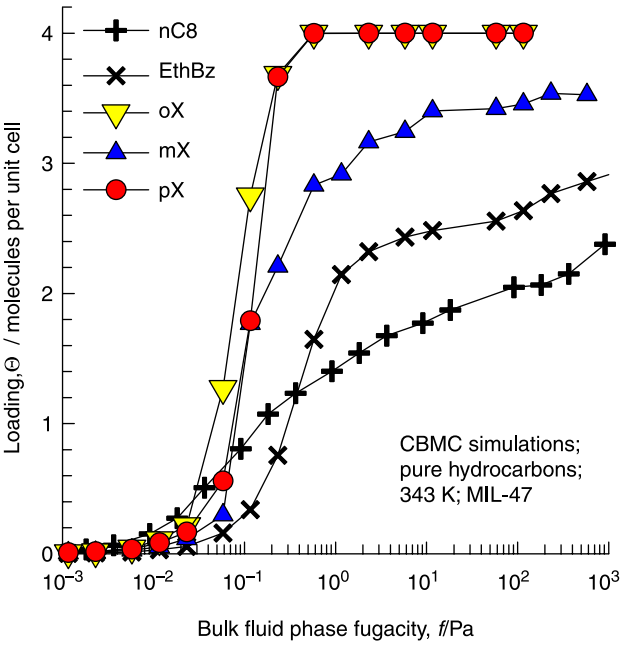

Figure 2. CBMC simulations of pure-component isotherms for *n*C8, EtBz, *o*-, *m*- and *p*-xylenes (*o* X, *m* X and *p* X) in MIL-47 at 343 K.

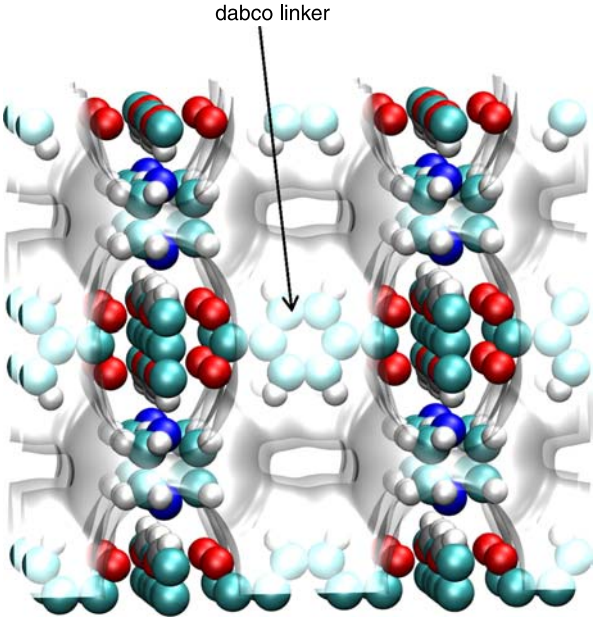

Figure 3. Pore landscape and structure of Zn(bdc)dabco. The structural and simulation details are available in the supplementary material accompanying this publication.

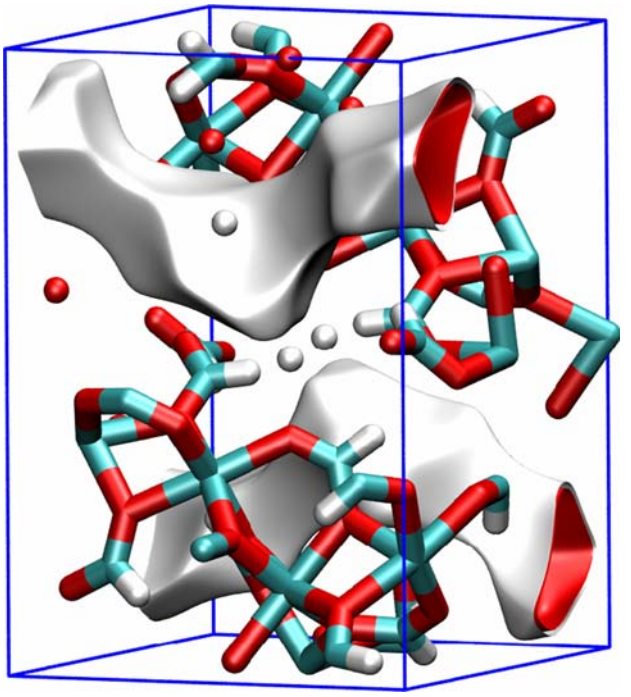

Figure 4. Pore landscapes and structure of Co-FA.

For the atoms in the guest metal-organic framework, the generic UFF [24] was used. The DREIDING [25] force field was used for the organic linker atoms. The Lorentz–Berthelot mixing rules were applied for calculating σ and ε/k_B for guest–host interactions.

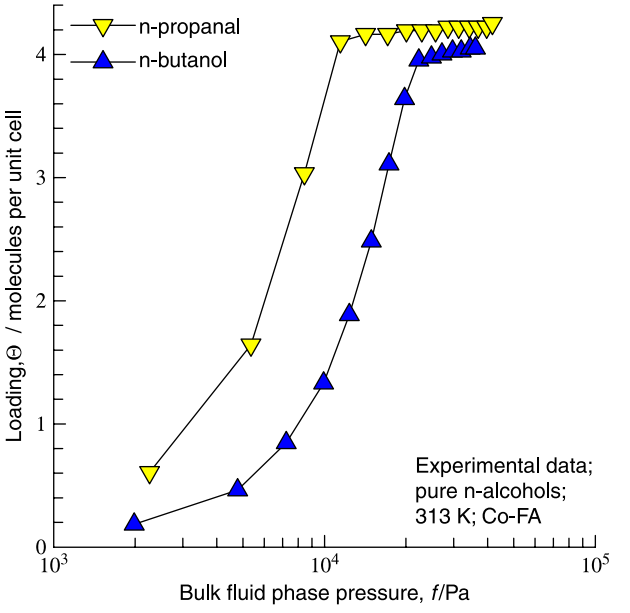

Figure 5. Adsorption isotherms for propanol and *n*-butanol in Co-FA. Experimental data of Li et al. [22]. See supplementary material for the unit cell dimensions and the conversion of loadings to units of molecules per unit cell.

Further simulation details, including structural information, CBMC and MD simulation methodologies, tabulated force fields, pore landscapes, snapshots showing the location and conformation of *n*-alkanes within the pores and simulation data are available in the Supplementary material accompanying this publication.

3. Adsorption of linear alkanes in Co-FA

Consider the CBMC simulations of the adsorption isotherms of linear alkanes in Co-FA at 300 K (see Figure 6(a)). The hierarchy of adsorption strengths for C1,

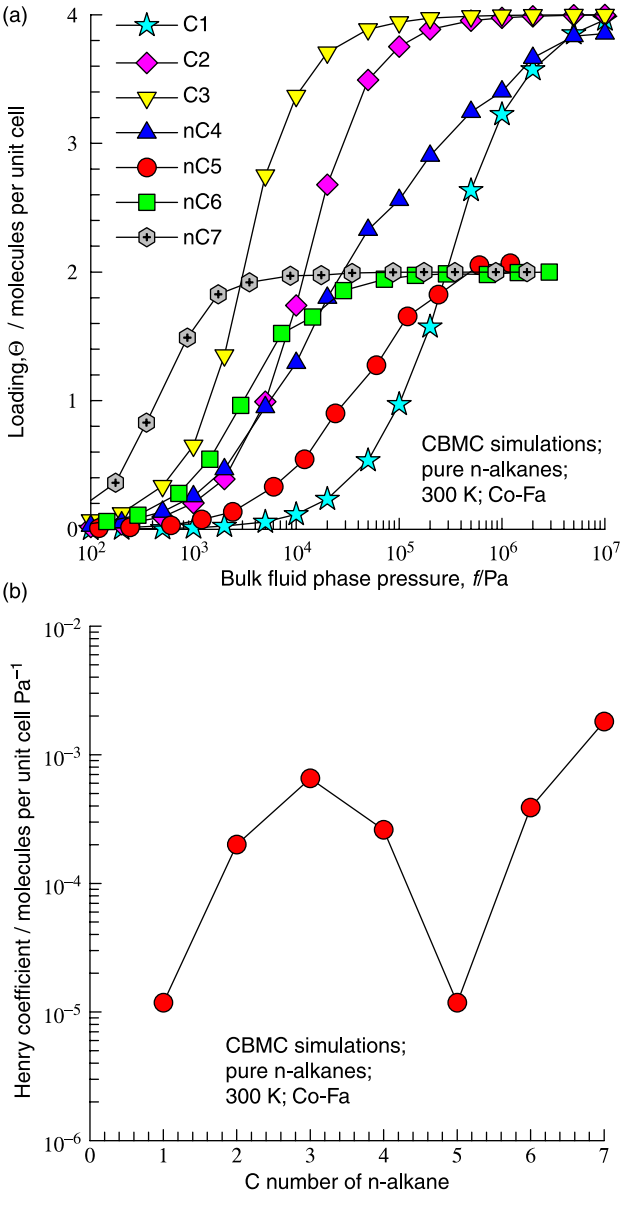

Figure 6. (a) CBMC simulations of adsorption isotherms for C1, C2, C3, *n*C4, *n*C5, *n*C6 and *n*C7 in Co-FA at 300 K. (b) Henry coefficients as a function of C number.

C2 and C3 is as expected; increasing chain length results in higher adsorption strength; see Henry coefficient data in Figure 6(b). However, with increasing chain lengths beyond C3 we note an unusual adsorption hierarchy: C3 > *n*C4 > *n*C5. Further increase in chain lengths result in the expected hierarchy, i.e. *n*C7 > *n*C6 > *n*C5. The saturation capacity for C1, C2 and C3 is found to be four molecules per unit cell, corresponding to one molecule per channel segment. Snapshots of the location of molecules along the one-dimensional zigzag channels of Co-FA confirm that each channel segment contains no more than one molecule each of C1, C2 and C3 (see Figure 7). *n*C5, *n*C6 and *n*C7 have conformations that make these molecules straddle two channel segments, and this is also reflected in the saturation capacities of these molecules of two molecules per unit cell, i.e. corresponding to one molecule in two channel segments. *n*C4 has an intermediate character; at low pressures, the *n*C4 has a conformation with a tendency to occupy a small portion of the adjoining segment. At very high pressures, *n*C4 adopts a more 'cramped' configuration, with each molecule occupying one channel segment and yielding a saturation capacity of four molecules per unit cell. When a molecule has a tendency to straddle two channel segments (*n*C4 at low pressures, *n*C5, *n*C6 and *n*C7), not all of the C atoms can effectively interact with the atoms of the framework; this leads to lower adsorption strength and a non-monotonous adsorption hierarchy witnessed in the Henry coefficient data in Figure 6(b). It is interesting to note that non-monotonous behaviour of the Henry coefficient for *n*-alkanes has also been observed for cage-type zeolites such as CHA, ERI and LTA, caused by commensurate–incommensurate adsorption within cages [26–28].

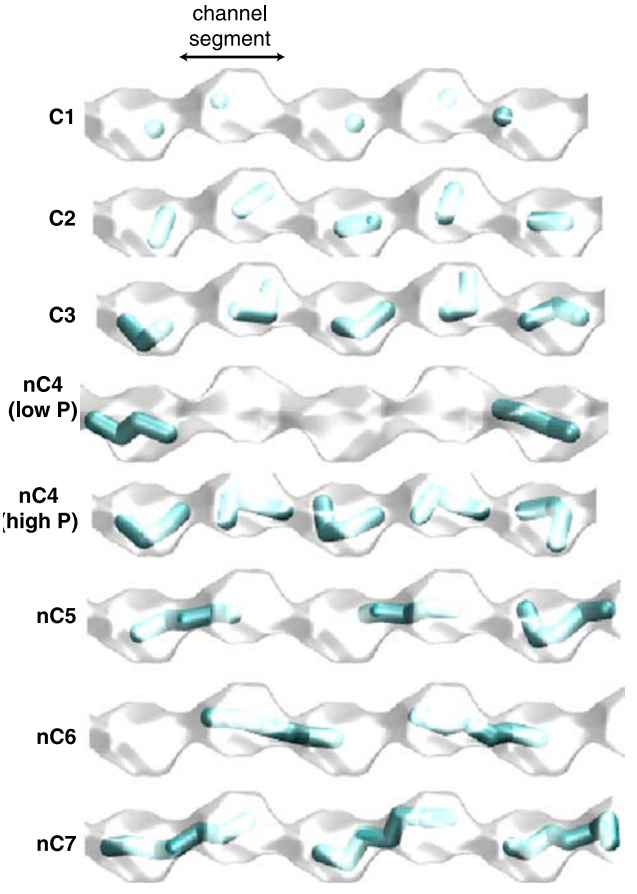

Figure 7. Snapshots showing the location of C1, C2, C3, *n*C4, *n*C5, *n*C6 and *n*C7 molecules in Co-FA.

The non-monotonous adsorption characteristics, along with differences in saturation capacities, can be exploited to achieve unusual separation possibilities. Consider a mixture of C3 and *n*C6. From the pure-component adsorption isotherms in Figure 6 we note that at low pressures the adsorption strengths of C3 is nearly the same as that of *n*C6. However, the saturation capacity of C3 is twice that of *n*C6. We can device a strategy for separating C3 from *n*C6 by exploiting the differences in the saturation capacities. CBMC simulations of the component loadings for a mixture with equal partial fluid phase fugacities, $f_1 = f_2$, are shown in Figure 8(a). When operating at partial fugacities in excess of 1 MPa, with a bulk *liquid* phase, we note that the adsorbed phase contains practically no *n*C6 and is predominantly C3.

Analogously, for *n*C4–*n*C5 liquid mixtures, the adsorbed phase contains the shorter alkane, almost exclusively (see Figure 8(b)). For the C3–*n*C4 and *n*C4–*n*C6 mixtures the separation is somewhat less selective. The CBMC simulation results in Figure 9 show that at high loadings the adsorbed phase is not exclusively the shorter alkane but also contains a small proportion of the longer alkane. The separations indicated in Figures 8 and 9 have possible industrial potential, and needs to be experimentally confirmed. It is perhaps relevant to point out here that earlier we had used molecular simulations to demonstrate the feasibility of separating *n*-alkane mixtures by exploiting differences in the saturation capacity in cage-type zeolites such as CHA, ERI and AFX zeolites [29]. More recently, the experimental work of Denayer et al. [30] has provided experimental confirmation of the separation potential anticipated by the molecular simulations.

4. Diffusion of linear alkanes in Co-FA

MD simulations of self-diffusivities of C1, C2, C3, *n*C4, *n*C5, *n*C6 and *n*C7 in Co-FA are shown in Figure 10(a) for a variety of loadings. At a loading of one molecule per unit cell, the values of the self-diffusivities are plotted in Figure 10(b) as a function of C number. The hierarchy of diffusivities of C1, C2 and C3 is as expected; the molecule with the longer chain length has the lower diffusivity. With increasing chain length, we observe a non-monotonous

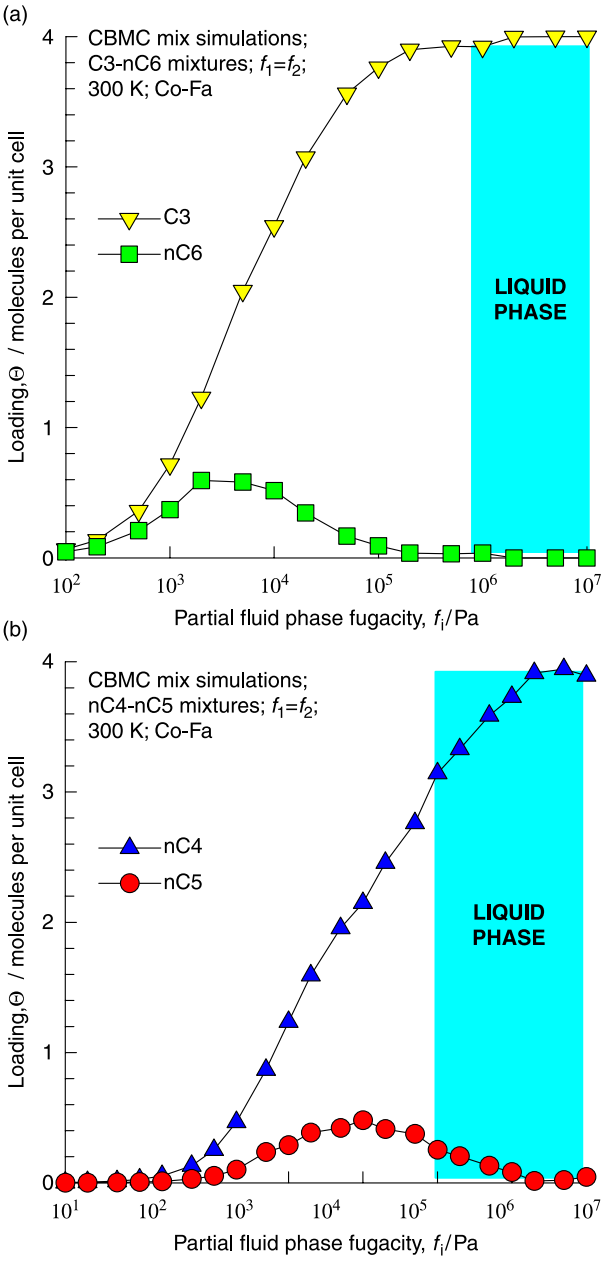

Figure 8. CBMC simulations of component loadings for (a) C3–*n*C6 and (b) *n*C4–*n*C5 mixtures in Co-FA at 300 K.

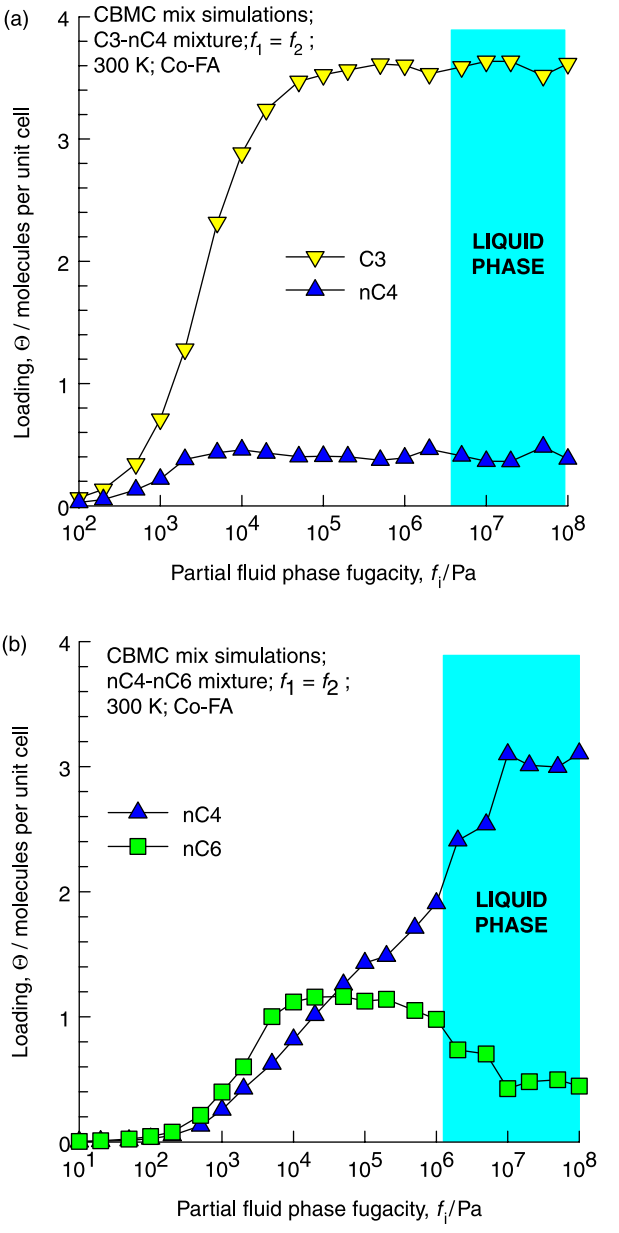

Figure 9. CBMC simulations of component loadings for (a) C3–*n*C4 and (b) *n*C4–*n*C6 mixtures in Co-FA at 300 K.

behaviour with the hierarchy: *n*C5 > *n*C4 > C3 ≈ *n*C6. The hierarchy of diffusivities is an exact mirror image of the hierarchy of Henry coefficients (compare Figures 6(b) and 10(b)). Put another way, if the molecular length is incommensurate with the channel segment length, the adsorption strength is low, but its diffusivity is high.

In the context of separation process development, it must be emphasized that since adsorption and diffusion run counter to each other, we should aim for either an equilibrium- or a diffusion- (i.e. kinetic) based separation. A combination of the two, for example, in a MOF membrane separation will not work, as the two effects may cancel each other out.

5. Conclusions

CBMC and MD simulations of adsorption and diffusion of linear alkanes within the one-dimensional channels of cobalt formate frameworks have revealed a non-monotonic behaviour in Henry coefficients and diffusivities as a function of the *n*-alkane chain length. The non-monotonicity is caused due to commensurate–incommensurate effects in adsorption; C3 has a molecular length that

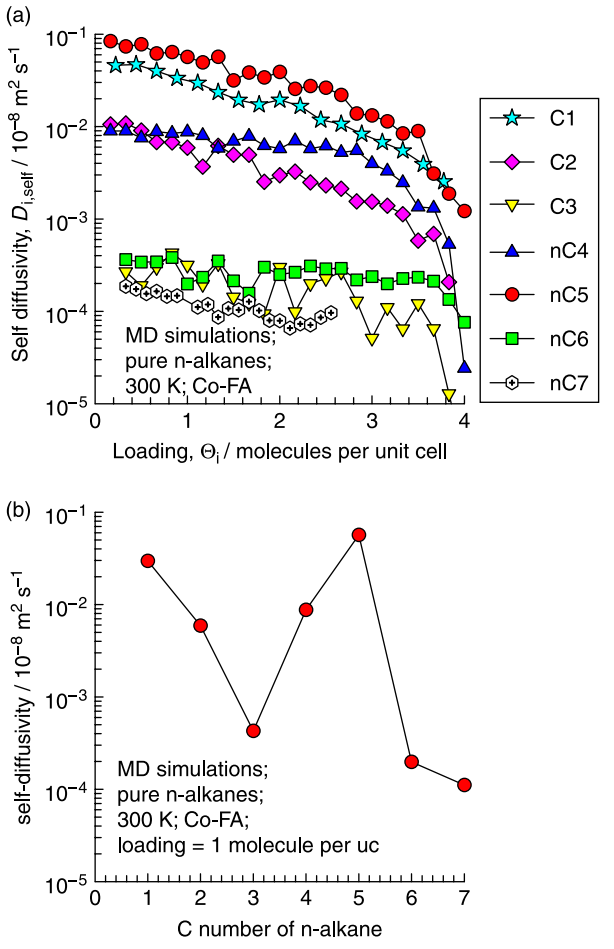

Figure 10. (a) MD simulations of self-diffusivities of C1, C2, C3, *n*C4, *n*C5, *n*C6 and *n*C7 in Co-FA at 300 K. (b) Diffusivities, at a loading of one molecule per unit cell, as a function of carbon number.

commensurates with the channel segment length. *n*C4, *n*C5, *n*C6 and *n*C7 have conformations that make these molecules straddle two channel segments; this leads to lower adsorption strength due to inefficient interaction with the framework atoms. The hierarchy of diffusivities is inverse of the hierarchy of adsorption strengths.

CBMC simulations also reveal the possibility of separating C3–*n*C6, C3–*n*C4, *n*C4–*n*C6 and *n*C4–*n*C5 *liquid* mixtures for which the adsorbed phase contains predominantly the *shorter* alkane.

Manganese formate frameworks are isostructural to Co-FA, and a similar non-monotonicity in adsorption and diffusion behaviours is observed from molecular simulations; details are available in the supplementary material.

Our study underlines the ability of molecular simulations to provide a molecular-level understanding of observed experimental phenomena, and also to unravel novel separations with structured nanoporous materials such as MOFs.

Supplementary material

Supplementary material associated with this article can be found with the online version at the journal's website.

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