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Probing cooperative jump-diffusion in zeolites: Neutron spin–echo measurements and molecular dynamics simulations of benzene in NaX

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Dedicated to the late Denise Barthomeuf, George Kokotailo and Sergey P. Zhdanov in appreciation of their outstanding contributions to zeolite science

Abstract

We report neutron spin–echo measurements of transport diffusivities for perdeuterated benzene in NaX zeolite. Corrected diffusivities from these neutron measurements were obtained for comparison with recently reported molecular dynamics simulations. Experimental diffusivities were measured with benzene loadings of 1, 2, 3 and 4.5 molecules per NaX cage, and at 300, 350 and 400 K. Both corrected and transport diffusivities increase from 1 to 3 molecules per cage, then decrease sharply to 4.5 molecules per cage. The comparison between experiment and simulation shows remarkably good agreement in both the loading dependence and in the overall magnitudes of the corrected diffusivities, with values mostly in the range 10^{-12}–10^{-11} m^2 s^{-1}.

Keywords: Diffusion; Benzene; NaX; Neutron spin–echo; MD simulations

1. Introduction

The transport properties of confined molecules [1,2] play a central role in applications of zeolite–guest systems [3]. A great many experimental and simulation studies have shed light on self-diffusion in zeolites, with a focus on alkanes in siliceous zeolites. These studies have revealed several important phenomena such as single-file self-diffusion [4–6], as well as persistent discrepancies among various microscopic and macroscopic measurements of self-diffusion [7]. Despite these findings, more work is needed before we can use our knowledge of these transport properties to design new processes in zeolites. In particular, more research is needed to understand how the Maxwell–Stefan (also corrected or cooperative) diffusivity, which pertains to non-equilibrium transport, depends on loading and temperature for motion in zeolites [8–11]. In addition, we need greater insights into the transport of unsaturated molecules in non-siliceous zeolites. To address these issues, we report below a combined experimental and simulation study of benzene cooperative diffusion in NaX zeolite.

Among the microscopic methods for measuring diffusion in porous materials, quasi-elastic neutron scattering (QENS) offers the possibility of extracting the self-diffusivity from incoherent neutron scattering, as well as the transport or Fickian diffusivity from coherent neutron scattering

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[12]. Transport diffusivities have been measured by coherent QENS for CF_4 [13], N_2 [14], CO_2 [14] and ethane in silicalite [15], all systems exhibiting relatively facile guest diffusion. The neutron spin–echo (NSE) method provides a way to apply coherent QENS to probe more sluggish motion in zeolites, consisting of rare site-to-site or cage-to-cage jumps. This is crucial for understanding diffusion controlled by shape selectivity. Transport diffusivities of xylenes in BaX [16] and benzene in silicalite [17] have been measured by NSE, which can probe diffusivities two orders of magnitude smaller than those measurable by standard (time-of-flight) QENS. Good agreement between transport diffusivities simulated by molecular dynamics and measured by time-of-flight QENS has been obtained for CF_4 [13], N_2 [14], CO_2 [14], and ethane in silicalite [15]. However, to date no comparison between simulations and NSE transport diffusivities has been reported. Below we pursue this comparison for benzene in NaX, a system with a long history of discrepancies among various probes of diffusion [7].

The direct output from molecular dynamics simulations of cooperative diffusion is the Maxwell–Stefan diffusivity, obtained by correlating collective displacements or velocities [2]. This is related to the transport diffusivity by the equation $D_T = D_{MS} \times \Gamma$, where D_T is the transport diffusivity, D_{MS} the Maxwell–Stefan diffusivity, and Γ is a thermodynamic factor that deviates from unity when the adsorption isotherm exhibits non-ideality [18,19]. Because D_{MS} is a purely dynamical quantity, whereas D_T mixes dynamical and thermodynamic effects, the Maxwell–Stefan diffusivity is often used as the fulcrum for comparing simulations and experiments. For multi-component adsorbed phases, the Maxwell–Stefan diffusivity plays a fundamental role in mixing theories for predicting binary diffusivities from single-component data [20].

Benzene diffusion in NaX is complicated by the interplay of rare site-to-site jumps and strong guest–guest interactions. Kinetic Monte Carlo (KMC) is the method of choice for treating jump diffusion; molecular dynamics is extremely convenient for modeling strong guest–guest interactions; but no simulation method is particularly good at treating both effects. Auerbach and co-workers applied KMC to simulate the loading dependence of benzene self-diffusion in NaX with a rather approximate treatment of guest–guest interactions [21,22]. Though this gave reasonable agreement with the loading dependence of pulsed field gradient (PFG) NMR self-diffusivities [23], we sought in more recent work to relax the assumptions associated with the KMC lattice model. In particular, we applied high temperature molecular dynamics to model both self- and cooperative diffusion of benzene in NaX, yielding excellent agreement for the loading and temperature dependencies of self-diffusion when compared with QENS and PFG NMR data [24]. However, when the simulated Maxwell–Stefan diffusivities were used to compute fluxes for comparison with the membrane permeation data of Nikolakis et al. [25], the simulated fluxes were found to be too high by one or more orders of magnitude [26]. This discrepancy, which may stem from defects in the polycrystalline NaX membranes, calls for a comparison between simulations and a *microscopic* measurement of cooperative benzene diffusion in NaX. Such is provided by the NSE data reported below.

To generate sufficient sampling of cage-to-cage jumps, the molecular dynamics simulations of Ramanan et al. were performed in the temperature range 600–1500 K [24]. In contrast, the NSE data below were obtained at 300–400 K. To compare the two data sets, we extrapolated the simulation results to ambient temperatures as described below. The resulting comparison between experiment and simulation shows remarkably good agreement in both the loading dependence and the absolute Maxwell–Stefan diffusivities, with values mostly in the range 10^{-12}–10^{-11} $m^2 s^{-1}$. This level of agreement augurs well for our growing understanding of cooperative diffusion in complex zeolite–guest systems.

The remainder of this article is organized as follows. In Section 2, we outline the experimental and simulation methods, in Section 3, we give the results, in Section 4, we discuss our findings, and in Section 5, we give a brief summary.

2. Methods

Here we describe the overall system under study, the neutron scattering methodology, and the molecular dynamics simulations.

2.1. System

The FAU framework structure is formed from sodalite cages connected by hexagonal prisms (see Fig. 1). This structure features a large cavity or supercage with four tetrahedrally-located windows (diameter ≈7.5 Å), resulting in a three-dimensional channel system. The unit cell has cubic symmetry and contains eight supercages and eight sodalite cages per unit cell [27]. NaX is a FAU-type zeolite with a Si:Al ratio between 1.0 and 1.5. The material with Si:Al = 1.2 is the most common and thus is studied below; this has 86 Na cations per unit cell compensating the negative charge from the 86 Al atoms in the framework. Benzene readily physisorbs in NaX, binding strongly to Na cations in sites SII, SIII and SIII′ (see Fig. 1). The saturation capacity of benzene in NaX is more than 5 molecules per supercage. Benzene diffusion occurs through jumps among cation sites, leading to cage-to-cage migration and intra-crystalline diffusion.

2.2. NSE measurements

The NaX zeolite (Si:Al = 1.23) previously used for QENS measurements on hydrogenated benzene [28], was activated by heating to 673 K under oxygen flow, and pumped to 10^{-4} Pa at the same temperature. Perdeuterated benzene was adsorbed after cooling. Perdeuterated benzene