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An alternative approach for *ab initio* fitted potentials: The *n*-pentane/silicalite-1 system

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Abstract

Quantum chemical calculations at the second-order Møller–Plesset perturbation (MP2) levels were performed to evaluate *n*-pentane/*n*-pentane and *n*-pentane/silicalite-1 interactions where several hundred configurations of the pair were generated. The silicalite-1 crystal structure was represented by a 10-T ring, in which the chemical composition is O[10]Si[10]H[20]. The energies of these configurations were fitted to analytical functions. Our goal was to reproduce both the experimental heat of adsorption (Q_{st}) as well as the self-diffusion coefficient (D_s). The MP2/6-31+G(d,p) was applied and the collision constants were introduced into the *ab initio* fitted potential function. The extrapolated Q_{st} from the newly developed function of 52.28 kJ/mol is 9.39% lower than that of the experiment and the dependence of the D_s as a function of temperatures is in good agreement with that observed experimentally. The obtained function was applied for a series of molecular dynamics simulations by varying temperatures and the concentration of *n*-pentane. The obtained structural data were interpreted in terms of residence distributions. Their changes were, then, described in terms of a competition between potential fields exerted by the zeolite and molecular movement. The attractive potential fields dominate the molecular movement at low temperature and this dominance decreases when the temperature increases.

Keywords: Pentane; Silicalite-1; Diffusion; Heat of adsorption; MD simulation; Potential

1. Introduction

Zeolites are molecular sieves that are of importance for many refinery and petrochemical processes such as the separation of linear and branched alkanes, and the conversion of linear to branched hydrocarbons [1]. The performance of these molecular sieves in such processes depends critically on the match between sieve topology and the shape and size of the adsorbate [2]. ZSM-5, a kind of zeolite whose pore sizes are of the same order of magnitude as those of the adsorbed hydrocarbons, shows selective adsorptions on its channels. Diffusion and adsorption of molecules in the pores of zeolites are fundamental attributes of many industrial separation and also catalytic processes [3–6]. Many hydrocarbon/zeolite potentials based on force field parametrizations are available [7–10]. These models are different in details, *e.g.*, some are all-atom representations, some include three-body interactions. Despite the potentials being expressed as functions of energies which depend on atomic coordinates, they all were parametrized through experimental data, mostly adsorption data, which are macroscopic properties. From different approaches and different experimental data, different parameter sets have been published. An alternative approach for developing the function that

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represents interaction between pairs of molecules or the interaction of a molecule with the lattice is to obtain the potential function from the *ab initio* energy points. An advantage of this approach is that the function is directly fitted to molecular interactions, *i.e.*, the energy obtained from the function is in one-to-one correspondence with the *ab initio* data. There are several successful cases for the *ab initio* fitted functions [11–15] in which the structural properties were in good agreement with the experimental data. Complications arise when the total value of the interaction energy obtained from *ab initio* calculations (*i.e.*, of one molecule with the lattice) is split into pair contributions attributed to interactions of the atoms (or united atoms) in the molecule with single lattice atoms because the contributions of the single atomic pairs to the molecular interaction is actually unknown and *ab initio* calculations give only one energy value for each whole configuration. This does not exhibit a problem in dealing with structural properties, but can lead to serious discrepancy when thermodynamic, perhaps also, dynamic properties are concerned [14,16,17]. Beside the development of the guest/host and guest/guest potential functions using the energy data calculated from the *ab initio* calculation, the aim of this study extends also to figure out the optimal ratio of the atomic pairs in the molecular pair potential. Therefore, scope of this work was set up to (i) develop the *ab initio* fitted *n*-pentane/silicalite-1 and *n*-pentane/*n*-pentane intermolecular potentials that reproduce thermodynamic and dynamic properties and (ii) apply the newly validated function to study molecular properties of the *n*-pentane/silicalite-1 system for varying *n*-pentane concentrations and temperatures.

2. Methodology

2.1. Potential development

2.1.1. Fragment representing silicalite-1

MFI-type zeolites are build of 10-membered oxygen ring systems and consist of bidirectional straight and sinusoidal channels connected via intersections. The size of straight and sinusoidal channel openings is 5.3 Å × 5.6 Å and 5.1 Å × 5.5 Å, respectively [18]. A unit cell of the zeolite has a dimension of 20.07 Å × 19.92 Å × 13.42 Å. This contains two straight channels and four sinusoidal channels with four intersections between them. The length of the straight channels is equal to 19.92 Å, while the sinusoidal channels are of 6.65 Å in size (see Fig. 1a) and the diameter of the intersections is 5.4 Å [19]. To develop the *n*-pentane/silicalite-1 potentials, it is not possible to perform quantum chemical calculations using the complete unit cell of the crystal. Therefore, a fragment consisting of 10 oxygen and 10 silicon atoms, or 10 O-membered ring, has been used to represent the silicalite-1. The fragment was, then, saturated with hydrogen atoms as shown in Fig. 1b.

Positions and orientations of the hydrogen atoms were optimized at the Hartree–Fock (HF) level with 6-31G(d).

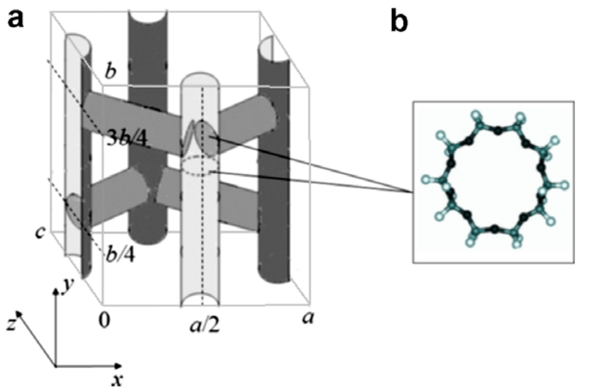

Fig. 1. Schematic representation of (a) the channel system within one unit cell of silicalite-1 ($a = 20.07$ Å, $b = 19.92$ Å, $c = 13.42$ Å) and (b) a 10-oxygen membered ring-fragment of silicalite-1.

2.1.2. Ab initio calculations

Energies for the *n*-pentane/silicalite-1 fragment and for the *n*-pentane/*n*-pentane interactions were calculated for configurations which were generated as follows.

2.1.2.1. n-Pentane/silicalite-1. The *n*-pentane molecule was initially positioned at the center of the fragment in the configuration shown in Fig. 2a. Then, 189 configurations were generated by varying coordinates of *n*-pentane in terms of molecular translation and rotation along *x*-, *y*- and *z*-axes. Quantum chemical calculations were performed. The MP2 method [17,20] with 6-31+G(d,p) basis sets was chosen to perform quantum calculations. The basis set superposition error (BSSE) was also taken into account for all data points.

2.1.2.2. n-Pentane/n-pentane. Similar procedures as performed for the guest/host intermolecular potential, were also applied to the guest/guest system. The center of mass of the first *n*-pentane was located at the origin and that of the second one at 3 Å on *x*-axis (Fig. 2b). Positions and orientations of the second *n*-pentane were varied in terms of its translation and rotation along the *x*-, *y*- and *z*-axes. The distance between the two molecules was extended until the interaction approaches zero. In addition, flexibility of

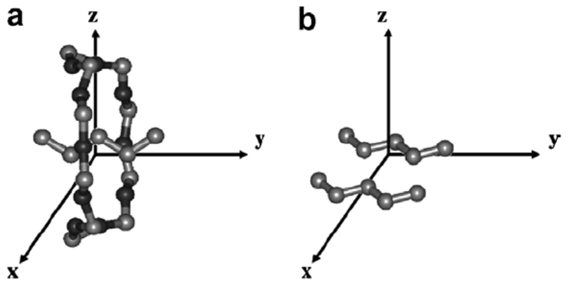

Fig. 2. Schematic representation of (a) *n*-pentane/silicalite-1 complex where *n*-pentane was positioned at the origin of the cartesian coordinates and (b) *n*-pentane/*n*-pentane dimer (hydrogen atoms connected to heavy atoms are not displayed).