Separation and Purification Technology 73 (2010) 151–163

Contents lists available at ScienceDirect

Separation and Purification Technology

journal homepage: www.elsevier.com/locate/seppur

Diffusion in zeolites: Extension of the relevant site model to light gases and mixtures thereof in zeolites DDR, CHA, MFI and FAU

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ARTICLE INFO

Article history:
Received 26 October 2009
Received in revised form 11 March 2010
Accepted 19 March 2010

Keywords:
DDR
MFI
FAU
CHA
Maxwell–Stefan
Zeolite diffusion
Molecular Dynamics
GCMC
Self-diffusivity
Relevant site model
Loading dependency

ABSTRACT

The recently introduced relevant site model (RSM) (Van den Bergh et al., J. Phys. Chem. C, 113 (2009), 17840) to describe the loading dependency of diffusion in zeolite DDR is successfully extended to a variety of light gases (CH_4, CO_2, Ar and Ne) and binary mixtures thereof in other zeolite topologies, DDR, CHA, MFI and FAU, utilizing the extensive diffusivity dataset published by Krishna and van Baten for this variety of zeolite-guest systems (e.g. Chem. Eng. Sci., 63 (2008), 3120 (supplementary material)).

The RSM is formulated around the central idea of segregated adsorption in structures consisting of cages connected by windows, distinguishing cage and window adsorption sites. Only the molecules located at the window site (i.e. the relevant site (RS)) are able to make a successful jump to the next cage. The RSM is based on the Maxwell–Stefan framework for mass transport but includes only one extra parameter that describes the adsorption properties of the 'relevant site'. Key feature of the RSM as applied to mixtures is that competitive adsorption effects and 'speeding up and slowing down' (exchange) effects between guest molecules are related to the relevant site loading and composition instead of to the overall loading, which can be very different.

From the RSM approach a measure for the level of adsorption segregation is derived: the ratio of the RS and total occupancy. The predicted level of adsorption segregation correlates well with the level of confinement of a molecule at the RS: the molecule diameter to zeolite pore diameter. The predicted degree of adsorption segregation of the studied light gases in DDR is in good agreement with molecular simulations results, indicating the physical meaningfulness of the estimated RS adsorption parameters.

The binary mixture diffusivity modelling points out that in case of the small-pore zeolites (DDR and CHA) the data is described best with equal RS saturation loadings for both components. For the large pore zeolite FAU the ratio of the RS saturation loadings equals that of the bulk saturation loadings. The geometry of the RS strongly influences the RS saturation loading: in case of the small-pore zeolites the RS (= window site) is restricted to only one molecule but when the RS becomes larger its saturation loading becomes similar to that of the bulk.

1. Introduction

Zeolites are commonly applied as adsorbents and catalysts in industry. Moreover, zeolite membranes have found their first application in alcohol dehydration [1,2]. A potential new application for 8-membered ring zeolite membranes (e.g. DDR [3–6]) is natural gas purification (CO_2/CH_4 separation). For membrane process and module design, an accurate description of mass transport in these micro-porous materials is required on a macroscopic level. Much progress has been made in recent years and the most successful approach is based on the Maxwell–Stefan framework for mass transport [7–10]. A recurring problem is the loading dependency of the diffusivity that complicates modelling. Recently, we proposed a new model to describe this loading dependency. This so-called relevant site model (RSM) was successful in describing single component diffusivity data of N_2, CO_2, Ar and Ne in zeolite DDR [11–13]. Moreover, a good prediction of diffusivity data for binary mixtures of CO_2/N_2 and Ar/Ne in DDR was obtained [12]. Key feature of the RSM is that the transport at a specific site (the relevant site (RS)) is rate controlling in the diffusion process. The observed loading dependency is explained from segregated adsorption in the zeolite: in DDR the RS occupancy is typically significantly lower than the total occupancy which leads to the observed loading dependency. The RSM was proposed as an alternative to the so-called 'Reed–Ehrlich' approach put forward by Krishna and co-workers

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doi:10.1016/j.seppur.2010.03.018

[14–18]. These authors explain the observed loading dependencies from inter-molecular repulsions. In our previous work [11,12] the two approaches are compared in detail.

In this paper the application of the RSM to zeolite topologies other than DDR is investigated. The vast majority of the considered single component diffusivity data and all mixture diffusivity data used are taken from Krishna and van Baten [19].

Originally the RSM model was derived for mixture diffusion under the assumption of equal RS saturation loading for each component [12]. Here, the RS is extended to systems with unequal saturation loadings. Firstly, the basics of the RSM approach are presented. The model is used to describe the loading dependency of the single component MS diffusivity of a series of light gases (CO_2, CH_4, Ar and Ne) in zeolites of quite different topologies (CHA, MFI and FAU). Previous modelling results of CO_2, N_2, Ar and Ne in DDR are also included in the discussion. Specific attention is paid to CH_4 in DDR for which new MS and self-diffusivities are calculated as a function of the loading by molecular dynamic (MD) simulations at 300, 373, 473 and 573 K. Moreover, the corresponding adsorption isotherms of CH_4 in DDR are computed using grand canonical Monte Carlo (GCMC) simulations.

The estimated single component diffusivity parameters are used to predict the self- and MS diffusivities of several binary equimolar mixtures (CO_2/Ne, Ar/Ne, CO_2/Ar and CH_4/Ar) in zeolites CHA, MFI and FAU.

2. Simulation technique

To compute adsorption isotherms of CH_4, Monte Carlo (MC) simulations in the grand canonical (GC) ensemble (μVT) were used [20–22]. In these simulations, a fixed chemical potential (or fugacity) of the sorbent is imposed, resulting in a certain average number of sorbate molecules adsorbed in the zeolite. The zeolite is modelled as a rigid structure [23] with atomic positions taken from the Atlas of Zeolite Structures [24]. We only consider all-silica frameworks, i.e. no non-framework atoms or cations are present. The sorbate–zeolite and sorbate–sorbate interactions are modelled by the sum of Lennard–Jones (LJ). LJ interactions were truncated and shifted at 12 Å. Methane is modelled as a chargeless united atom with parameters taken from Ref. [25]. For more information on the force field and simulation details, we refer the reader to Ref. [26].

The self- and Maxwell–Stefan diffusivities are computed from equilibrium molecular dynamics (MD) simulations in the NVE ensemble using the same force field as for the adsorption calculations. Again, the zeolite is considered as a rigid structure. A time step of 0.001 ps was used to integrate the equations of motion. The starting positions of the sorbate molecules are taken from well-equilibrated MC simulations. Diffusivities are calculated from the mean-square displacements computed using the order-n algorithm of Refs. [27,28]. We refer the reader to Ref. [29,30] for details on how to extract diffusivities from equilibrium MD simulations. Simulations of at least 20 ns are needed to be in the regime of diffusion to calculate the diffusivities [31].

3. Theory

The diffusivity in zeolites can be a strong function of the amount adsorbed on the zeolite [14,32,33]. Particularly zeolite topologies consisting of cages connected by narrow windows show strong and peculiar loading dependencies, especially for molecules that are strongly confined in the window opening [15]. In this case a strong increase of the diffusivity is observed with increasing loading, passing through a maximum and decreasing to very low values when approaching saturation loading [14]. The RSM was previously introduced to account for these effects for single component systems [11] and mixtures with equal RS saturation loadings [12]. In view of the strong confinement for the considered cases, the assumption of equal saturation loadings for the different components at the RS was made. Upon moving to other topologies this restriction is relaxed allowing unequal RS saturation loadings. Below, the foundations of the RSM are discussed and the model is extended to mixtures with unequal RS saturation loadings.

3.1. Relevant site model

The RSM is based on the Maxwell–Stefan (MS) approach to mass transport for diffusion in zeolites [8–10]. In the MS approach the fundamental driving force for mass transport under isothermal conditions is considered to be a gradient in chemical potential ($\nabla\mu_i$) of component i. This driving force is balanced with 'friction' that a component with a certain velocity (u_i) has with the zeolite and with other species in the system. The interaction, or 'friction', with the zeolite is characterised by the MS diffusivity Đ_i and the interaction with other components by the exchange diffusivity Đ_{ij}. θ_i is the occupancy of i and is defined as the ratio of its loading and its saturation loading $\left(q_i/q_i^{sat}\right)$.

$$-\nabla\mu_i = RT\frac{u_i}{\text{Đ}_i} + \sum_{j=1}^{n}\theta_j RT\frac{u_i-u_j}{\text{Đ}_{ij}}, \quad i=1,2,\ldots n. \tag{1}$$

In essence the RSM model follows the same principles, however, the main difference is that a distinction is made between the total loading (q) and the relevant site (RS) loading (q^*). This difference implies segregated adsorption, which is a phenomenon frequently observed in zeolites. A classical example is the adsorption of alkanes in MFI where a distinction between channels and intersections is made [22,34,35]. But segregated adsorption has also been observed in zeolite CHA, DDR and ERI [36].

The main assumption in the RSM is that mass transport is determined by the RS: transport at the RS is rate controlling. As a case study DDR was selected [11,12], a zeolite consisting of cages connected by window openings. Krishna and van Baten [36] have shown that adsorption in DDR is segregated; a distinction between window sites and cage sites can be made. Molecules can reside in the cage or in the window region.

In the RSM it is assumed that only the molecules in the window region are able to make a successful jump to the next cage. Since it is now assumed that the diffusivity is determined by molecules that reside at the RS, Eq. (1) can be expressed in terms of the RS properties:

$$-\nabla\mu_i = RT\frac{u_i^*}{\text{Đ}_i^*} + \sum_{j=1}^{n}\theta_j^* RT\frac{u_i^*-u_j^*}{\text{Đ}_{ij}^*}, \quad i=1,2,\ldots n. \tag{2}$$

All RS related properties are denoted with an asterisk. The flux of component i (N_i) is defined as the product of its average velocity $\left(u_i^*\right)$, the zeolite density (ρ) and the loading at the RS $\left(q_i^*\right)$:

$$N_i \equiv \rho q_i^* u_i^*. \tag{3}$$

Eq. (2) can then be cast into:

$$-\rho\theta_i^*\frac{\nabla\mu_i}{RT} = \sum_{j=1}^{n}\frac{q_j^*N_i - q_i^*N_j}{q_i^{sat*}q_j^{sat*}\text{Đ}_{ij}^*} + \frac{N_i}{q_i^{sat*}\text{Đ}_i^*}, \quad i=1,2,\ldots n. \tag{4}$$

By inverting equation (4) the following expression for the fluxes is obtained:

$$(N) = -\frac{\rho}{RT}[B^*]^{-1}[q^*](\nabla\mu), \tag{5}$$

where matrix q^* is an $n\times n$ matrix with diagonal elements $q_1^*, q_2^*, \ldots, q_n^*$ and all off-diagonal elements are zero. The elements