NUMERICAL SIMULATION OF ADSORPTION PROCESS IN ZEOLITE

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Abstract

As nanomaterial applications in industry grow, particular nanostructures become better understood, widening the horizons for research. Achievements in mathematical modeling for predictive purposes significantly boost the capabilities for manufacturing research, and expedite unprecedented developments in hi-tech composites.

The focus of the research being presented was adsorption properties of Zeolites manufactured to render selective properties for separating mixture components, based on differences in molecular size, shape, and polarity. Whether multicomponent adsorption isotherms can be obtained from single and binary mixture simulations was also investigated.

Experimental determination of multicomponent adsorption parameters is far more difficult and time consuming compared to that for single component adsorption. Furthermore, determinations by experimental methods are far costlier and slower than computer-based numerical methods.

Numerical models were developed for pure component and subsequently multicomponent adsorption processes. Using Configurational Biased Monte Carlo (CBMC) approach in grand canonical ensemble, both process types were simulated numerically, replicating benchmark experimental data. Classical theoretical models based on application of ideal (IAST) and real adsorbed solution theory (RAST) to predict mixture adsorption in nanopores, were also used and are presented for comparison purposes.

The reported are computer simulations on the adsorption of alkanes in the all-silica zeolites MFI (channel type) and DDR (cage type), which match experimental data on adsorption of light hydrocarbons - alkanes - such as methane, ethane, propane and butane. Included are binary and ternary mixtures.

The numerical approach developed can be an accurate, powerful, cost and time saving tool to predict process characteristics for different molecular-structure configurations.

Keywords: nanomaterial, simulation, zeolite, adsorption, CBMC

1. INTRODUCTION

Zeolites are crystalline nanoporous materials widely used in the chemical industry. Owing to the molecular structure and physical properties, Zeolites – comprised of silica-based molecules – have played a pivotal role in the application of nanotechnology in various applied science and engineering fields, as ion exchangers, catalysts, and adsorbents [1]-[3] in separation processes. For development of separation technologies the calculation of the mixture sorption characteristics for a wide range of operating conditions (pressures, temperatures, and chemical compositions) is needed. Compared to the experimental data available on pure component adsorption isotherms [4]-[11] there is considerably less data on mixture isotherms [6], [11]. The lack of mixture data is due to the difficulties with experimental research. In some cases mixture isotherms can be calculated from pure component isotherm data using the Ideal Adsorbed Solution Theory, but in general, thermodynamic non-ideal effects [12] need to be taken into consideration.
In this work the properties of all-silica zeolites – for channel MFI and cage DDR type molecular-structure configurations – were studied by Configurational Biased Monte Carlo (CBMC) numerical simulation [13], [14] in grand canonical (GC) ensemble [15].

Furthermore, the molecular simulations of the adsorption on binary as well as ternary mixtures of the above-mentioned alkanes were generated and compared with experimental data. Ideal adsorbed solution theory (IAST) is a thermodynamic method for predicting multicomponent adsorption equilibria data from isotherms for single gases [16]. Whereas the non-ideal real adsorbate solution theory (RAST) [17], [18] requires consideration of activity coefficients. Depending on the ideal or non-ideal behavior of the interacting elements either IAST or RAST is applied.

2. SIMULATION METHOD

In the simulations the zeolite frameworks have been constructed from silicon and oxygen atoms, only - with no cations involved. The MFI and DDR zeolites structures were modeled from the crystallographic structure taken from all-silica topology elsewhere [19]-[21] in which all Al atoms are substituted by Si atoms. All-silica structures are representing homogeneous hydrophobic surface within a porous crystal [22], therefore they stronger adsorb non-polar organic molecules.

Simulations were performed in the low and high coverage (high and low pressure) regimes using Configurational Biased Monte Carlo (CBMC) in the grand-canonical ensemble [15]. In the CBMC scheme, the molecules are grown bead by bead (segment) biasing the growth process towards energetically favorable configurations. The fundamental advantage of CBMC method is that it avoids the inherent limitations of 'conventional' Monte Carlo methods as adsorbate (molecule) chain lengths increase. In standard Monte Carlo simulations, the probability of accepting a random insertion of a chain molecule into void region of the zeolite structure decreases rapidly with increasing chain length. More details on this simulation technique can be found elsewhere [13], [23]-[25].

In the represented simulations the zeolite lattices have been kept rigid during simulations [24], [25]. The alkanes are described with a united atom model, in which the CH4, CH3 and CH2 groups of alkanes’ molecules are treated as a single interaction center [26]. The non-bonded interactions such as adsorbate-adsorbate, adsorbate-zeolite and intramolecular interactions (for beads in alkane molecule chain, separated by more than three bonds), are described by a well known Lennard-Jones (LJ) potential, as follows:

\[
U_{\text{non-bonded}} = U_{LJ} = \sum 4\varepsilon_{ij} \left[ \frac{\sigma_{ij}}{r_{ij}} \right]^{12} - \left( \frac{\sigma_{ij}}{r_{ij}} \right)^{6}
\]

or by

\[
U_{\text{non-bonded}} = U_{LJ} = \sum 4\varepsilon_{ij} \left[ \frac{\sigma_{ij}}{r_{ij}} \right]^{12} - \left( \frac{\sigma_{ij}}{r_{ij}} \right)^{6} - E_{\text{cut}}
\]

where \( r_{ij} \) is the distance between the pseudoatoms \( i \) and \( j \), \( \varepsilon_{ij} \) is the energy parameter (or strength parameter), \( \sigma_{ij} \) is the size parameter, \( E_{\text{cut}} \) the energy at the cutoff radius \( r_{\text{cut}} \), and \( U_{\text{non-bonded}} = 0 \) when \( r_{ij} > r_{\text{cut}} \).

Simulations of adsorption in MFI zeolite were performed using the TraPPE model [27] for describing the alkane molecules, and for the adsorbate-zeolite interactions the force field of Vlugt et al. [24] was used. For adsorption of alkanes in DDR structure the force field developed by Dubbeldam et al. [25] was used. Simulations for pure components were performed at 300 K, 308 K and for mixtures at 300 K.

3. MODELS OF ADSORPTION ISOTHERMS
Single, binary and ternary component adsorption isotherms in Silicalite-1, measured by Abdul-Rehman et al. [6], and the experimental data of Sun et al. [5] for MFI and the data of Himeno et al. [28] for DDR (only methane) have been studied and compared with simulation results.

The known models for adsorption isotherms such as the Dual-Site Langmuir (DSL) and the Three-Site Langmuir (3SL) have been chosen as the best fitting model for pure component adsorption in MFI and DDR zeolite structures, correspondingly, for the whole temperature range. The analytic expressions of these models are given below:

Dual-Site Langmuir model (DSL):

$$N = N_m \frac{b_1 P}{(1 + b_1 P)} + N_m \frac{b_2 P}{(1 + b_2 P)}$$

Three-Site Langmuir model (TSL):

$$N = N_m \frac{b_1 P}{(1 + b_1 P)} + N_m \frac{b_2 P}{(1 + b_2 P)} + N_m \frac{b_3 P}{(1 + b_3 P)}$$

where $N$, $N_m$, $b_i$, $P$ are total loading, maximum loading, Langmuir constant and pressure (or fugacity), respectively. The postscripts 1, 2 and 3 refer to the adsorption sites of the zeolites. The calculated fit parameters were fitted to the entire adsorption isotherm at particular temperature. The results on MFI zeolite structure are shown in Fig.1.

Figure 1. Comparison of MC simulations with experimental data [6] for Silicalite-1: Pure component adsorption isotherms of Methane, Ethane and Butane in MFI zeolite structure.

4. ADSORBATE SOLUTION THEORY

The main problem in design of adsorptive separation processes is estimation of multicomponent equilibria. One of the most widely used models on prediction of mixture adsorption is the ideal adsorbed solution theory (IAST), developed by Myers and Prausnitz [16]. Later a real adsorbate solution theory (RAST) [17], [18] which incorporates activity coefficients in the multicomponent isotherm equations to account for the deviations from ideal behavior, was applied. In this work the activity coefficients of the adsorbed phase are determined from the simulated data (by the GCMC approach) using the Wilson model [29] and so called spreading pressure dependence (SPD) models [17], [30].
Experimental determination of a mixture isotherm involves not only measuring the weight increase of the zeolite but also the change in composition of the gas mixture. Therefore, the measurements of multicomponent systems are difficult and time consuming compared to the measurement of single (pure) component adsorption isotherms. The fundamental equation of equilibria for mixture adsorption is described as follows:

\[ P_i \phi_i = P_i^0(z) \phi_i^0 x_i \gamma_i \]  
with \( \sum_{i=1}^{n} x_i = 1 \) and \( \sum_{i=1}^{n} y_i = 1 \)  
(5)

where \( \phi_i \) is the fugacity coefficient of the \( i \)-th component at the pressure, temperature, and composition of the mixture; \( P_i^0(z) \) is a saturation pressure at a chosen value of reduced spreading pressure \( z \); \( \phi_i^0 \) is the fugacity coefficient of pure \( i \) component at its reference pressure \( P_i^0(z) \); \( x_i \) is the mole fraction in adsorbed phase, and \( \gamma_i \) is an adsorbed phase activity coefficient.

In IAST model, for predicting the phase diagrams, only the knowledge of single component isotherms is required, and \( \gamma_i \) is set to 1. The RAST model requires correlation with binary data to predict multicomponent data [17]. Both IAST and RAST models applied here require fit parameters of single component adsorption isotherms described by Dual-Site Langmuir and Three-Side-Langmuir models.

Simulated adsorption isotherms in MFI zeolite structure for different mixtures (binary and ternary) at the fixed pressure of 3.45 bars, are compared with IAST as well as experimental data [6] in Silicalite-1, and shown in Fig. 2. According to the results obtained, the binary and ternary mixtures in Silicalite-1 are well predicted by CBMC-GC simulations as well as by IAST model.

![Figure 2. Comparison of MC simulations with IAST and experimental data [6] for Silicalite-1 at 300 K and 3.45 bars: (a) binary mixture of Ethane (C2) – Propane (C3), and (b) ternary mixture adsorption of Methane (C1) – Ethane (C2) – Propane (C3).](image)

An interesting non-ideal behavior was noticed for ethane-butane binary mixture in DDR at 2 bars (Fig. 3a). The simulation results deviate from IAST model calculations. The RAST prediction turned out excellent, where Wilson and SPD models were used for calculating the activity coefficients in adsorbed phase. Such a kind of non-ideal behavior is caused by the zeolite pore geometry, and size effect between adsorbed molecule and zeolite. DDR structure has two types of cages of different size which leads to a segregation of adsorbed molecule of different size, i.e., molecules are predominantly adsorbed within the cages [31]. Thus, a segregated adsorption could not be accurately predicted by ideal adsorbed solution theory.
5. CONCLUSION

The approach presented allowed accurate prediction of pure component and mixture adsorption isotherms, and was similarly found to be an accurate tool for predicting functional properties of zeolites for separation processes. The key feature of the Monte Carlo simulation used is that it can predict –based on the known, governing physical principles and how the ranges of estimates are set up – the probabilistic outcomes for the mathematical model. This approach is effective for predicting process parameter as well as cell characteristics. It can potentially predict quality and quantity characteristics for zeolites as candidate materials for a process of interest.

REFERENCES


