

## The seventh industrial fluid properties simulation challenge<sup>☆,☆☆</sup>



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### ABSTRACT

The goal of the seventh industrial fluid properties simulation challenge was to test the ability of molecular simulation methods to predict the adsorption of organic adsorbates in zeolite materials. Zeolite adsorbents are used in a variety of applications due to their high surface area and abilities to adsorb or desorb sorbates depending upon the applied conditions. With increasing numbers of applications, the ability to predict the performance of zeolites for a wide range of adsorbates would be very valuable in pre-optimizing systems and reducing product development time. The seventh challenge focused, in particular, on the adsorption of perfluorohexane in BCR-704 Faujasite Zeolite. Entrants were challenged to predict the adsorption of perfluorohexane in the zeolite at 293 K and at relative pressures of 0.01, 0.05, 0.1, 0.2, 0.4, 0.6, and 0.8. The relative pressure is defined as that relative to the bulk saturation pressure predicted by the model at a given temperature (293 K in this case). The predictions were judged by comparison to a benchmark set of experimentally determined values. Overall good agreement and consistency were found between the predictions of most entrants.

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## 1. Introduction

### 1.1. Background and motivation

As with the previous six challenges [1–7], the seventh industrial fluid properties simulation challenge (IFPSC) is focused on predicting properties of high industrial importance. Sorbent adsorption, in general, has many applications including water purification, removal of volatile organic compounds from air, removal of toxic gases from air and storage of corrosive or reactive chemicals during shipping. Zeolites are used in sorbent adsorption applications due to their high surface area and abilities to adsorb or desorb sorbates depending upon the applied conditions. With an increasing

number of applications, the ability to predict the performance of adsorbent materials such as zeolites for a wide range of adsorbates would be very valuable to aid in pre-optimizing systems and reducing product development time. Molecular simulation techniques, in principle, could be ideal for predicting adsorption in zeolites with various chemistries.

Adsorption in porous media has been an area of extensive activity in the field of molecular simulation (e.g. in zeolites [8,9], metal–organic frameworks [10,11], nanotubes [12], and other porous carbons [13–15]). Although studies of adsorption equilibria by molecular simulation employing both Monte Carlo [16–18] and molecular dynamics [19,20] techniques have become relatively common, adsorption has not yet been the focus of the IFPSC. Organizing a simulation challenge to assess the capability of molecular simulation methods and force fields to accurately predict adsorption in porous media for practically relevant and moderately complex chemical systems is of interest in order to benchmark the state-of-the-art capability in this important application area.

The application of molecular simulation methods has several benefits beyond the ability to quantitatively predict a wide variety of properties and phenomena. Qualitatively, molecular simulation methods provide molecular level insights to aid in

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understanding structures, physical phenomena, transport mechanisms, and adsorption mechanisms. Many of these molecular level insights are not directly available via experimental methodologies. The increased understanding can lead to ideas for new materials and more optimal processes not previously arrived at via experimental efforts. Molecular simulation can also be used to supplement experimental results. This is particularly useful in distinguishing between contradictory experimental measurements or conflicting interpretations of experimental data [21–23].

### 1.2. History of the IFPSC

Formal detailed plans for the first industrial fluids simulation challenge came about as a result of discussions held at the Workshop on predicting the thermophysical properties of fluids by molecular simulation in May 2001. The Workshop, held at NIST, was attended by scientists from a variety of companies, national laboratories, and universities.

The first challenge, held in 2002, focused on predicting vapor-liquid equilibria, density, and viscosity [2,24–31]. Challenge entrants were asked to predict a P<sub>x</sub> curve for a mixture of dimethyl ether and propylene and the pressure and composition of an azeotropic point for a mixture of nitroethane and propylene glycol monomethyl ether.

The second challenge, held in 2004, focused on problems involving vapor pressures, heats of vaporization, Henry's law constants, and heats of mixing [3,32–39]. Challenge entrants were asked to predict: vapor pressures and heats of vaporization for acetone and butyramide; Henry's law constants for N<sub>2</sub>, CO<sub>2</sub>, CH<sub>4</sub>, and O<sub>2</sub> in ethanol; and heats of mixing for n-butylamine and n-heptane. Predicting heats of mixing proved to be especially challenging for alkylamine/water systems.

The third challenge, held in 2006, focused on assessing the transferability of molecular simulation methods and force fields [4,40–48]. The molecular simulation community was challenged to predict shear viscosities across a range of diols and triols as well as bubble point pressures for mixtures of 1,1,1,2,3,3,3-heptafluoropropane and ethanol at 343 K, given data at 283 K.

The fourth challenge was held in 2007 and focused on testing the transferability of molecular simulation methods and force fields when applied to the prediction of a wide variety of physical properties for an industrial relevant molecule [4,49–54], namely ethylene oxide. The fifth challenge, held in 2008, focused on predicting octanol–water partition coefficients and infinite-dilution activity coefficients for 1-ethylpropylamine and 3-methyl-1-pentanol [5,55–58]. The sixth challenge, held in 2010, focused on prediction of the mutual solubilities of water and a glycol ether (PROGLYDE DMM) in liquid–liquid equilibria as a function of temperature [6,59–64].

## 2. The challenge

The focus of the current challenge is to assess the ability of molecular simulation methods and force fields to predict the adsorption of organic compounds in zeolite materials. Specifically, the challenge focused on predicting the adsorption isotherms of n-perfluorohexane in BCR-704 Faujasite type zeolite.

Perfluorohexane was chosen as the adsorbate for the challenge for several reasons. These include: (1) it is an example of a class of important commercial perfluorinated solvents; (2) it is computationally tractable; (3) it is moderately challenging from a force field development standpoint (compared to less complex compounds such as hexane); and (4) it is a strong global warming potential compound of universal importance. In addition, until the

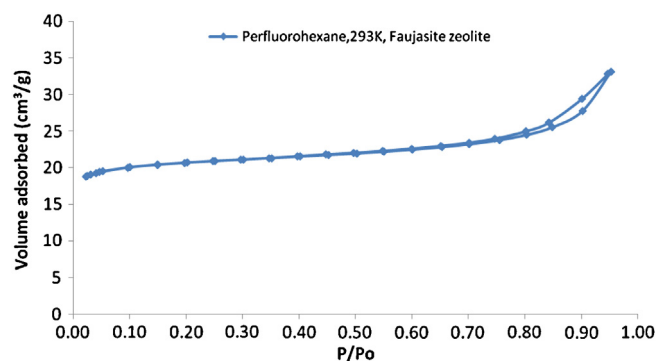


Fig. 1. Experimental adsorption of perfluorohexane in BCR-704 Faujasite zeolite at 293 K (where  $P/P_0$  is relative pressure).

current publication, there were no previously published studies of the adsorption of perfluorohexane in zeolites.

The certified reference material BCR-704 Faujasite type zeolite was used as the zeolite substrate. BCR-704 zeolite material is supplied by the Institute of Reference Materials and Measurement (IRMM) and can be obtained from Sigma–Aldrich. This zeolite was chosen, in part, due to the large number of highly reproducible previous characterization studies carried out by multiple research groups [65].

Elemental analysis had been carried out for the BCR-704 Faujasite type zeolite prior to the challenge and was available to challenge entrants via the IRMM report EUR 21065 “Certification of the Specific Micropore Volume and the Median Micropore Width of Two Microporous Reference Materials According to Draft-DIN 66135-4, BCR-704, BCR-705” [65]. Argon adsorption studies in the zeolite are also given in the report.

Argon and nitrogen adsorption isotherm studies were carried out by Quantachrome Instrument scientists to further characterize the BCR-704 zeolite. The results of the argon and nitrogen adsorption studies were provided to challenge entrants to aid in validating their simulation methods and forcefields. The argon and nitrogen isotherms are reported in the paper: “Perfluorohexane Adsorption on BCR-704 Faujasite Zeolite Benchmark Studies for the Seventh Industrial Fluid Properties Simulation Challenge” [66] which accompanies the current paper in a special section of fluid phase equilibria.

Experimental benchmark adsorption studies for n-perfluorohexane ( $n\text{-C}_6\text{F}_{14}$ ) adsorbed in BCR-704 zeolite were also carried out by Quantachrome scientists. Three independent adsorption studies were carried out from which averaged adsorption data was used to assess the ability of the molecular simulation entries to predict the adsorption of n-perfluorohexane in the BCR-704 zeolite. Graphical and tabular forms of the adsorption isotherm data for the first study are shown in Fig. 1 and Table 1, respectively. Further details of the experimental n-perfluorohexane isotherms are reported in the accompanying paper: “Perfluorohexane Adsorption on BCR-704 Faujasite Zeolite Benchmark Studies for the Seventh Industrial Fluid Properties Simulation Challenge” [66].

Challenge entrants were asked specifically to compute the adsorption isotherms for n-perfluorohexane in BCR-704 zeolite at a temperature of 293 K and at relative pressures of 0.01, 0.05, 0.1, 0.2, 0.4, 0.6, and 0.8. The relative pressure is defined as that relative to the bulk saturation pressure predicted by the model at a given temperature (293 K in this case).

Challenge champions along with first, second, and third runners-up and an honorable mention were awarded. Entries were scored by comparing the predicted adsorption isotherm data to the experimentally-measured data. Full credit was awarded for a prediction that fell within the experimental error. A weighted scale of

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