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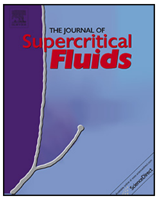

Highly selective separation and adsorption-induced phase transition of SF_6-N_2 fluid mixtures in three-dimensional carbon nanotube networks

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ABSTRACT

The separation of an equimolar SF_6-N_2 fluid mixture in a three-dimension porous carbon nanotube network has been investigated by means of classical molecular dynamics simulations at ambient conditions. The calculations performed have shown that the SF_6 molecules are preferentially adsorbed over the nitrogen ones, yielding a high selectivity for sulfur hexafluoride. The adsorbed mixture is much denser than the bulk supercritical fluid, exhibiting a liquid-like behavior, which is reflected on the static structural, transport and dynamic properties of the confined mixture.

1. Introduction

Due to the combination of its physicochemical properties, such as its weak dielectric properties, low toxicity and high stability, sulfur hexafluoride (SF_6) became the most important insulation and switching medium for electrical power transmission equipment, especially under very high voltage [1–4]. However, SF_6 is a very potent greenhouse gas; its global warming potential is 24,000 times larger than the carbon dioxide's one [5,6] and its atmospheric lifetime is estimated to be up to 3200 years [1]. Due to its contribution to global warming, SF_6 was included in the list of gases of the Kyoto protocol, whose goal is to diminish emissions of the main anthropogenic gases. SF_6 falls also under the European F-Gas regulation, limiting in this way its use for several applications [7]. To overcome the problems related to its use as an insulator in high voltage and circuit breakers, the development of efficient methods to handle and recover SF_6 after its industrial use becomes indispensable.

In this framework, it has been found that when mixing sulfur hexafluoride with nitrogen, even at high nitrogen compositions the fluid mixture maintains the high dielectric strength of pure SF_6 [8,9]. At the same time this mixed fluid insulator is much more environmental friendly and cheaper. However, when mixing these two fluids the difficulty of recovering and recycling SF_6 increases [10]. In this case, the development of processes for the effective separation of SF_6-N_2 mixtures is required. Adsorption [10–14] and membrane separation [15–19] have been recently proposed as low energy and cost alternatives to liquefaction using refrigeration [19].

Physisorption-based separation methods, using porous materials as molecular sieves, are amongst the most environmental friendly and economically feasible methods to achieve efficient removal of SF_6 from SF_6-N_2 mixtures. The development of porous materials effective for such kind of separations depends on the modification of their pore size, volume and chemical functionality in order to increase their permeation selectivity and adsorption capacity. Since the synthesis of materials for these particular applications can be a difficult and time consuming task, computational modeling can be a very helpful tool for the rational design of novel adsorbent materials.

Abbreviations: PNN, porous nanotube network; MD, molecular dynamics; GCMC, grand canonical monte carlo; rdf, radial distribution function; tcf, time correlation function.

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In the recent literature, experimental studies have tested the ability of two-dimensional carbon-based nanopores [20], to separate SF_6/N_2 mixtures. Carbon-based materials exhibit a superior structural stability to a wide range of processing conditions, making them suitable for a wide range of applications. The key factor towards the rational design of carbon-based materials for gas storage and separation is the development of nanostructures with large surface areas and pores. In such a way the stability and light framework of carbon-based materials could be combined with larger surface areas and high porosity, which is one of the disadvantages of two-dimensional carbon nanotube networks [21,22]. Recent studies have revealed that the synthesis of 3D carbon nanotube networks is possible [23–25]. The porosity in such novel carbon superstructures could be appropriately tuned, yielding several types of candidate materials for gas storage and separation. In a previous study we designed a novel three-dimensional (3D) porous nanotube network (PNN) [22], consisting of interconnected (8,8) single-walled carbon nanotubes forming a 3D orthogonal network. Our previous molecular dynamics simulation studies have also shown that this material could be also used as an effective medium for the separation of CO_2/CH_4 [26] and CO_2/N_2 [27] mixtures.

The main aim of the present study was to investigate the separation of an equimolar SF_6/N_2 mixture at ambient temperature in these porous nanotube networks, by employing molecular dynamics (MD) simulation techniques. Such an investigation could assist towards the rational design of carbon-based nanomaterials suitable as media for the separation of SF_6/N_2 mixtures. This paper is organized as follows: the computational methodology is presented in Section 2. Results and discussion are presented in Section 3. General conclusions are presented in Section 4.

2. Computational methodology

When simulating the adsorption of fluids in nanoporous materials, the main aim is to bring the material in equilibrium with a virtual gas reservoir, where the value of the chemical potential inside the porous material becomes equal to that one of the bulk gas. In such a way this stationary flux is being achieved. To do so in our MD study, we employed a technique used in several previous studies [26–30]. The initial configuration of the system was built by initially placing the cubic 3D PNN in the center of the simulation box. From both sides of the PNN (along the z-axis direction) two orthogonal parallelepiped boxes containing the equilibrated bulk fluid mixture were placed. These boxes had the same x- and y-axis length with the cubic PNN (41 Å) and a much larger z-axis length corresponding to the simulated number of molecules and the bulk fluid's desired density. Then the system was simulated for a period of 2 ns in the canonical (NVT) ensemble, where the filling process of the nanotubes started taking place. Representative snapshots, depicting a part of the overall simulation box during this filling process are presented in Fig. 1. After calculating the amount of adsorbed molecules in the nanopore in the initial run, a subsequent MD run was performed by putting at the center of the simulation box the nanopore with the adsorbed gas molecules and by placing again left and right of the nanopore—adsorbed gases system the boxes containing the bulk gas mixture (which were initially used in the first configuration). From each simulation the amount of adsorbed molecules was calculated and this procedure was repeated several times until the amount of adsorbed SF_6 and N_2 reaches a constant value and saturation has been achieved. When saturation was achieved, a final MD simulation with 15 ns duration was performed and the mole fraction profiles of each gas constituent were calculated, attaining in this way the bulk values for each constituent outside the nanopore. The density of the system outside the nanopore also corresponds to the density of the bulk mixture.

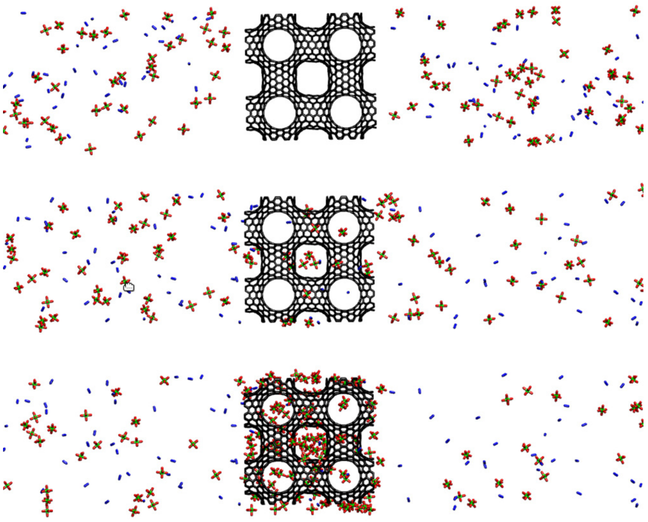

Fig. 1. Representative snapshots, depicting a part of the overall simulation box during the filling process with the SF_6/N_2 fluid mixture.

This procedure of consecutive MD simulations until there is no net adsorption (i.e. the nanoporous material is saturated) can thus be seen as a stationary flux of gas flowing over a nanoporous material. In this sense the results obtained by this method can be considered as totally equivalent with the ones obtained with the commonly employed Grand Canonical Monte Carlo, since in this method (GCMC) the main idea is to bring the material in equilibrium with a virtual gas reservoir and to insert (or reject) gas molecules until the value of the chemical potential inside the porous material becomes equal to that one of the bulk gas [31]. In such a way this stationary flux is being achieved. Although the equilibrium in GCMC can be probably achieved faster than with this MD method, dynamic and kinetic effects, as well as interfacial properties may also be calculated in a very straightforward manner.

The equimolar bulk fluid mixture in our simulations consisted of 250 SF_6 and 250 N_2 molecules and the thermodynamic point under investigation corresponded to 2 MPa and 300 K. To estimate the density of the bulk fluid mixture, an isothermal-isobaric (NPT) simulation of the bulk mixture was performed, using a cubic simulation box. Then, when the density was determined, a parallelepiped box containing 250 SF_6 and 250 N_2 molecules at the desired density was constructed, keeping the x- and y-length equal to the size of the PNN cell. A NVT-MD simulation of this box was then performed for 2 ns, in order to equilibrate the bulk mixture and to use it in the consecutive NVT-MD runs described above.

To estimate the structural, transport and dynamic properties of the SF_6 and N_2 molecules inside the PNN, an additional NVT-MD simulation was performed. In this simulation the initial configuration in the central simulation box consisted just of the PNN containing the average number of SF_6 and N_2 molecules which were adsorbed and were calculated from the previous simulations. The estimated average numbers of adsorbed SF_6 and N_2 molecules in the PNN were 302 and 17, respectively. The total duration of the simulation was 2 ns. The first nanosecond was considered as an equilibration period; structural, transport and dynamic properties were calculated during the rest 1 ns. The properties of the bulk fluid were also obtained by performing a NVT-MD simulation of a mixture of 250 SF_6 and 250 N_2 molecules at the calculated density corresponding to 2 MPa.

The intermolecular interactions among the molecules in the fluid, as well as among the molecules in the fluid and the car-