

A force field assessment on adsorption of HFC-32 on MFI

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Abstract

Among the greenhouse gases the hydrofluorocarbons (HFCs) present higher global warming potential (GWP) values compared to CO₂. Therefore, many efforts have been made in order to developed processes to recover and repurpose them. One potential process is the adsorption on porous materials such as zeolites. In this work, an evaluation of the effect of different adsorbent and adsorbate force fields over the prediction of HFC-32 on MFI zeolite type was conducted, using Monte Carlo simulation. The effect of slightly different MFI structures was also evaluated. To describe the HFC-32 the force fields proposed by Raabe [1] and Agbodekhe et al. [2] were used. The framework atoms positions were taken from Olson et al. [3] and Koningsveld et al. [4]. The TraPPE-Zeo [5] force field and another one proposed by the group were used to account the framework atoms interactions. The results indicated that despite of quantitative changes presented by the combinations of different force fields, the combinations tested yield good prediction of the isotherm behavior of this system (MFI-HFC-32). Thereby, these combinations can be used to explore the capacity of different zeolite frameworks

Keywords: HFC-32; Adsorption; zeolite; GCMC; force field

1. Introduction

The global warming caused by greenhouse gases such as the hydrofluorocarbons (HFCs) are nowadays a big concern. Therefore, international initiatives aimed at reducing HFC emissions have recently been adopted, such as EU Regulation No. 517/2014 [6]. However, the HFCs mixtures currently used are characterized by an almost azeotropic behavior, which makes the separation process by cryogenic distillation difficult and expensive. Therefore, it is necessary to develop new, more efficient and lower cost separation processes. According to Gonzalez-Olmos and Llovéll [7] currently there is no available standardized technology to recover low and moderate GWP compounds from existing refrigerant blends. Adsorption processes are recognized for having a lower energy cost, compared to distillation processes, and also for being selective in the separation of complex mixtures such as isomers. Currently, especially due to the exponential growth in the speed and calculation capacity of computers, the use of Molecular Simulation (MS) became a powerful tool in understanding important natural phenomena, essential for the development and optimization of complex processes, such as adsorption. However, the accuracy of MS's results are attached to the right geometric and energetic representation of the

molecules involved. In the adsorption's case we can highlight three fundamentals aspects: the solid framework, the solid force field and fluid force field. In this work we present a study of how these three aspects can affect the results of simulations of difluoromethane (HFC-32) on MFI zeolite type.

2. Methodology

The MFI is an orthorhombic zeolite that presents two different kinds of channels: straight and zig-zag which intersect each other promoting a wide opening pore. Two slightly different crystalline structure, reported by Olson et al [3] and Koningsveld et al. [4] were used in order to access the effect of the geometry of MFI over the HFC-32's isotherm. The geometric characteristics of these two structures are presented in Table 1. Two different force fields for HFC-32 were also evaluated. The force fields proposed by Raabe [1] and Agbodekhe et al. [2] were chosen. The parameters of these two force fields are presented in Table 2 and 3. A force field, not publish yet, developed by the group, based on Kislev model to describe the energetic interactions of the framework atoms were used to obtain the HFC-32 isotherm on MFI at 298 and 323K. The results of this force field were compared to simulations reported by Marin-Rimoldi et al. [8],

who used the TraPPE-Zeo force field, proposed by Bai et al. [5] in order to obtain the isotherms. Table 4 presents the parameters of framework atoms of these two force fields. The results were also compared to experimental data reported by Marin-Rimoldi et al. [8] at 298 and 323K and Sosa et al. [9].

Table 1. MFI unit cell length sizes.

Ref.	unit cell length		
	a (Å)	b (Å)	c (Å)
Olson [3]	20.070	19.92	13.420
Koningsveld [4]	20.022	19.899	13.383

Table 2. Non-bonded HFC-32 parameters used

Atom	Raabe [1]		
	ϵ/k_B [K]	σ [Å]	$q[e]$
C	54.6	3.15	0.43960
F	44.0	2.94	-0.26138
H	7.9	2.2293	0.04158
Atom	Agbodekhe et al. [2]		
	ϵ/k_B [K]	σ [Å]	$q[e]$
C	55.6481	3.7992	0.4054670
F	39.1405	2.7427	-0.250783
H	3.6644	1.9689	0.0480495

Table 3. Bonded HFC-32 parameters used

	Bond - r_0 [Å]			
	Raabe [1]		Agbodekhe et al. [2]	
C-H	1.094		1.0961	
C-F	1.369		1.3497	
	Bending			
	Raabe [1]		Agbodekhe et al. [2]	
	K_θ [*]	θ [deg]	K_θ [*]	θ [deg]
H-C-H	146.54	113.6	163.2	110.20
H-C-F	367.61	108.7	213.8	108.79
F-C-F	249.92	108.6	296.6	107.36

* $\text{kJmol}^{-1}\text{rad}^{-2}$

Simulations Details

The simulations were conducted using a Grand-Canonical ensemble implemented in the open-source Monte Carlo package Cassandra. Details such as the configurational-biased sampling scheme and acceptance rules are very well described at Shah et al. [10]. A supercell 3x3x3 were built in order to access low pressure range.

Table 4. Parameters of zeolite force fields.

Force Field	Atom	Parameters		
		ϵ/k_B [K]	σ [Å]	$q[e]$
TraPPE-	O	53.2	3.304	-0.75
Zeo [5]	Si	22.2	2.31	1.5
This	O	73.5	3.155	-0.9
work	Si	-	-	1.8

The potential energy (U) of the system was evaluated by the sum of terms related to the interactions between bonded (U_B) and nonbonded (U_{NB}) atoms:

$$U = U_B + U_{NB} \quad (1)$$

The term related to the interactions between nonbonded atoms was evaluated considering short-range, using the Lennard-Jones potential and long-range interactions:

$$U_{NB} = 4\epsilon_{ij} \left[\left(\frac{\sigma_{ij}}{r_{ij}} \right)^{12} - \left(\frac{\sigma_{ij}}{r_{ij}} \right)^6 \right] + \frac{q_i q_j}{4\pi\epsilon_0 r_{ij}} \quad (2)$$

The parameters related to unlike atoms were accounted by Lorentz-Bertholot combining rule:

$$\epsilon_{ij} = \sqrt{\epsilon_i \epsilon_j} \quad (3)$$

$$\sigma_{ij} = \frac{\sigma_i + \sigma_j}{2} \quad (4)$$

The bonded energy term is related only to the bend term, accounted the harmonic potential, since the bond length are kept constant:

$$U_B = U_{bend} = \frac{K_\theta}{2} (\theta - \theta_0)^2 \quad (5)$$

Previous to conduct simulations on the adsorbed phase, GCMC simulations were run in gas phase at the desired temperature in order to obtain the relationship between chemical potential and pressure. In gas phase a cutoff of 40% of the box size was used for van der Waals and electrostatic interactions. Details of these procedure are explained on [10]. The adsorption isotherms were obtained via GCMC simulations in which the box has the shape and size of the supercell used. In these simulations a cutoff of 13 Å without applying analytic tail corrections to the Lennard-Jones potential was used. The electrostatic contributions were accounted by Ewald summation method. Translation, rotation, regrowth, insertion and deletion moves were used with equal probability. The 10 million steps were used to equilibrate the system and then more 10 million steps were performed in production step.

3. Results

Figure 1 presents our simulation results using the zeolite proposed force field by our group along with GCMC results reported by [8]. To highlight only the effect of the zeolite force field used, our simulations presented at this figure were performed using the same MFI structure (Koningsveld[4]) and HFC-32 force field (Agbodekhe [2]) used by Marin-Rimoldi[8]. The results indicate that both force fields present similar performances. It is important to highlight the proposed zeolite force field presents just a single interaction van der Waals site, in opposition to TraPPE-Zeo [5] which presents 2 sites.

The effect of the slight differences on the MFI structure is presented at Figure 2. The results of GCMC performed using the Agbodekhe et al. [2] force field to describe HFC-32; the proposed force field to MFI in combination with the Olson et al.[3] and Koningsveld et al.[4] structures are compared to experimental data reported by Marin-Rimoldi et al. [8] and Sosa et al. [9]. Even if the structures are very similar a considerable difference is observed in the region from 0.05 to 0.4bar. However, at high pressures the results are almost identical, what indicate that the structures present almost the same accessible pore volume.

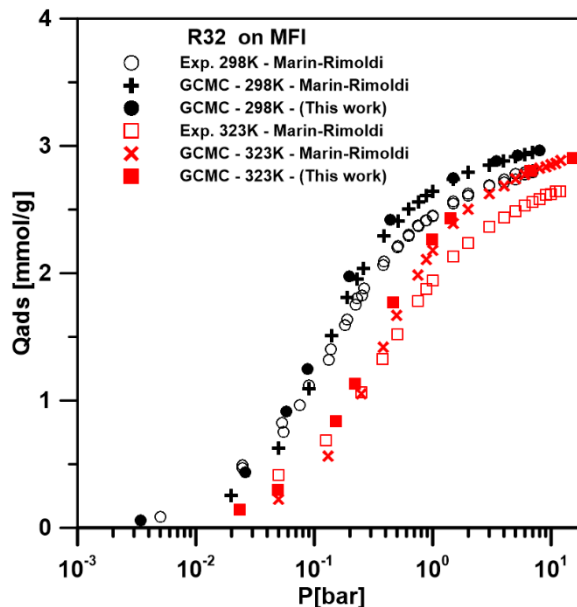


Fig. 1. Adsorption of HFC-32 on MFI. Effect of MFI force field

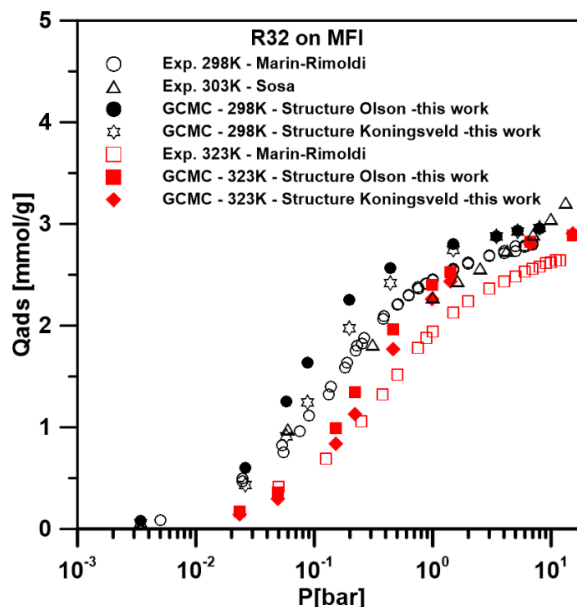


Fig. 2. Adsorption of HFC-32 on MFI. Effect of MFI structure.

The Figure 3 presents the effect of HFC-32 force field over its adsorption on MFI. The results of adsorption isotherms at 298 K by GCMC using the combination of Koningsveld et al [4] structure, the zeolite force field proposed by the group and the HFC-32 force fields proposed by Raabe [1] and Agbodekhe et al. [2] are presented with the experimental data reported by Marin-Rimoldi et al [8] and Sosa et al. [9]. Both HFC-32 force fields were able to present a good prediction of isotherm behavior.

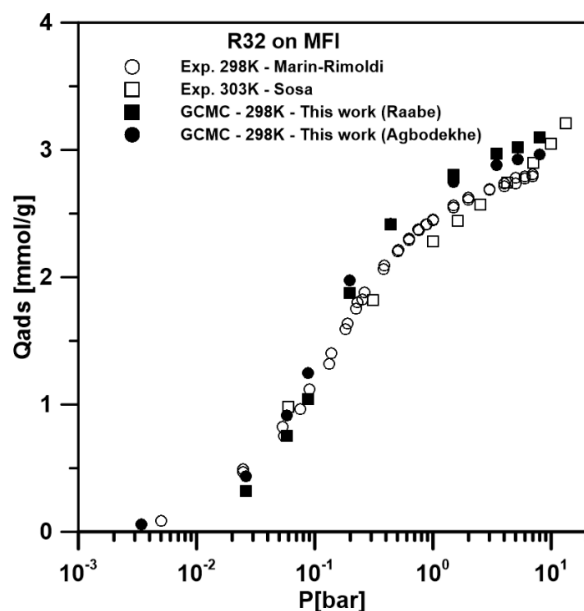


Fig. 3. Adsorption of HFC-32 on MFI. Effect of HFC-32 (R32) force field. Experimental data

4. Conclusions

The effect of the three main variables on the adsorption isotherms prediction using molecular simulations were evaluated. The results showed that even if there are differences on the results presented by the combination of different force fields and zeolite structures, if the models of individual contributions are good, the results produced will be in a good agreement with experimental data. The results reinforces that the molecular simulation is a powerful tool in order to screening materials.

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References

- [1] Raabe, G. Molecular Simulation Studies on the Vapor–Liquid Phase Equilibria of Binary Mixtures of R-1234yf and R-1234ze(E) with R-32 and CO₂, *J. Chem. Eng. Data* 2013, Vol. 58, pp. 1867–1873.
- [2] Agbodekhe, B. Marin-Rimoldi, E., Zhang Y., Dowling, A.W., Maginn E.J., Assessment and Ranking of Difluoromethane (R32) and Pentafluoroethane (R125) Interatomic Potentials Using Several Thermophysical and Transport Properties Across Multiple State Points, *J. Chem. Eng. Data*, 2024, Vol. 69, pp. 427–444.
- [3] Olson, D.H.; Kokotailo, G.T.; Lawton, G.T.; Meier, W.M. Crystal Structure and Structure-Related Properties of ZSM-5. *J. Phys. Chem.* 1981, 85(15), pp. 157-171.53.
- [4] Van Koningsveld, H., Van Bekkum, H., Jansen, J., On the location and disorder of the tetrapropylammonium (TPA) ion in zeolite ZSM-5 with improved framework accuracy, *Acta Crystallogr., Sect. B: Struct. Sci.*, 1987, Vol. 43, pp.127–132.
- [5] Bai, P.; Tsapatsis, M.; Siepmann, J. I. TraPPE-Zeo: Transferable Potentials for Phase Equilibria Force Field for All-Silica Zeolites. *J. Phys. Chem. C*, 2013, Vol. 117, pp. 24375–24387.
- [6] Schulz, M., Kourkoulas, D., 2014. Regulation (EU) No 517/2014 of the European Parliament and of the Council of 16 April 2014 on fluorinated greenhouse gases and repealing Regulation (EC) No 842/2006. *Off. J. Eur. Union* 2014.
- [7] Gonzalez-Olmos, R., Llovell, F., Life cycle assessment of fluorinated gas recovery from waste refrigerants through vacuum swing adsorption, *Sustainable Materials and Technologies*, 2024, Vol.39.
- [8] Marin-Rimoldi, E., Yancey, A.D., Shiflett, M.B., Maginn, E.J. Adsorption of difluoromethane (HFC-32) and pentafluoroethane (HFC-125) and their mixtures in silicalite-1: An experimental and Monte Carlo simulation study, *J. Chem. Phys.*, 2024, Vol. 161, pp.074701-1-12.
- [9] Sosa, J.E., Malheiro, C., Castro, P.J., Ribeiro, R.P.P.L., Piñeiro, M.N. Plantier, F., Mota, J.P.B., Araújo, J.M.M., Pereiro, A.B., Exploring the Potential of Metal–Organic Frameworks for the Separation of Blends of Fluorinated Gases with High Global Warming Potential, *Global Challenges* 2023, Vol. 7, 2200107.
- [10] Shah, J.K.; Marin-Rimoldi, E.; Mullen, R.G.; Keene, B.P.; Khan, S.; Paluch, A.S.; Rai, N.; Romanielo, L.L.; Rosch, T.W.; Yoo, B.; Maginn E.J. Cassandra: An Open Source Monte Carlo Package for Molecular Simulation. *J. Comput. Chem.* 2017, 38, 1727-1739.

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