

Selective Paraffin Removal from Olefin/Paraffin Mixtures by Adsorption to Aluminum Methylphosphate- α : A Molecular Simulation Study

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In this work the selective paraffin removal from olefin/paraffin mixtures by adsorption to the hybrid inorganic-organic material aluminum methylphosphonate polymorph alpha is investigated using Grand Canonical Monte Carlo simulations. This material selectively adsorbs the paraffin from ethane/ethylene mixtures as well as ethyl chloride/vinyl chloride mixtures. Therefore, the key factor determining the selectivity is found to be the molecular interaction between the methyl group of this material and the methyl group of the paraffin.

Introduction

The olefin/paraffin separation is the most energy intensive separation carried out in the petrochemical industry. Currently, high-pressure distillation is used as purification method, which is energy-intensive and expensive. A cheaper, more efficient, less energy-intensive and cleaner method for separating olefins from paraffins would be very desirable. One of these alternative separation methods is adsorption, which is still in the research-phase. Commonly, it is the olefin that is preferentially adsorbed using this separation method, because of the strong interaction between the unsaturated bond of the olefin and a metal ion on the surface of the adsorbent material, forming a π -complex. Because the olefin is preferably adsorbed, it is the paraffin that is easily obtained in its pure form. Unfortunately, in industrial processes the desired product is the olefin (raw material for polymers) and not the paraffin. Therefore, adsorption is not an option to replace the current distillation columns (yet). However, when it is the paraffin that is selectively adsorbed, the olefin can be easily obtained in its pure form, which would make the adsorption process a very attractive alternative.

Recently, for the first time, an adsorption material was found that was able to selectively adsorb the paraffin instead of the olefin. This research involved the selective absorption of ethyl chloride compared to vinyl chloride using the hybrid inorganic-organic material aluminum methylphosphonate polymorph alpha (AlMePO- α) [1]. The study was performed by a combined experimental-molecular simulation approach. However, it is still unclear why AlMePO- α selectively adsorbs the ethyl chloride compared to the vinyl chloride, and whether this material is also suited for other olefin/paraffin separations. Here, we will use molecular simulations in order to understand the key factors determining the selective paraffin adsorption by AlMePO- α (molecular interactions, steric effects, rigidity) and to investigate the suitability of this material for other olefin/paraffin separations. The molecular model used for the material is the same developed in previous work [2], while appropriate force fields are

used for the different olefins and paraffins under consideration. As an example, the selective adsorption of ethane from ethane/ethylene mixtures by AlMePO- α is investigated.

Methodology

Molecular models: The AlMePO- α material is modeled as consisting of single Lennard-Jones spheres for the individual atoms, where the Lennard-Jones parameters of the Al, P and O atoms were taken from Schumacher *et al.* [3] and the methyl groups are represented as single Lennard-Jones sites located at the positions of the C-atom [2]. The parameters used in this work are given in table 1. The simulation cell consists of 96 aluminium atoms, 144 phosphorus atoms, 432 oxygen atoms, and 144 methyl groups.

Table 1: Lennard-Jones parameters of AlMePO- α used in the simulations [2,3]

Site	σ (nm)	ε/k_B (K)
Al	-	-
P	-	-
O	0.2655	128.13
CH ₃	0.3500	120.15

Both ethane and ethylene are modeled using three different force fields: two united-atom molecular models i.e. the OPLS-UA model [4] and the TraPPE model [5], and a two-center Lennard-Jones force field with point quadrupole potential i.e. the 2CLJQ model [6,7]. The first two models with fixed bond lengths (l_0) between the united-atom groups (CH₃ or CH₂) only use the Lennard-Jones intermolecular potential (ϕ_{LJ}) for the non-bonded interactions, where ε/k_B and σ are model parameters [4,5]:

$$\phi_{LJ} = \sum_{i=1}^2 \sum_{j=1}^2 4\varepsilon_{ij} \left[\left(\frac{\sigma_{ij}}{r_{ij}} \right)^{12} - \left(\frac{\sigma_{ij}}{r_{ij}} \right)^6 \right] \quad (1)$$

The 2CLJQ model describes the total fluid-fluid potential as a sum of the Lennard-Jones interactions (ϕ_{LJ}) and the quadrupolar interactions (ϕ_{QQ}), where the quadrupole moment of the fluid (Q) is an additional model parameter located at the geometric center of the molecule:

$$\phi_{QQ} = \frac{3}{4} \frac{Q^2}{(4\pi\varepsilon_0)r_{ab}^5} \left[1 - 5(c_i^2 + c_j^2) - 15c_i^2c_j^2 + 2(c - 5c_ic_j)^2 \right] \quad (2)$$

with:

$$c_i = \cos \theta_i \quad (3)$$

$$c_j = \cos \theta_j \quad (4)$$

$$c = \cos \theta_i \cos \theta_j + \sin \theta_i \sin \theta_j \cos \phi_{ij} \quad (5)$$

where i and j refer to the LJ sites on the molecules, r_{ij} is the distance between the centers of molecules i and j , r_{ab} is the center-to-center distance amongst molecules, θ_i and θ_j are the polar angles of the molecular axis with respect to a line joining the molecular centers, ϕ_{ij} is the difference in azimuthal angles and ϵ_0 is the vacuum permittivity.

The LJ parameters for the CH₃ groups of ethane and the CH₂ groups of ethylene for the three different models and the quadrupole moment for the 2CLJQ model are shown in table 2.

Table 2: Force fields and parameters for ethane and ethylene used in the simulations [4-7]

Component	Force field	Parameters			
		ϵ/k_B (K)	σ (Å)	l_0 (Å)	Q (B)
Ethane	OPLS-UA	104.1	3.775	1.53	
	TraPPE	98.0	3.75	1.54	
	2CLJQ	136.99	3.4896	2.3762	0.8277
Ethylene	OPLS-UA	70.44	3.850	1.34	
	TraPPE	85.0	3.675	1.33	
	2CLJQ	76.95	3.7607	1.2695	4.331

Simulation details: With Grand Canonical Monte Carlo (GCMC) simulations, the number of molecules adsorbed versus the activity is obtained. In order to change the activity into pressure, the virial equation of state in terms of activity is used [8]:

$$\frac{p}{p_0} = \frac{2\xi\xi_0^2 + (\rho_0 - \xi_0)\xi^2}{(\rho_0 + \xi_0)\xi_0^2} \quad (6)$$

where ξ_0 and ρ_0 are the activity and density of the saturation state point of pure ethane or ethylene at the needed temperature. The state points were calculated from bulk simulations and can be found in table 3.

Table 3: State points of ethane and ethylene at different temperatures

Component	T (K)	P (kPa)	ρ (mol/l)	ξ (Å ⁻³)
Ethane	273.15	2390.73	1.5550	0.0264
	298.15	4201.45	3.5906	0.0362
	323.15	6906.72	6.9481	0.0498
Ethylene	273.15	4101.03	3.5787	0.0423
	298.15	6957.74	7.5649	0.0618
	323.15	11152.44	8.7048	0.0808

The positions of the atoms of the adsorbent material were fixed during the simulations. This implies that the solid-solid interactions do not affect the calculations, as they cancel out when energetically comparing simulated configurations. Hence, only solid-fluid and fluid-fluid interactions were calculated. The Lorentz-Berthelot mixing rules were used to calculate the Lennard-Jones parameters between sites of different types.

The simulations required 2×10^7 configurations to reach the equilibrium. Average properties were calculated over blocks with 5×10^5 configurations once the equilibrium was reached. The fluid-fluid potential was cut at $r_c = 6 \sigma_{ff}$ as recommended by Duque and Vega [9].

In order to compare with previous experimental and simulation data on ethyl chloride/vinyl chloride adsorption, the number of ethane/ethylene molecules adsorbed was converted to the amount of ethane/ethylene adsorbed on AlMePO- α in excess to what is present in the bulk.

Results and Discussion

In figure 1 the simulated isotherms for ethane with the three different models are shown at 273.15 K, 298.15 K and 323.15 K. The error bars are so small that they fall within the symbols representing the data points. It can be seen that the three models give similar results.

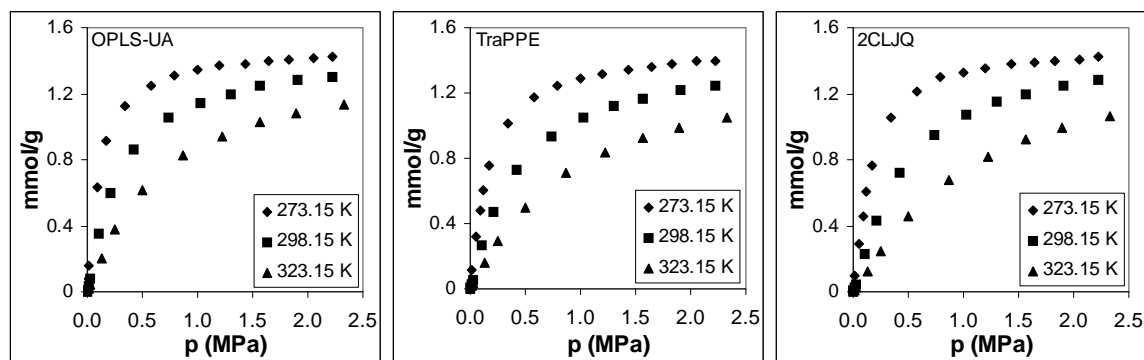


Figure 1: Adsorption isotherms of ethane in AlMePO- α at 273.15 K, 298.15 K and 323.15 K using the OPLS-UA model, theTraPPE model and the 2CLJQ model

Figure 2 shows the simulated isotherms for ethylene with the three different models at 273.15 K, 298.15 K and 323.15 K. Again, the three models give similar results.

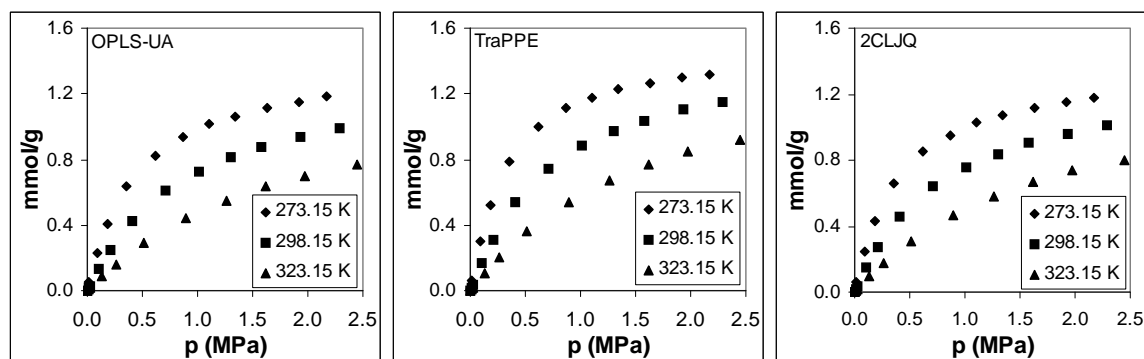


Figure 2: Adsorption isotherms of ethylene in AlMePO- α at 273.15 K, 298.15 K and 323.15 K using the OPLS-UA model, theTraPPE model and the 2CLJQ model

When comparing figures 1 and 2, it can be noticed that the adsorption of pure ethane is always higher than the adsorption of pure ethylene, so preferential adsorption of the paraffin by AlMePO- α is also observed for ethane/ethylene mixtures. Figure 3 compares the adsorption of ethane and ethylene at 273.15 K, 298.15 K and 323.15 K using the OPLS-UA model. It can be noticed that the adsorption of both ethane and ethylene is higher at lower temperatures, whereas the selectivity to ethane (=paraffin) adsorption is higher at higher temperatures. The optimal separation temperature is therefore a trade-off between a higher overall adsorption at lower temperatures and a higher selectivity at higher temperatures.

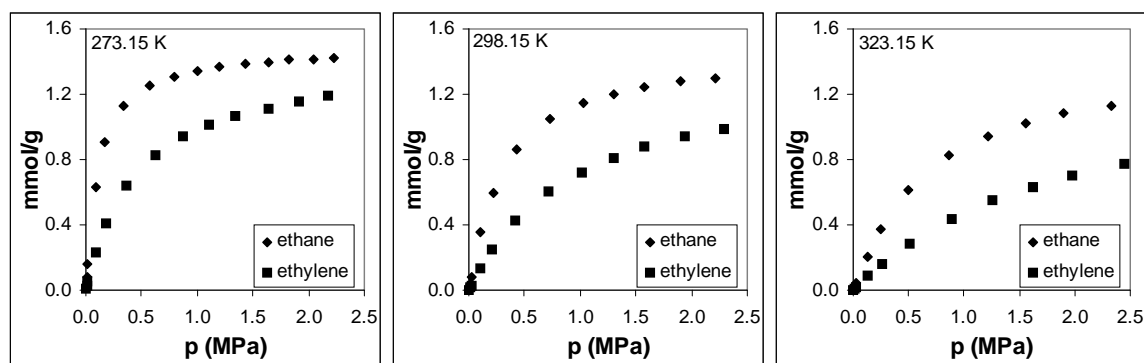


Figure 3: Adsorption isotherms of pure ethane and ethylene at 273.15 K, 298.15 K and 323.15 K using the OPLS-UA model

The obtained isotherms for ethane and ethylene were also compared to the isotherms determined previously for ethyl chloride and vinyl chloride [1], which are shown in figure 4. It can be seen that the adsorption of pure ethyl chloride is also always higher than the adsorption of pure vinyl chloride. Also, the difference in adsorption between ethyl chloride and vinyl chloride is increasing with increasing temperature, although this difference seems a little larger compared to the difference in adsorption between ethane and ethylene. However, the maximum amount of both ethyl chloride (1.05 mmol/g) and vinyl chloride (0.90 mmol/g) adsorbed is lower than the maximum amount of both ethane (1.4 mmol/g) and ethylene (1.25 mmol/g) adsorbed. Thus, both ethane and ethylene adsorb better to AlMePO- α than ethyl chloride and vinyl chloride.

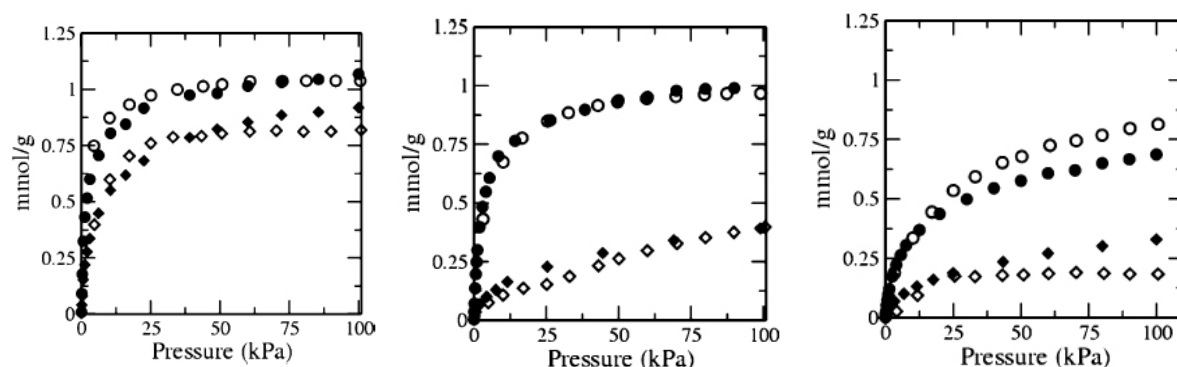


Figure 4: Adsorption isotherms of pure ethylene chloride and vinyl chloride at 293.15 K (left), 323.15 K (middle) and 323.15 K (right) [1]. Ethyl chloride experimental data (o), ethyl chloride simulated results (●), vinyl chloride experimental data (◇), and vinyl chloride simulated results (◆)

Because AlMePO- α shows selectivity for paraffin adsorption for both ethane/ethylene mixtures and for ethyl chloride/vinyl chloride mixtures, it is expected that the molecular interaction between the material and the paraffin is the key factor determining the selectivity and not the steric effects, as ethyl chloride and vinyl chloride are much larger than ethane and ethylene. This also follows from the snapshots shown in figure 5, where the ethane, ethylene, ethyl chloride and vinyl chloride molecules arrange exactly in the same way in the material AlMePO- α , with the methyl groups of the AlMePO- α directed towards the methyl groups of ethane and ethyl chloride.

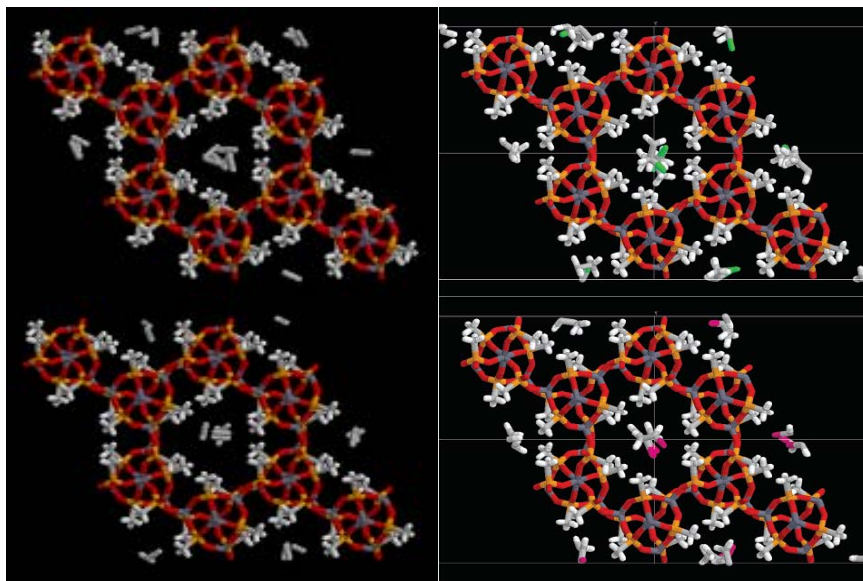


Figure 5: Snapshots at maximum loading for ethane (upper left), ethylene (below left), ethyl chloride (upper right) and vinyl chloride (below right)

Conclusions

The material AlMePO- α shows selective paraffin adsorption for both ethane/ethylene mixtures and ethyl chloride/vinyl chloride mixtures. Therefore, the key factor determining the selectivity is found to be the molecular interaction between the methyl group of this material and the methyl group of the paraffin.

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