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University of Aveiro & Ordem dos Engenheiros

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# Separation of hexane isomers in metal organic framework ZIF-8

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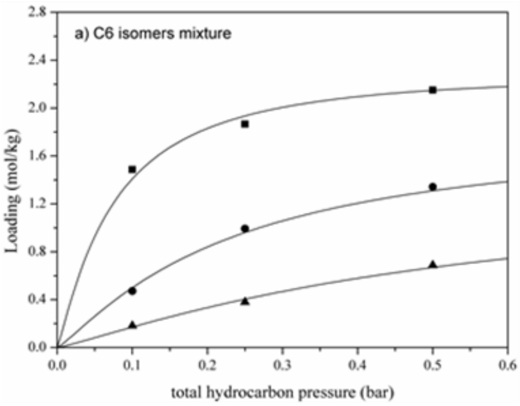

The performance of porous metal organic framework ZIF-8 in the separation of all five hexane isomers (nHEX, 2MP, 3MP, 23DMB, 22DMB), is evaluated through a series of multicomponent breakthrough adsorption experiments, at the temperatures of 373, 423 and 473 K and up to partial pressures of 0.5 bars. The reported data shows for all experiments the following sorption hierarchy: nHEX >> 2MP > 3MP >> 23DMB > 22DMB. It is also demonstrated that the sorption of nHEX is equilibrium based in contrast with the sorption of branched isomers which is kinetic controlled. The experimental data is also simulated through a mathematical model developed in MATLAB code, being the results in qualitatively agreement. This paper shows that it possible to separate the hexane isomers in ZIF-8 by classes linear/mono-branched/di-branched if proper experimental conditions are set-up, being the result of importance for the octane upgrading of gasoline.

The separation of hydrocarbon mixtures has become one of the most important topics in the petrochemical industry, including the separation of paraffins isomers in the range C5/C6 for the octane upgrading of gasoline. These processes separate low Research Octane Number (RON) linear paraffins [e.g., n-hexane (nHEX: RON 24)] from their respective branched isomers with higher RON content [e.g., 3-methylpentane (3MP: RON 74.5), 2-methylpentane (2MP: RON 73.4), 2,3-dimethylbutane (23DMB: RON 101.7) and 2,2-dimethylbutane (22DMB: RON 91.8. In this context, the newest class of crystalline porous material, the metal organic frameworks (MOF´s), have been studied for this separation target [1-4]. Due to their chemical and thermal stability, Zeolite Imidazolate Frameworks are of interest, specially ZIF-8 [5].

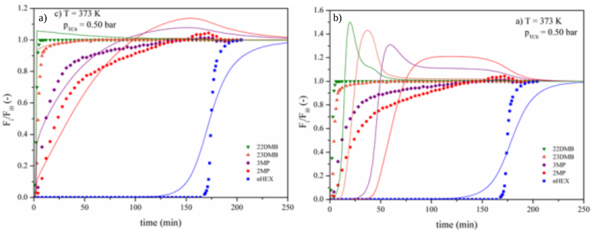

Figure 1. Breakthrough curves for an equimolar mixture of hexane isomers in ZIF-8 at 373 K and total hydrocarbon pressure of 0.50 bar.

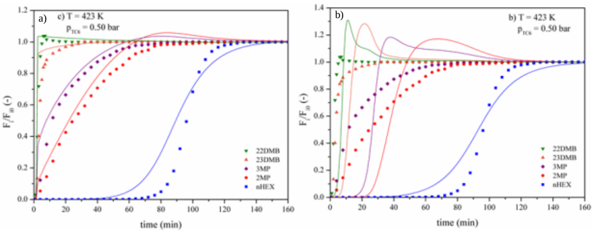

Figure 2. Breakthrough curves for an equimolar mixture of hexane isomers in ZIF-8 at 423 K and total hydrocarbon pressure of 0.50 bar.

The goal of this work is to contribute to a better understanding of the adsorption of hexane isomers on ZIF-8 through fixed bed adsorption experiments. For the first time, experimental breakthrough curves with an equimolar quinary mixture of all 5 isomers (nHEX, 3MP, 2MP, 23DMB and 22DMB) are measured. The influence of temperature and total hydrocarbon pressure are analyzed to evaluate the sorption dynamics behavior. Moreover, the data obtained are modeled by the Langmuir-Freundlich isotherm model and finally, all calculated data are used to development of a mathematical model, in MATLAB code, to predict the experimental breakthrough curves and validate the thermodynamic isotherm model.

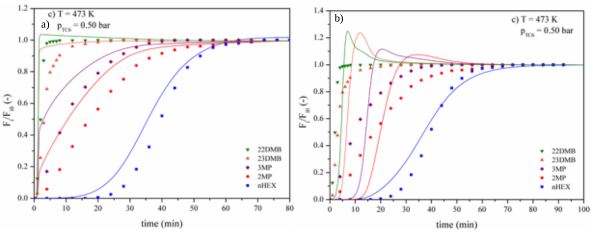

Figure 3. Breakthrough curves for an equimolar mixture of hexane isomers in ZIF-8 at 473 K and total hydrocarbon pressure of 0.50 bar.

The adsorption behavior of all five hexane isomers nHEX, 2MP, 3MP, 23DMB and 22DMB in ZIF-8 was investigated by performing a set of multicomponent equimolar breakthrough curves. The experiments were performed at temperatures 373, 423 and 473 K, total hydrocarbon pressure of 0.10, 0.25 and 0.50 bar and using helium to set-up a total pressure in the column of 1 bar.

A mathematical model was used to simulate the adsorption in a fixed bed column by using a system of partial differential equations (PDE´s), constituted by the mass and energy conservation laws, a general isotherm to describe the adsorption equilibrium and a control mechanism for the kinetic mass transfer from the bulk gas phase to the adsorbent. The adsorption data was described by the Langmuir-Freundlich isotherm [6]:

$$q_i = q_{maxi} \frac{b_i p_i^{n_i}}{1 + \sum_{k=1}^{j} b_k p_k^{n_k}}$$

where $q_{maxi}$ is the maximum saturation loading, $b_i$ is the adsorption equilibrium affinity constant, $p$ is the hydrocarbon partial pressure and $n_i$ is the heterogeneity index. When $n$ is 1 the material has a homogeneous surface and the model reduces to Langmuir isotherm applicable for ideal surfaces. The index $i$ refers to component and $j$ is the number of components present in the mixture.

Figures 1, 2 and 3 show the breakthrough curves for 373, 423 and 473 K, respectively, at a total hydrocarbons pressure of 0,50 bars, plotted in terms of normalized molar flowrate $F/F_0$ (-) and as a function of time (min) where the points are the experimental data and the continuous lines correspond to the numerical simulations. Globally, the results shown in these Figures indicate that the sorption hierarchy of hexane isomers in ZIF-8 is always nHEX >> 2MP > 3MP >> 23DMB > 22DMB (normal hierarchy), just like the order of the normal boiling point of the compounds. However, the shape of the breakthrough curve of nHEX is always different from the branched ones, which means that its sorption is essentially equilibrium based. In contrast, the branched isomers start their elution practically at the contact time of the gas in the column due to strong diffusional limitations. But, the approach to feed concentration of the branched isomers is different since the di-branched isomers 22DMB and 23DMB rapidly saturate at the early stage of the experiments, in contrast with the mono-branched isomers 3MP and 2MP that due to less diffusion limitations produce a less sharp approach to inlet concentration. These observations show that ZIF-8 separates the hexane isomers by classes linear>mono-branched>di-branched, which is an important result for petrochemical applications viewing the octane improvement of gasoline.

The Graphical Abstract shows the adsorption equilibrium isotherms of a mixture of hexane isomers in ZIF-8. Points are experimental data and the continuous lines represent the Langmuir–Freundlich model predictions for a mixture loading with the temperature at 373 K (□), 423 K (○) and 473 K (Δ). The experimental data was satisfactorily represented, and the isotherms are pronounced as type I in IUPAC classification. Next, the experimentally determined isotherm fits (Graphical Abstract) were inserted in the mathematical model developed in MATLAB code. Figures 1, 2 and 3 show that the numerical model developed is capable to describe the profiles of the breakthrough curves of hexane isomers very well. To prove that the separation between nHEX and branched isomers, and mono-branched 2MP/3MP from di-branched 22DMB/23DMB in flow system is kinetically driven, we decided to perform numerical simulations assuming thermodynamic equilibrium. Figure 1, 2 and 3 b) shows the simulations performed at the three studied temperatures and at total hydrocarbon pressure of 0.5 bar. In this case, the breakthroughs from equilibriums simulations show a completely different approach for the branched isomers in comparison with experimental data. Their shapes become more sharped and a pronounced roll-up for the branched isomers can be seen, reaching more than 1.5 of the feed concentrations for 22DMB and 23DMB at 373 K in Figure 1 a). One should also note that the overshoot of mono-branched isomers 2MP and 3MP is much higher that obtained from experimentally breakthrough curves. These overshoots are an evidence of the interactions occurring in the material in equilibrium separations, disregarding the strong diffusional limitations.

Concluding, this is the first experimental work dealing with the sorption of all five hexane isomers nHEX / 2MP / 3MP / 23DMB / 22DMB on ZIF-8. A series of multicomponent (equimolar) breakthrough curves were measured analyzing the effect of temperature and partial pressure on the hexane isomers sorption. All experiments showed a normal sorption hierarchy *n*HEX >> 2MP > 3MP >> 23DMB > 22DMB, being the di-branched isomers 22DMB and 23DMB completely sieved from the others. In addicting, the parameters obtained by the Langmuir-Freundlich model fitting were used to develop a mathematical model in MATLAB code for better understanding the sorption of all five hexane isomers in a fixed bed with ZIF-8. Firstly, the numerical simulation proves that the nHEX sorption is essentially equilibrium based while branched isomers are kinetically driven, since the experimental breakthrough curves of branched isomers were qualitatively reproduced by accounting for diffusional influences. Secondly, the contact time between the gas and the solid in the bed has extremely importance, once very low contact times doesn't allow the penetration of mono-branched isomers 2MP and 3MP in the structure of ZIF-8. Thirdly, in a global view, the results of numerical simulations clearly show that the agreement between the experimental data and the Langmuir-Freundlich model is reasonably good considering the wide range of studied conditions. Fourthly, this work has proved the great importance of using mathematical modelling to describe and understand experimental results and for futures designs of adsorptive processes.

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