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Separation of Amyl Alcohol Isomers in ZIF-77

Rocio Bueno-Perez,^[a] Juan J. Gutiérrez-Sevillano,^[a] David Dubbeldam,^[b] Patrick J. Merkling,^{*,[a]} and Sofia Calero^{*,[a]}

The separation of pentanol isomer mixtures is shown to be very efficient using the nanoporous adsorbent zeolitic imidazolate framework ZIF-77. Through molecular simulations, we demonstrate that this material achieves a complete separation of linear from monobranched—and these from dibranched— isomers. Remarkably, the adsorption and diffusion behaviors follow the same decreasing trend, produced by the channel size of ZIF-77 and the guest shape. This separation based on molecular branching applies to alkanes and alcohols and promises to encompass numerous other functional groups.

The industrial production of alcohols yields complex mixtures that depend on the process used. In the case of amyl alcohols (pentanols) that are obtained by low-pressure rhodium-catalyzed hydroformylation (oxo process) of butenes and subsequent hydrogenation, mainly 2-methyl-butanol and 1-pentanol are obtained in a catalyst-dependent ratio.^[1] If amyl alcohols are produced through the hydration of pentenes, other mixtures are obtained, for example 76% 2-pentanol and 24% 3-pentanol from 2-pentene. Pentanols are also found in fuel oils and in the fermentation of starch-containing products, but their recovery is uneconomical at present.^[2]

The fact that amyl alcohols possess an odd number of carbon atoms endow them with peculiar physical and solubility properties and make them attractive solvents, surfactants, extraction agents, and gasoline additives.^[1] Separation and purification of a wide range of alcohol isomers is therefore an important task. The main separation technique employed is distillation, an energetically costly step due to the high vaporization enthalpy of alcohols. Additionally, obtaining pure compounds is difficult because of the very similar boiling points of some of them, that is, 2-pentanol, 3-pentanol, 3-methyl-2-butanol, and 2,2-dimethylpropanol^[2–3] and the fact that they form azeotropes.^[2] A different strategy consists in separating these isomers over appropriate adsorbents. In this sense, the separation

of a few alcohols, mostly biobutanol and bioethanol has been studied over some ZIFs, especially ZIF-8, ZIF-71 and ZIF-90.^[4]

A recent computational study on a number of microporous materials suggested that ZIF-77^[5] is very well suited for the separation of hydrocarbons at high temperature,^[6] favoring linear over branched molecules, and these over dibranched ones, presenting the degree of branching as the driving force, a fact that has been also described experimentally, albeit on a different type of MOF.^[7] No flexibility, breathing nor phase changes have been reported for this structure. Also, the most similar structure to ZIF-77 that has been looked into for breathing is ZIF-78, in which the thermal expansion of the cell length is below 0.1%.^[8] In addition, the channel system in ZIF-77 is similar to those in zeolites, and no gate-opening effect is expected where flexibility could have a strong influence. Given that no reliable, well-tested flexible force field for the adsorbent is available, we deemed it safer to assume that the structure would be retained under loading and used a rigid framework. This would additionally provide us with a lower bound for diffusion coefficients. Several papers have reported the effect of flexibility on adsorption due to a change in structure.^[9,10] ZIF-77 exhibits very high selectivity, combined with a quite large adsorption capacity. Figure S1 of the Supporting Information (SI) shows that this structure possesses narrow channels along the z-direction interconnected with even smaller zig-zag channels along the x-direction, forming a two-dimensional system. The fact that zig-zag channels are narrower than the straight ones lets bulkier molecules diffuse only along the z-axis. Due to the zeolitic nature of the framework, metal centers are not accessible from the channels, in the same way that Si or Al atoms are not in a zeolite. The partial charge of the atoms exposed to the channels, including the nitro group, are small, therefore the channels present low polarity. In this study, we investigate the ability of ZIF-77 to separate the eight structural isomers of pentanol: 1-pentanol (1P), 2-pentanol (2P), 3-pentanol (3P), 3-methylbutanol (3MB), 2-methylbutanol (2MB), 3-methyl-2-butanol (3M2B), 2-methyl-2-butanol (2M2B) and 2,2-dimethylpropanol (22DMP). For the sake of the discussion, these structural isomers can be divided in four categories based on their heavy-atom skeleton, that is, ignoring hydrogen atoms: 1P would therefore be a linear molecule, 2P, 3P, 3MB and 2MB monobranched molecules, while 3M2B, 2M2B and 22DMP would be dibranched molecules. We find it useful to separate the latter three into molecules dibranched on different carbon atoms (3M2B) or on the same carbon atom (2M2B and 22DMP).

For a material to be an efficient adsorbent it should not suffer from diffusional limitations. The propensity of guest molecules to move through the porous environment can be ex-

[a] R. Bueno-Perez, Dr. J. J. Gutiérrez-Sevillano, Prof. P. J. Merkling, Prof. S. Calero
Department of Physical, Chemical and Natural Systems
University Pablo de Olavide
Ctra. Utrera, km. 1, 41013 Seville (Spain)
E-mail: pjmerkling@upo.es
scalero@upo.es

[b] Dr. D. Dubbeldam
University of Amsterdam
Science Park 904, 1098XH
Amsterdam (The Netherlands)

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pressed by the self-diffusion coefficients (D) and were obtained in this work by molecular dynamics simulations. The sets of force field parameters used are known to produce results in agreement with available experimental data and have high predictive capability.^[11] The model for the adsorbent is rigid and based on UFF^[12] force fields (Figures S1 and S2 and Table 1S, SI). The point charges used were derived specially for zeolitic imidazolate frameworks to improve the reliability of adsorption results based on UFF force field parameters.^[13] The adsorbates have been modelled using flexible united-atom models based on TraPPE force fields^[14] (Figure S3 and Table 2S, SI).

The results for the structural isomers of pentanol at low coverage and 298 K are shown in Table 1. These are directionally averaged self-diffusion coefficients. Diffusion takes place only along the z -direction, with the exception of 1P (Table 3S, SI)

Molecule	D [$10^{-10} \text{ m}^2 \text{ s}^{-1}$]	Molecule	D [$10^{-10} \text{ m}^2 \text{ s}^{-1}$]
1P	1.15 ± 0.25	3MB	0.074 ± 0.02
2P	0.12 ± 0.03	3M2B	0.067 ± 0.02
3P	0.17 ± 0.04	2M2B*	— ^[a]
2MB	0.20 ± 0.5	22DMP*	— ^[a]

[a] The self-diffusivities were too low to be computed by MD.

and its magnitude is similar to the one in the bulk.^[15] Independently from the temperature, 1P is the alcohol that diffuses the most. The linear 1P alcohol is able to wind efficiently through the channels. 2P, 3P and 2MB, molecules with one branching point as defined previously, have a self-diffusion coefficient an order of magnitude lower. Next, 3MB and 3M2B diffuse another factor 2 slower than the previous group of compounds. Whereas 3M2B possesses topologically two branching points, 3MB is ranked amongst the monobranched molecules but performs unexpectedly badly. Two structures, 2M2B and 22DMP, are seen to have negligible diffusion: due to their bulkiness around the central carbon, they cannot enter the pores. We will therefore exclude them from further consideration. To illustrate the accessible part of the structure for each alcohol, the diffusion trail and the density profile of a randomly inserted molecule is recorded. Diffusion trails are represented in Figure 1 for 1P, 2P, 3M2B and 22DMP. These and other views and molecules, as well as density profiles are shown in Figures S4, S5, S8 and S9 of the SI. As appears in Figure 1, the molecule in 1P is able to access the two-dimensional void space spanned by interconnected x - and z -channels. 2P and 3M2B molecules are restricted to moving through the z -channel in which they initially entered. Finally, 22DMP can only be generated in the central region of a pore cavity due to its bulkiness in all directions. Therefore, this molecule would be limited to the pore cavity.

To place these results in a broader context, diffusion data for alkanes were obtained at 298 K (Table 2 and Tables 3S and 4S of the SI). Alkanes engage in simpler intermolecular interac-

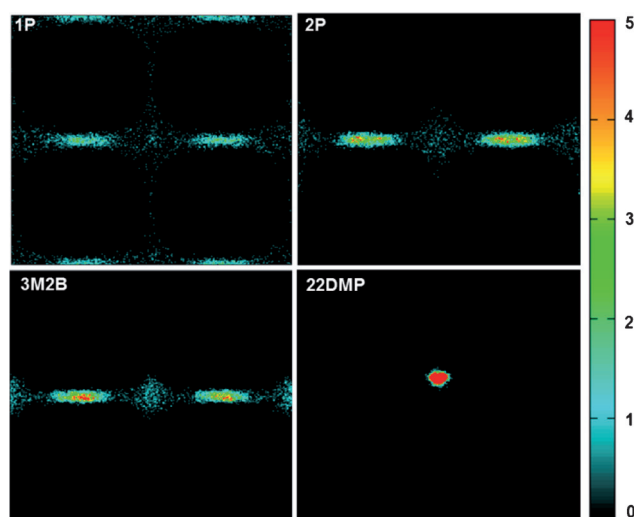


Figure 1. Molecular dynamics trajectories of adsorbates within the framework in a zx -view for four adsorbates: 1P (top left), 2P (top right), 3M2B (bottom left) and 22DMP (bottom right).

Molecule	D [$10^{-10} \text{ m}^2 \text{ s}^{-1}$]	Molecule	D [$10^{-10} \text{ m}^2 \text{ s}^{-1}$]
nC6	0.8 ± 0.2	23DMB	0.13 ± 0.02
2MP	0.13 ± 0.03	22DMB	— ^[a]
3MP	0.13 ± 0.04		

[a] The self-diffusivities were too low to be computed by MD.

tions than alcohols given that they lack the ability to form hydrogen bonds. They should therefore reflect the effect on diffusion of flexibility and shape of the molecule, and of van der Waals interactions. If we substitute the hydroxyl (OH) group for a slightly larger methyl (CH_3) group to form a related alkane, based on the principle that the molecule retains a similar size and shape, we obtain a set of alkanes and can establish a correspondence between alcohols and alkanes that is helpful in the comparison of both classes of molecules. In this way, the analogue of 1-pentanol is n -hexane (nC6), the one of 2P is 2-methylpentane (2MP), and so forth. Similarly to the case of alcohols, the single linear molecule diffuses faster than the monobranched alkanes, and these faster in turn than the alkane dibranched on different carbon atoms. As already observed in alcohols, molecules dibranched on the same carbon atom are not able to diffuse as they do not cross pore windows. In the case of alkanes, no exception to this ordering principle is observed. The alcohols and their related alkane diffuse at similar rates, the slight increase in size of the alkane makes up for the polarity of the alcohol in this rather hydrophobic environment. Nevertheless, in spite of the related topologies of alkanes and alcohols, the small differences in the dynamics of the pore are influenced by the position of the hydroxyl group, given the difference in size and nature between hydroxyl and methyl groups.

The latter can be evaluated through isosteric heats and Henry constants (Table 5S, SI) and relate to adsorption at low loading. However, both the linear alkane and alcohol fit neatly both in the large (*z*-) and small (*x*-) channels. Therefore, these molecules interact more strongly with the framework and adsorb better than mono- or dibranched molecules at low loading. The next best adsorbates are the monobranched 2P and 3P, and finally other alcohols. This is related to the behavior in alkanes, in which both monobranched isomers adsorb better than the dibranched ones.^[6] Obviously, the picture in alcohols is a more mixed one, given that 2MB and 3MB are also monobranched molecules, but are not able to interact that effectively with the framework as 2P and 3P do.

Adsorption isotherms of liquid feeds of equimolar composition at 298 K were computed using configurational bias Grand-Canonical Monte Carlo simulations.^[16] Liquid phase fugacities were computed from the saturated vapor pressures of the components, the liquid phase activity coefficients, and the external pressure of the system. The latter were calculated from the experimental vapor–liquid equilibrium data.^[17]

Figure 2 shows the adsorption values of the most adsorbed component and its selectivity versus the second most adsorbed one for equimolar mixtures containing up to six isomers. Thus, in ZIF-77, an equimolar mixture of all isomers (ex-

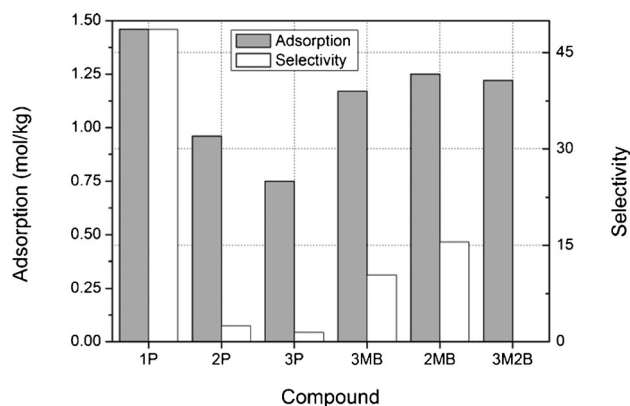


Figure 2. Histogram of the adsorption properties for the separation of equimolar mixtures: adsorption of the most adsorbed species and selectivity with respect to the second most adsorbed species. Moving one position from left to right in the figure means dropping the most adsorbed species from the equimolar mixture. The mixture on the left has six isomers (1P, 2P, 3P, 3MB, 2MB, 3M2B).

cluding 2M2B and 22DMP) adsorbs selectively 1P. The mixture containing the remaining isomers adsorbs mainly 2P, and its selectivity over 3MB is shown in Figure 2 as explained. By removing successively the most adsorbed species, we obtain the preferential order of adsorption in ZIF-77, which can be seen from left to right in this figure: $1P \gg 2P > 3P > 3MB > 2MB \gg 3M2B$. Data are obtained at fugacity conditions that led to saturation adsorption values and high selectivities with respect to the second most adsorbed species. Therefore, 1P can be separated efficiently from all other isomers. On the contrary, 2P cannot be separated efficiently from 3P, 3MB and 2MB, or any

mixture containing significant amounts of these. These four compounds may thus be grouped together based on their topology and these results show that similarity in shape makes separation more difficult while it is less important where the hydroxyl group is actually located. Finally, any of these four can be easily separated from 3M2B. In comparison, alkanes exhibit a similar adsorption pattern: the linear alkane is strongly favored over the monobranched ones and these over the dibranched one. Once again, the shape determines the behavior.

As seen from this study, ZIF-77 is unusual in that the molecules that diffuse best also achieve highest adsorption in a multicomponent mixture. This combination would be especially helpful in a membrane-based separation process. In this context, the overall separation ability for a mixture of two components *i* and *j* is estimated through permselectivity. The permselectivity can be approximated by the formula^[18] $S_{perm(ij)} = D_{x,y} / D_{x,y_i}$, where *x* and *y* represent the fraction of the components in the adsorbent and the feed, respectively.

For each of the multicomponent equimolar mixtures considered previously, one value of permselectivity has been selected and is shown in Table 3. It corresponds to the pair of the most adsorbed species of the mixture (molecule *i*), whereas molecule

Table 3. Permselectivity for alcohol molecules in ZIF-77 at 298 K.

Molecule <i>i</i>	Molecule <i>j</i>	S_{perm}
1P	2P	500
2P	3MB	4.0
3P	2MB	2.5
3MB	2MB	4.6
2MB	3M2B	39

j is its closest competitor. The separation between linear and monobranched molecules turns out to be far better than could be anticipated from adsorption results, and the one between monobranched molecules and the dibranched one is also significantly improved. This is remarkable, because generally the higher the affinity for a molecule (and therefore the selectivity), the lower its diffusion. Within the group of monobranched molecules, separation is confirmed to be difficult. Results for alkanes show a similar pattern, permselectivity between linear and monobranched molecules is higher than adsorption selectivity.

Selectivities in this ZIF have been found to be governed essentially by the branching of the molecules, as can be seen both in alcohols and their corresponding alkanes. The hydroxyl groups affect guest–guest interactions and framework–guest interactions when exposed in the molecule but the hydrocarbon chains moderate this effect. The logarithm of the octanol–water partition coefficient ($\log K_{OW}$) can give a measure of how polar a molecule is and how it behaves in different solvents or molecular environments. This value for the alcohols studied spans from 0.89 to 1.51, for 2M2B and 1P, respectively,^[19] while for alkanes the values are around 3.70. Many chemical compounds possess $\log K_{OW}$ values within this range. Given a proper length of the hydrocarbon chain, linear molecules of

ketones, acids, aldehydes, cis/trans alkenes, thiols and ethers should also be separated from their branched isomers by ZIF-77. Thus, an efficient adsorption relies just as much on enough interactions between hydrocarbon chains and the adsorbent as it could possibly on strong dipolar or hydrogen-bond interactions. So we expect that in the low-polarity environment inside ZIF-77 linear molecules of a wide range of chemical classes are better suited for diffusing and adsorbing than branched ones.

This work shows that ZIF-77 is a promising material for the separation of pentanol isomers. The order of preferential adsorption and diffusion is linear over mono-branched over di-branched molecules on different C-atoms. Molecules di-branched on the same C-atom are not able to enter the framework. The same is true for alkanes, indicating that the hydroxyl group does not significantly affect the separation behavior, but that it is instead sterically driven. It is thus able to achieve the separation of polar, hydrogen-bond-forming molecules with a hydrocarbon tail on one side and of nonpolar molecules altogether on the other. This makes ZIF-77 a prime candidate for the separation of linear from branched molecules of intermediate size (five to six carbon atoms), independently of the chemical functional group involved, at least as long as it retains the hydrophobic character in part of the molecule.

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