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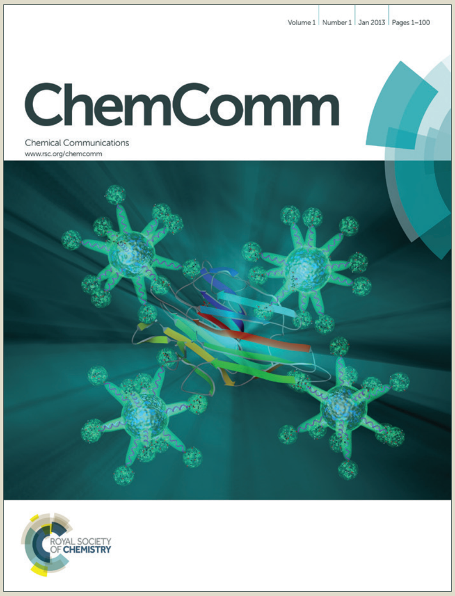

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Separation of polar compounds using a flexible metal-organic framework

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A flexible metal-organic framework constructed from a flexible linker is shown to possess the capability of separating mixtures of polar compounds (propanol isomers) by exploiting the differences in the saturation capacities of the constituents. Transient breakthrough simulations show that these sorption-based separations are in favor of the component with higher saturation capacity.

Separation and purification of organic liquid isomers is a scientifically important industrial technology and has received considerable attention worldwide.[1] Distillation is clearly the dominating separation process, accounting for more applications than all the other chemical-separation processes combined. In fact, distillation columns consume more than 50% of the total energy used in the chemical industry worldwide. Even more challenging is separation of an azeotrope mixture that forms when certain compositions of liquid isomers are present by weight. Specifically, the separation of water, alcohols, and ketones often is made difficult because of azeotrope formation. Separating these mixtures using fractional distillation or using polymeric membranes is energy-intensive and is highly complex.[2] Alternatively, these processes sometimes require the addition of a separating agent, called entrainers, that alter the vapor/liquid equilibrium in a favorable manner to achieve the desired separation, but the recovery of such entrainers later in the process not only requires an additional distillation step but also incurs an increased over all energy penalty. The largest opportunities for energy reduction in this area are offered by replacing distillation or membrane-based separations by low-cost adsorption-based systems. The success of such replacement strategies is crucially dependent on development of suitable adsorbents, but there is very limited information available on adsorptive-based separation of azeotropes using porous media.

Recent developments in porous metal-organic frameworks (MOFs) have gained much attention because of the outstanding properties and ability to fine tune the pore apertures and high stability towards the desired application.[3],[4] Such remarkable properties of MOFs make them an interesting class of materials for adsorption,[5] and separation applications.[6] Specifically, studies of the gas separation are extensively reported in the literature; however, very limited information is available on the separation of polar molecules, including azeotropic mixtures. For example, Denayer et al used highly stable zeolitic imidazole frameworks (ZIF-8, ZIF-68) to separate butanol from aqueous mixtures in the presence of organic contaminants like ethanol.[7] Jie Zhang et al reported the separation of alcohol and water mixtures using a charge-polarized MOF that shows selectivity towards polar molecules under an electric field gradient.[8] Similarly, Kitagawa et al synthesized a copper-based coordination polymer that selectively adsorbs methanol and water from bioethanol.[9] Most of these studies focused on purifying bioethanol, but there are few reports that focus on the separation of mixtures of alcohols and other polar molecules such as chloroform and acetone.[6g, 10] Our experimental adsorption studies coupled with transient breakthrough simulations confirm the separation of propanol isomers and various azeotropes. To our knowledge, this is the first report on the separation of mixtures of propanol isomers and other binary mixtures containing alcohols, chloroform, and acetone using flexible MOFs.

TetZB, the flexible porous framework used in this communication, was synthesized using a flexible tetrahedral organic linker, tetrakis[4-(carboxyphenyl)-oxamethyl]methane **1** (Scheme S1) and then was used effectively for the sorption and separation of polar solvents. The synthesis method and associated sorption properties of TetZB were reported by us previously.[11] For this study, we chose adsorption experiments of polar solvents such as C1–C3 alcohols, water, acetone, chloroform, and benzene, respectively. Experimentally measured vapor sorption capacities were obtained using an Intelligent Gravimetric Analyzer (IGA) from Hiden Instruments. The TetZB sample was activated at 473K under dynamic vacuum before sorption studies. To evaluate the separation efficiency of TetZB, we initially considered 1-propanol /2-propanol isomers for the sorption studies. After sample activation, the MOF sample was exposed to 1-propanol vapors and the sorption behavior was plotted against pressure. The adsorption curve shows a sudden increase in uptake at relative pressure (P/P_0) of 0.15 reaching the first saturation capacity of 7.8 wt%. At a relative pressure of P/P_0 of 0.27, TetZB shows another step adsorption and reaching second saturation capacity of 26 wt% or 4.55 mmol/g (Figure 1). Such two-step adsorption was observed in TetZB with other gas/vapors and was shown to expand and contract the framework upon guest removal and re-adsorption of the same or different guest molecule. The flexibility arises from the twisting of benzoate moieties around the central quaternary carbon atom through ethereal links of the tetrahedral building block that result from diverse ligand geometries such as tetrahedral, irregular, or near-flattened. Such building block flexibility has been observed both by us and other researchers. The desorption curve does not follow the adsorption, rather, it shows a sudden decrease in the sorption capacity at a P/P_0 ratio of 0.03 (Figure S1). Similarly, when a freshly activated MOF sample was exposed to 2-propanol vapors, the first uptake isotherm reached its first plateau at P/Po = 0.3; this was followed by a step adsorption with approximately 2.5 times higher capacity (25 wt%, 4.1 mmol/g at P/Po = 0.8), and then the saturation point was reached. Another significant difference between these two sorption isotherms is the rates at which they sorb onto the TetZB framework. Sorption profiles indicate that both propanol isomers can enter the pores of TetZB, but 1-propanol with its kinetic diameter of 4.7 Å has slightly higher uptake when compared to 2-propanol with the same kinetic diameter. This may be attributed to the flexibility of the 1-propanol, which is a linear chain that can enter the pore more easily than a branched isomer. The density functional theory (DFT) estimated dipole moment values of 2-propanol is slightly higher (1.56D) than 1-propanol (1.49D), which shows the 2-propanol molecule is more likely to be polarized by the TetZB pore structure, thus having a sharper uptake at relatively low pressure compared to 1-propanol.[12]

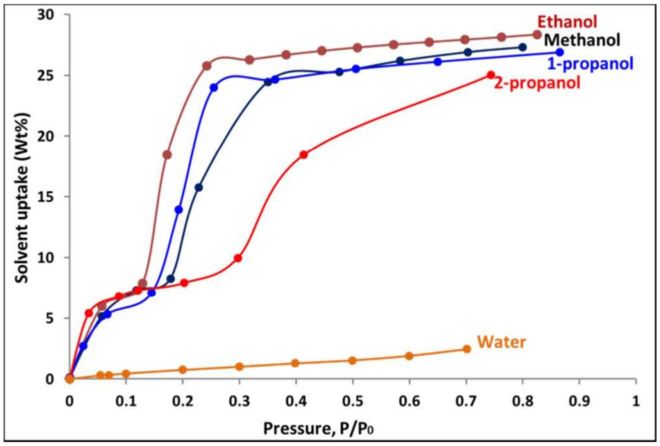

Figure 1. Adsorption isotherms of alcohol adsorbents and water in TetZB at 298 K.

To gain further insights on sorption behavior, we performed grand canonical Monte Carlo (GCMC) simulations using the MuSic program where the simulation box consisted of one unit cell of MOF and the periodic boundary conditions were used in all three dimensions. [13] Because the host framework considered has a rigid structure, the breathing phenomenon was not observed, but the overall solvents uptake matched the experimental results at 25°C (Figure S6). In agreement with experimental results, the simulations of 2-propanol sorption curve appears to be steeper at lower loadings when compared to 1-propanol. To understand this behavior, we computed the interaction energies between the TetZB framework and propanol isomers as function of loading. The simulated results clearly showed more negative interaction energies for 2-propanol when compared to 1-propanol at lower loadings (Figure S6), but the overall uptake is slightly higher for 1-propanol. These intriguing experimental and simulation results suggest vapor sorption experiments of 1-propanol and 2-propanol using the flexible TetZB has a potential for separating propanol isomers, which motivated us to undertake further IAST breakthrough simulations.

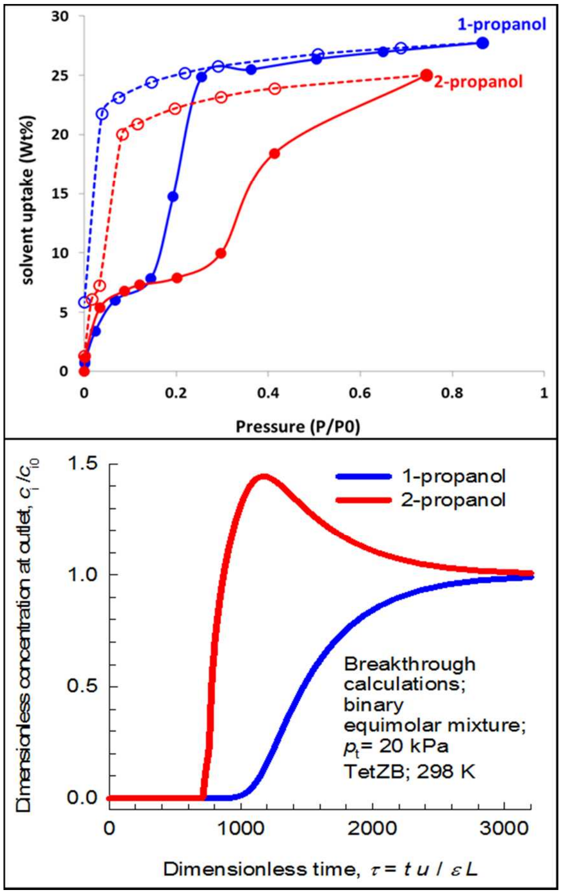

Figure 2. Adsorption and desorption isotherms of 1-/2-propanol in TetZB (top) and corresponding transient breakthrough simulation characteristics of an adsorber packed with TetZB for separation of 50/50 mixtures of 1-propanol from 2-propanol (bottom)

We then focused our attention on lower chain alcohols such as methanol and ethanol. The sorption isotherm of methanol shows a sudden increase at a P/P_0 ratio of 0.18 and then reaches 27 wt% at a P/P_0 ratio of 0.8. For ethanol after the first uptake at low relative pressure, the isotherm reaches its first plateau (7.8 wt% at a P/Po ratio of 0.12) followed by a step adsorption with approximately four times higher capacity of ethanol (25.7 wt%, 6 mmol/g at P/Po = 0.25). Because of the hydrophobic nature of the TetZB framework, water sorption studies show a low uptake until the P/P_0 ratio reaches

0.7, and the isotherm does not reach saturation even at a P/Po ratio of 0.95. The saturated loadings of alcohols decrease as the size increases from methanol to propanol because adsorption near saturation is mainly directed by the entropic (size) effect as fewer propanol molecules can be adsorbed compared to methanol (Figure S2). Further, interestingly when TetZB is exposed to acetone vapors, the first plateau is reached at a very low relative pressure (P/Po = 0.05). Chloroform and benzene show a type-I isotherm that exhibit significant uptakes at low vapor pressures. The distinct behaviors of the solvent molecules with the host framework definitely reveal a potential for application in separation technologies that should be studied.

To investigate the separation potential of TetZB, the experimentally measured loadings of 1- and 2- propanols, methanol, ethanol, acetone, benzene, chloroform, and water were fitted with the dual-site Langmuir-Freundlich model, and the fits are excellent over the entire range of pressures. The details of simulation methodology and the breakthrough simulations using IAST calculations are outlined in the supporting information. The transient breakthrough simulations suggest TetZB has the potential to separate mixtures of alcohols by differentiating on the basis of chain length and conformation as can be observed for 1-propanol/2- propanol mixtures (Figure S7-S9). The separation of 1-propanol from 2-propanol is governed by molecular packing effects that favor the adsorption of the linear alcohol when operating under conditions corresponding to pore saturation. The better packing efficiency of 1-propanol is reflected in its higher saturation capacity compared to 2-propanol. It is important to note that this separation is not dictated by differences in binding energies that are higher for 2-propanol (Figure S6b). For other mixtures of 1-alcohols, in the Henry regime, at pressures below 1 kPa, selectivity favor alcohols with longer chain lengths; however, at pressures above 10 kPa, selectivity favors alcohols with shorter chain lengths. This is because of the higher saturation capacity of the shorter chain alcohols. The IAST calculations also imply that sharp separations of alcohol mixtures are possible using TetZB provided the operating pressures are greater than 10 kPa. This is confirmed in the transient breakthrough simulations presented in for 50/50 mixtures of methanol/ethanol, ethanol/1-propanol, and ethanol/2-propanol at a total pressure of 100 kPa (Figure 3, Figure S9-S12). It is interesting to compare the separations of TetZB with those obtained with ZIF-8 and CHA zeolite. The shorter chained alcohol is eluted later than the longer chain alcohol, which is in agreement with the corresponding results for other microporous materials such as SAPO-34, and ZIF-8 reported previously.[7b, 14] Comparisons of ethanol/1-propanol adsorption selectivity, and uptake capacity of ethanol for equimolar ethanol/1-propanol mixtures in TetZB, ZIF-8, and CHA zeolite are shown in Figure S10. We note that TetZB has both higher selectivity and higher uptake capacity, making it more suitable for separation of mixtures of 1-alcohols (Figure S11-S16). Figure 3f shows the separations of water/ethanol mixture of azeotropic composition using TetZB. The separation is selective to water that has the higher saturation capacity; similar water-selective separations, achieved as a result of molecular packing effects, have been reported for CuBTC.[15] The methodology adopted for the breakthrough simulations are provided in the Supporting Information. Also available as ESI are seven video animations of the breakthroughs.

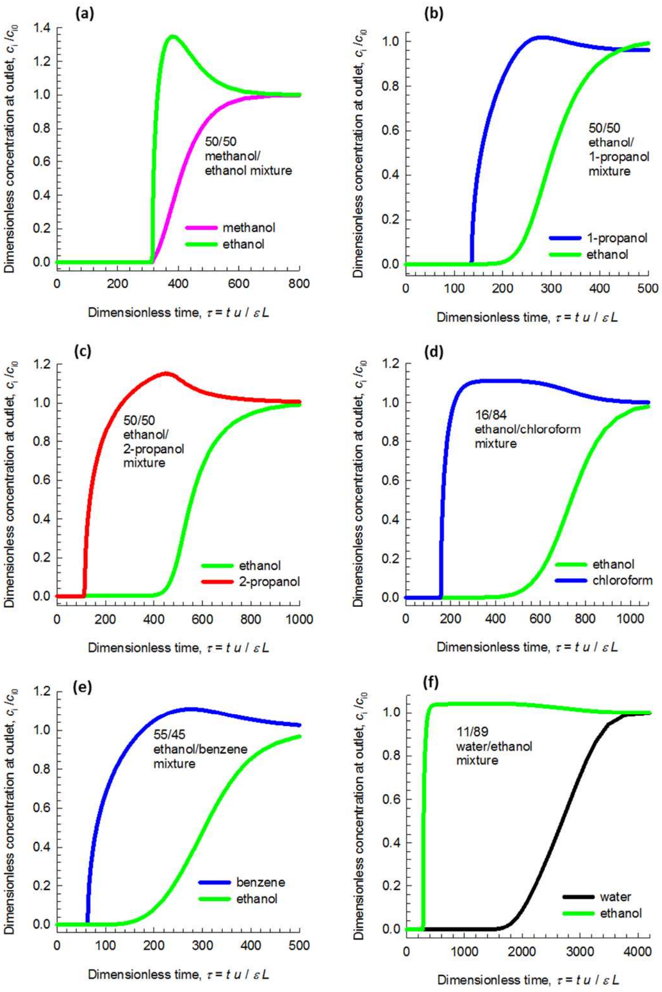

Figure 3. Transient breakthrough simulation characteristics of an adsorber packed with TetZB for separation of ethanol from various solvent mixtures of (a) methanol, (b) 1-propanol, (c) 2-propanol, (d) chloroform (e) benzene, (f) water at 298K. The total pressure is 100 kPa.

The experimental and modeling sorption analysis shows that the hydrophobic –CH_2 and aryl groups of the tectonic acid and phenyl groups of the 4,4’-bipyridine molecules are exposed inside the pore, thereby creating a hydrophobic environment.[11] To illustrate such an environment, we painted all the hydrophobic groups in green and the hydrophilic groups in red where it is clearly evident that hydrophobic groups dominate the surface of the pore (Scheme S1, Figure S6). The metal atoms and the carboxylate groups that are more hydrophilic are buried deep inside and are not easily accessible to the guest molecules. Polar alcohols such as methanol, ethanol molecules consisting of hydrophobic and hydrophilic groups interact favorably with pore components, leading to higher uptake rates with high adsorption energies. To our knowledge, this is the first report of the separation of propanol isomers, mixtures of 1-alcohols with acetone, and chloroform ketones using MOFs.

In conclusion, we report that hydrophobic TetZB, a flexible metal organic framework generated from a flexible tetrahedral building block, shows remarkable affinity and separation capability of alcohols and ketones, specifically separation of propanol isomers. If the operating conditions are chosen such that pore saturation is achieved, separation using TetZB strongly favors the component with the higher saturation capacity. For mixtures of alcohols, the separation is selective for the alcohol with the shorter chain length. For separation of water/alcohol mixtures, the separation favors water. Of particular interest is the separation of azeotropic water/ethanol mixtures; see Figure 3(f).

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† Electronic Supplementary Information (ESI) available: (a) material synthesis, characterization; (b) pure component isotherms and dual-Langmuir-Freundlich models; (c) adsorption energy calculations, (d) GCMC simulation studies, (e) IAST calculations; (f) transient breakthroughs simulation methodology; (g) video animations for transient breakthroughs of several binary mixture separations. See DOI: 10.1039/c000000x/

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