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Unravelling the influence of carbon dioxide on the adsorptive recovery of butanol from fermentation broth using ITQ-29 and ZIF-8†

Ana Martin-Calvo, Stijn Van der Perre, Benjamin Claessens, Sofia Calero and Joeri F. M. Denayer*

The vapor phase adsorption of butanol from ABE fermentation at the head space of the fermenter is an interesting route for the efficient recovery of biobutanol. The presence of gases such as carbon dioxide that are produced during the fermentation process causes a stripping of valuable compounds from the aqueous into the vapor phase. This work studies the effect of the presence of carbon dioxide on the adsorption of butanol at a molecular level. With this aim in mind Monte Carlo simulations were employed to study the adsorption of mixtures containing carbon dioxide, butanol and ethanol. Molecular models for butanol and ethanol that reproduce experimental properties of the molecules such as polarity, vapor–liquid coexistence or liquid density have been developed. Pure component isotherms and heats of adsorption have been computed and compared to experimental data to check the accuracy of the interacting parameters. Adsorption of butanol/ethanol mixtures has been studied in absence and presence of CO2 on two representative materials, a pure silica LTA zeolite and a hydrophobic metal–organic framework ZIF-8. To get a better understanding of the molecular mechanism that governs the adsorption of the targeted mixture in the selected materials, the distribution of the molecules inside the structures was analyzed. The combination of these features allows obtaining a deeper understanding of the process and to identify the role of carbon dioxide in the butanol purification process.

Introduction

The production of bio-alcohols has gained immense interest as an alternative to petroleum-based fuels and chemicals, as a result of increasing fossil fuel prices and environmental issues. At this point, these renewable chemicals represent a great opportunity as bio-based materials pose a variety of high-value industrial uses. Additionally, their production costs and emissions of greenhouse gases during their processing are low. Among bio-alcohols, bio-butanol has shown superior properties such as higher energy and lower volatility and water miscibility. Traditionally, these green chemicals were obtained by fermentation of different feedstocks. However, the economical production of bio-butanol remains a major challenge as (1) the production of butanol by ABE (acetone/butanol/ethanol) fermentation processes, produces a mixture of the three components diluted in water, and (2) the solvent toxicity is a main limiting factor of fermentation process, since above a certain amount of solvent, the cellular metabolism of the bacteria responsible for fermentation ceases, leading to low productivity. In recent years, huge investments have been made in order to improve such fermentation processes and to make production more competitive. Among the most used techniques, adsorption on molecular sieves has been posted as the cheapest and most energy-efficient technique for the recovery of butanol from fermentation broth. A variety of porous solids such as activated carbons, zeolites, and Metal–Organic Frameworks (MOFs) have been studied for this purpose. Most studies focus on the separation of the main components from the aqueous phase in the fermenter. However, gases such as hydrogen or carbon dioxide are produced as well during the fermentation process, which causes a stripping of valuable compounds from the aqueous phase into the vapor phase (head space) above the liquid. The vapor phase recovery of butanol from the head space has some obvious advantages over liquid phase adsorption such as absence of cells and inorganic salts which could cause clogging of the adsorbents and absence of acids, fermentable carbohydrates and other competing species. Relative to water, the head space is enriched the acetone, butanol, and ethanol.
When using porous materials for the adsorptive recovery of butanol in vapor phase processes, at least two main steps have to be considered: (1) an adsorption step, using one or multiple adsorption columns, to selectively adsorb as much butanol as possible, while releasing the other components of the mixture, and (2) a desorption step to recover butanol. Since an important amount of carbon dioxide is present in the head space of the fermenter, an effect on the adsorption and separation of butanol, ethanol, acetone and water could occur. Therefore, the main goal of this work is to understand the effect that the presence of carbon dioxide may have on the adsorption of the ABE components and to explore if its use could be beneficial for the recovery process.

Only few studies address the vapor phase adsorptive recovery of butanol from the head space of the fermentor. In a recent study, we proposed a multiple step process in which the combined use of different types of hydrophobic, shape selective zeolites allows to obtain very high butanol purity at elevated butanol recovery. An inert stripping gas (helium) was used in the adsorption and desorption step. In other recent study, gas stripping with carbon dioxide was combined with an adsorption processes for butanol separation. The performance of an activated carbon F-400 on the separation of a butanol/water mixture, an ABE model solution, and a real fermentation broth was analyzed. It was demonstrated that the negative effect of fermentation side-products on the butanol adsorption were eliminated using this method. However, in a recent study of butanol separation on zeolitic imidazolate frameworks, it was observed that the use of humid CO₂ as stripping gas reduces the butanol adsorption capacity of many materials as a result of the formation of complex carbonates.46

With these results in mind, the current work wishes to extend our knowledge by studying the effect that carbon dioxide exerts on the recovery of butanol on two well-known families of porous materials (zeolites and MOFs) at a molecular level. This study focusses on two hydrophobic materials that were identified before as interesting adsorbents for the vapor phase recovery of biobutanol. In particular, zeolite ITQ-29 and the metal organic framework ZIF-8 are studied.

This work uses molecular simulations techniques to gain a general understanding of the role of carbon dioxide in the recovery of butanol from ABE fermentation broth. Adsorption properties such as adsorption isotherms, heats of adsorption, and molecular distribution inside the structures have been analyzed in both materials for pure components and mixtures containing CO₂, ethanol and butanol. For this purpose, new realistic models for butanol and ethanol have been proposed. The simulation results are compared to experimental results recently acquired in our group.

**Methods**

Computational calculations have been performed using the molecular simulation software RASPA. Characteristic molecular properties such as the vapor-liquid equilibrium curve or liquid density of the component of interest have been obtained through Gibbs- and NVT-ensemble simulations, respectively. Adsorption isotherms were calculated by Monte Carlo simulations in the grand canonical ensemble, while for heats of adsorption under diluted conditions, we used the Widom test particle method. Absolute adsorption is transformed into excess adsorption for comparison with experimental results. Pore Size Distribution (PSD) of the materials are computed geometrically. Rotation, translation, reinsertion and identity change in the case of mixtures are the movements applied to the molecules. Details of the simulation methods can be found elsewhere in literature.39–41

In this work, flexible models for butanol and ethanol, based on TraPPE models are proposed. Both molecules are defined using united atoms models for the aliphatic chain, where each CH₂ group is considered as a single interaction center, while in the hydroxyl group, oxygen and hydrogen are defined independently. Bonds are kept fixed while harmonic bend and TraPPE dihedral potentials are used for angles and torsions, respectively. Molecular parameters are taken from TraPPE, same as for Lennard-Jones and partial charges of oxygen and hydrogen atoms, as well as for the connecting CH₂ group.42 Lennard-Jones parameters of the other CH₂ groups are obtained from a previous work of Dubbeldam et al.43 Since this work adopts parameters from different publications, as a prior step to our study, it is crucial to validate these new models by reproducing experimental properties of the molecules such as their vapor-liquid equilibrium curve or liquid density. Fig. S1 from the ESL† shows the excellent agreement obtained for both properties.

For carbon dioxide, a full atom model with molecular and interacting parameters well validated and reported in the literature is used.45

The adsorbent materials ITQ-29 and ZIF-8 are considered as rigid frameworks, using their crystallographic position of the atoms (cubic unit cells of a = b = c = 11.8671 Å and a = b = c = 16.991 Å, respectively).46,47 Lennard-Jones parameters and partial charges of the atoms from the structures are taken from previous publications of Garcia-Sanchez et al. (ITQ-29) and Gutierrez-Sevillano et al. (ZIF-8), respectively. As mentioned before, both materials have a hydrophobic nature. ITQ-29 is a pure silica LTA zeolite, formed by sodalite cages connected to each other, resulting in large cavities. Sodalite cages are not accessible for the gases under study; therefore, their adsorption is limited to the so-called x-cages of ITQ-29 by a selective blockage of the structure. ZIF-8 is a MOF with sodalite topology, containing zinc at metal nodes and imidazole linkers. Even though ZIF-8 is well known for showing a window swing effect that may affect the adsorption behavior of the material in certain conditions, this structural flexibility is predictable for adsorption of butanol at room temperature, as demonstrated in our previous work. Although this flexibility could have an important effect on the dynamic properties, this is out of the scope of this work.

Adsorbate-adsorbent as well as adsorbate-adsorbate interactions are defined by Lorentz-Berthelot mixing rules (except for ITQ-29-adsorbate interactions, which are detailed in Table 1), while for coulombic interactions the Ewald summation method
is used with a relative precision of $10^{-6}$. Lennard-Jones and coulombic potentials are cut and shifted at a cutoff distance of 12 Å. The simulation box consists of $3 \times 3 \times 3$ unit cells for ITQ-29 and $2 \times 2 \times 2$ unit cells for ZIF-8, with periodic boundary conditions applied. As a validation of the interacting parameters, pure component isotherms at 313 K have been computed and compared to experimental values in Fig. 1.

As an additional validation of the model of ethanol, adsorption isotherms in DDR zeolite at different temperatures have been computed (Fig. S2 from the ESI†). The results obtained are also in accordance with experimental data from Kuhn et al.50 With our new model, the differences found in a previous publication where a standard TraPPE model was used, are overcome.

To compare the results obtained for mixtures, the adsorption selectivity of a component from a mixture, which is defined as the ratio between the adsorption loading of the molecules and their molar fraction in the mixture, was calculated following the expression:

$$x_j / y_j = \frac{y_j}{x_j}$$

where $y$ represents the adsorption loading of the molecules and $x$ their molar fractions.

To mimic the real conditions at the head of the fermenter, an estimation of the molar composition was obtained using AspenPlus 4.11. All components, present at the end of the fermentation process in the aqueous medium (input), were considered to determine the vapor phase composition (output). Table S1 from the ESI† shows the composition of the vapor phase for a typical ABE fermentation mixture at 35 °C and 5 kPa using the Wilson model in the software program. Then, since the mixtures under study in this work are more simplistic (binary and ternary mixtures), their molar fractions are stablished to reproduce the same molar-ratio between components than the obtained for the complete mixture.

### Results and discussion

After validation of butanol and ethanol models as well as their interacting parameters with the structures, pure component adsorption behavior was studied on both materials. As observed from Fig. 1, the butanol saturation capacity of ZIF-8 is almost the double of the ITQ-29 capacity. Looking at their pore size distribution, PSD (Fig. S3 from the ESI†), the differences in dimensions of the large cavity of both materials (from 10 to 11 Å in ITQ-29 and ZIF-8, respectively) are not large enough to be responsible for the differences in butanol capacity, despite the presence of inaccessible sodalite cages in ITQ-29 (5 Å in diameter). However, the accessible pore volume of both structures differs significantly, with ITQ-29 having about half the available pore volume (0.32 cm$^3$ g$^{-1}$) of ZIF-8 (0.57 cm$^3$ g$^{-1}$), readily explaining the differences in butanol saturation capacity on a volumetric basis.

The differences in size of the large cavities are decisive on the distribution of the molecules of butanol inside the structures. As seen in Fig. 2, butanol molecules are found in the main cavities of ITQ-29, while in ZIF-8, molecules are mainly located close to the walls of the cavities. Since ZIF-8 has larger cavities than ITQ-29, at the pressure under study this material is not fully saturated.

In a next step, the adsorption of a CO$_2$/butanol binary mixture was investigated. To this purpose and to mimic the process as realistic as possible, a 99.5 : 0.5 CO$_2$/butanol mixture was studied. This composition leads to a CO$_2$/butanol molar-ratio equivalent to the one found within a real mixture in the fermenter head space, where other byproducts are also present.

Fig. 3 shows that, despite being present at very low concentration in the mixture, the adsorption of butanol remains almost identical as that of the pure component, while the adsorption of carbon dioxide is very low in the whole pressure range in the two structures.

The significantly larger heat of adsorption of butanol compared to carbon dioxide (see Fig. 4a) explains this behavior. The higher heat of adsorption of butanol is mainly attributed to

<table>
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<th>Atoms</th>
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<tr>
<td>Oz-O$_{co2}$</td>
<td>78.98</td>
<td>3.237</td>
</tr>
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</table>

Fig. 1 Pure component isotherms of butanol, ethanol, and carbon dioxide at 313 K in ITQ-29 (left) and ZIF-8 (right). Comparison of experimental values (empty symbols) and simulated results (full symbols). Experimental results of butanol and ethanol are taken from previous publications.33,34
dispersive interactions and indicates a stronger interaction of the molecule with the structures. The larger size of butanol also favors commensuration of this molecule inside the cavities of the structures. As expected, the values of the heat of adsorption in ITQ-29 are larger than these in ZIF-8 since the cavities of the former are slightly smaller and therefore weaker van der Waals interactions are expected for ZIF-8. The distribution of the molecules is also representative of the observed behavior. While butanol molecules are found at the main cavities (Fig. 4b) with a similar distribution as observed for pure components (Fig. 2), carbon dioxide (Fig. 4b) can only be adsorbed in the remaining available space of the main cavities and at the windows between cavities since butanol molecules are too large to be adsorbed there.

A different behavior is observed when the differences in size between CO₂ and the competing molecules are not as large as for the CO₂/butanol couple. This is probed by studying the adsorption of a CO₂/ethanol mixture. In this case, a molar composition 99.85 : 0.15 is used to be representative for the fermenter head space composition. As shown in Fig. 5, the amounts of ethanol and CO₂ adsorbed are similar for the two adsorbents. Since these molecules are similar in size and have closer heats of adsorption, the molar composition of the mixture has a large effect on the relative amounts adsorbed of ethanol and CO₂. Since carbon dioxide is present in large excess, it is the most adsorbed component from the mixture in almost the full pressure range studied. However, both adsorbates reach a similar adsorption value at the highest pressure. As a consequence of their smaller size and their lower interaction with the adsorbents, compared to butanol, the amounts adsorbed of ethanol and CO₂ are reduced compared to the pure component behavior. This effect was not observed for butanol. (see Fig. 3). The low concentration of ethanol in the mixture is also translated into a significant shift in pressure while this effect is not evidenced for CO₂ since it is the main component of the mixture. Due to their similarity in terms of adsorption, the distribution of ethanol and CO₂ is comparable but with a larger concentration of carbon dioxide (Fig. S4 from the ESI†).

The adsorption of a ternary CO₂/butanol/ethanol mixture with relative molar composition 99.363 : 0.49 : 0.147 was also studied (Fig. S5 and S6 from the ESI†). To allow comparison with the results obtained from the binary CO₂/butanol (99.5 : 0.5) and butanol/ethanol (77 : 23) mixtures, the selectivity of butanol over...
carbon dioxide and ethanol is plotted as a function of total pressure in Fig. 6.

Fig. 6 shows a peak in butanol/CO₂ selectivity at 10 kPa for the two structures. This is the optimal pressure for an efficient separation of the components since butanol is almost at saturation while CO₂ has not started yet adsorbing. At higher values of pressure, the concentration of carbon dioxide in the structures increases while the amount of butanol remains constant. This leads to a reduction of the adsorption selectivity.

Comparing the results from the binary and the ternary mixtures, no large differences are observed. As a general trend, ITQ-29 shows higher selectivity than ZIF-8. Since ITQ-29 is the structure with smaller cavities and larger energies of interaction (see Fig. S3 (ESI†) and Fig. 4a), this structure discriminates better just based on the size of the adsorbates and their interaction energies (butanol > CO₂) to preferably adsorb the type of molecules that fit more efficiently inside the cavities (butanol).

Regarding the butanol/ethanol selectivity, some noise in the low pressure range is observed. This is consequence of the relatively large errors at low ethanol uptake at these values of pressure.
At pressure values above 100 Pa, the selectivity of ZIF-8 and IQ-29 is larger for the ternary mixture (containing CO₂) than for the binary mixture. As observed in Fig. 7 and Fig. S6 from the ESI, the adsorption of ethanol is lower in presence of CO₂, but the adsorption of butanol remains unaffected. The stronger competition between ethanol and CO₂ results in the increment of the butanol/ethanol adsorption selectivity, as can also be perceived from Fig. 6 (bottom). A maximum between 1 and 10 kPa is observed. This is, the optimal pressure range for an efficient separation of these components. As in the previous case, this maximum corresponds to the point of the isotherm where butanol is already at saturation while ethanol is starting to adsorb. This leads to a reduction of the selectivity at higher pressure. The larger selectivity of ITQ-29 compared to ZIF-8 (smaller cavities and with stronger interactions with the adsorbates) is attributed to the same reason.

Based on these findings, the efficiency of recovery of butanol from ABE mixtures can be modified by the presence of carbon dioxide depending on the properties of the materials. However, these differences are not due to the direct effect of carbon dioxide on the adsorption of butanol, but rather to the competition between carbon dioxide with other components from the mixture such as ethanol.

**Conclusions**

The adsorption of the main ABE components has been analyzed in ITQ-29 zeolite and ZIF-8. From the molecular simulation point of view, two new models for butanol and ethanol have been proposed and validated in terms of inner properties of the gases and adsorption behaviors. The adsorption of pure components (butanol and ethanol), binary (CO₂/butanol, CO₂/ethanol, and butanol/ethanol), and ternary (CO₂/butanol/ethanol) mixtures has been investigated providing information about the uptake, distribution of the molecules inside the studied materials, and the competition between molecules. The presence of carbon dioxide in the mixture enhances or hinders the adsorption and recovery of butanol from an ABE mixture attending to the features of the materials under consideration. However, it is the competition of
CO₂ with the other components of the mixture (ethanol) that result on the changes of butanol selectivity, while the adsorption of butanol remains almost unaffected.

Author contributions
The manuscript was written through contributions of all authors. All authors have given approval to the final version of the manuscript.

Conflicts of interest
There are no conflicts to declare.

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References