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# Adsorption equilibria of bio-based butanol solutions using zeolite

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ABSTRACT

1-Butanol can be produced by clostridial fermentations with acetone and ethanol as by-products. The butanol can be present up to $\sim$20 g L$^{-1}$ depending on process conditions and microbial strain. The high-silica zeolite CBV28014 has been proven to adsorb butanol selective over water, while showing higher affinity for butanol than for acetone and ethanol. Multi-component acetone–butanol–ethanol (ABE) adsorption on CBV28014 has been modeled using a single site extended Langmuir adsorption model and the ideal adsorbed solution (IAS) theory model. The IAS model describes multi-component adsorption of ABE in synthetic mixtures and ABE in filtered fermentation broth by CBV28014 more accurately than the single site extended Langmuir model.

## 1. Introduction

Production of biofuels is currently one of the key strategies in developing a sustainable economy. In all probability a whole range of biofuels, from hydrogen and ethanol to biodiesel, will appear on the transportation fuel market in the first half of this century [1]. In comparison to ethanol, e.g., 1-butanol is an attractive biofuel candidate as it has positive fuel characteristics such as carbon chain length, volatility, polarity and combustion value. Butanol can be biologically derived from carbohydrates by means of clostridial fermentations, with acetone and ethanol as principle by-products [2]. The highest butanol concentration obtained in clostridial fermentations is around 20 g L$^{-1}$ [3]. This limitation occurs because butanol increases the permeability of the microbial cells' membrane. Maintaining homeostasis becomes increasingly more difficult at higher butanol concentrations, leading to a complete stop of all microbiological activity. Microorganisms with a higher butanol tolerance are being discovered and developed, but elimination of the inhibiting characteristics of butanol is unlikely. Therefore, efficient recovery of butanol from dilute aqueous solutions is a prerequisite for development of a biobutanol production process. Adsorption has been shown to be a promising recovery technique [4]. Adsorption should allow separation of the butanol from the bulk aqueous fermentation broth, so that further downstream processing operations need to be performed on a relatively small amount of organic product phase only; thus providing the basis for energy efficient recovery. Hydrophobic adsorbents potentially show the desired high selectivity for butanol over water. Zeolitic hydrophobic sorbents have additional positive features such as stability, homogeneity and low heat capacity. The hydrophobicity of zeolites increases with increasing $SiO_2/Al_2O_3$ ratio, with silicalite containing no alumina. Silicalite-1 (ZSM-5 structure) has been shown to adsorb low amounts of water [5]. Commercially available zeolites with high silica over alumina content have been shown to adsorb organic components selectively over water [6]. Adsorption of butanol from fermentation broth has been reported for various zeolites for binary mixtures and some multi-component systems, e.g., with ethanol and acetic acid [7,8]. However, there is a lack of data on butanol adsorption by high silica zeolites in the presence of acetone and ethanol. Also, the butanol adsorption behavior of commercial high silica zeolites from aqueous mixtures or fermentation broth is lacking. Therefore, we have determined the adsorption of butanol and water by three structurally different commercially available high-silica zeolites. The competitive adsorption of acetone, butanol and ethanol from aqueous mixtures and fermentation broth has also been measured and mathematically modeled.

## 2. Materials and methods

### 2.1. Materials

The powdered zeolites, CBV28014, CBV901 and CBV811C-300 (abbreviated to CBV811) were from Zeolyst International, Conshohocken, PA, USA. All zeolites were calcined at 600 °C for 8 h. Further details on the zeolites are shown in Table 1.

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**Table 1**
Manufacturer's specifications of zeolite adsorbents and pore volume estimates.

| Name | Zeolite type | $SiO_2/Al_2O_3$ | Nominal cation | Surface area ($m^2/g$) | Estimated pore volume ($cm^3/g$) |
|---|---|---|---|---|---|
| CBV28014 | ZSM-5 (MFI) | 280 | Ammonium | 400 | 0.19 |
| CBV811 | Beta (BEA) | 360 | Hydrogen | 620 | 0.24 |
| CBV901 | Y (FAU) | 80 | Hydrogen | 700 | 0.50 |

**Nomenclature**

| | |
|---|---|
| $A$ | surface area of adsorbent ($m^2\,kg^{-1}$) |
| $C$ | liquid phase concentration ($kg\,m^{-3}$) |
| $C^o$ | single solute equilibrium liquid phase concentration ($mol\,m^{-3}$) |
| $K$ | Langmuir constant ($m^3\,kg^{-1}$) |
| $m$ | mass (kg) |
| $q$ | mass equilibrium solid phase concentration ($kg\,kg^{-1}$) |
| $q^o$ | single solute equilibrium concentration in solid phase ($mol\,kg^{-1}$) |
| $q_m$ | maximum adsorption capacity ($kg\,kg^{-1}$) |
| $R$ | gas constant ($J\,mol^{-1}\,K^{-1}$) |
| $T$ | temperature (K) |
| $V$ | liquid volume ($m^3$) |
| $x$ | solvent free liquid phase mole fraction (–) |
| $z$ | adsorbed phase mole fraction (–) |
| *Greek symbol* | |
| $\pi$ | spreading pressure ($N\,m^{-1}$) |
| *Subscripts* | |
| $i$ | sorbate species $i$ |
| $j$ | all sorbate species |
| $z$ | sorbent |
| 0 | initial condition |
| $T$ | total |
| *Superscript* | |
| $o$ | single-solute |

The pore volumes of the specific zeolites listed in Table 1 are not reported in the literature. For silicalite-1 (alumina free ZSM-5, MFI framework) the pore volume is 0.19 $cm^3/g$ [5]. The MFI framework has an intersecting channel system with both channel systems being 10-ring channels (0.53 nm × 056 nm) and (0.55 nm × 0.51 nm) [9].

Beta-type zeolites consist of faulted intergrowth of two separate 3-dimensional 12-ring pore structures. The two structures have a pore structure of channels with (0.73 nm × 0.60 nm) and (0.56 nm × 0.56 nm) dimensions [9].

The pore volume for CBV901 has been estimated at 0.24 $cm^3/g$ [10], but this value is surprisingly low in comparison to reported volume for NaY zeolites. The FAU-type framework of the zeolite has a large void volume, ~50%, which is easily accessible. FAU-type zeolites have 12-ring pore openings and a 3-dimensional channel system (0.74 nm × 0.74 nm) [9].

1-Butanol (Acros, purity 99.5%), acetone (Merck, purity 99.9%) and ethanol (Merck, purity 99.9%) were used. Samples from two clostridial fermentations were obtained from the Wageningen University and Research Centre. One sample was directly taken from the main fermentation broth. The other sample was filtered fermentation broth and contains no microbial cells. The fermentation broth contained 2.33, 9.02, 0.25, 0.45 $g\,L^{-1}$ acetone, butanol, ethanol and butyrate, respectively, according to gas chromatography (GC) analysis. The filtrate contained 1.72, 4.84, 0.14, 0.5 $g\,L^{-1}$ acetone, butanol, ethanol and butyrate. The pH of the fermentation broth and filtrate were 5.16 and 5.36, respectively.

### 2.2. *Experimental methods*

Experiments were carried out at temperatures in the range of 22–25 °C.

#### 2.2.1. *Gas phase equilibration experiments*

Gas phase equilibrium experiments were performed in a closed desiccator. A known amount of the calcined zeolite was placed next to an amount of liquid butanol or water. The mass increase of the zeolite after 72 h was used to calculate its adsorption of the species involved. The adsorption of the sorbate via gas phase equilibrium was measured after 90 h. It was verified equilibrium had been reached because no deviation in adsorption was seen after 264 h.

#### 2.2.2. *Liquid phase equilibration experiments*

Liquid phase adsorption equilibrium experiments were carried out in closed stirred vessels of 35–40 mL. The vessels contained known amounts of butanol, acetone, ethanol, water and adsorbent. Typically 0.25–1 g adsorbent was used. After 48 h equilibration, acetone, butanol and ethanol liquid phase concentrations were determined. The adsorption $q$ of a sorbate ($i$) on a zeolite ($z$) was calculated by means of mass balance as shown in Eq. (1). Over the concentration range the density of the mixtures varies by less than 0.3%. Therefore the density of the liquid phase was considered to be constant at the density of pure water. The volume was calculated using the initial total mass of acetone, butanol, ethanol and water. Competitive water adsorption by the zeolite material could not be measured by us and was not taken into account. The error that imposes on the calculation of the amount of adsorption of the other compounds is up to 3 times smaller than the error in the adsorption due to the GC measurements. The accuracy of a calculated adsorption is a function of the ratio between the aqueous concentration and available solid zeolite material used

$$q_i = \frac{(C_{i,0} - C_i) \cdot V_0}{m_{z,0}} \tag{1}$$

The measured adsorption isotherms were modeled using a Langmuir-type equation for single site adsorption, neglecting water adsorption. For multi-component mixtures containing ($j$) species the Langmuir model for adsorption of component ($i$) is shown in Eq. (2)

$$q_i = \frac{q_{m,i} \cdot K_i \cdot C_i}{1 + \sum_j K_j \cdot C_j} \tag{2}$$

The ideal adsorbed solution (IAS) theory has originally been developed to describe gas phase adsorption of volatile components. The IAS model has been modified to describe liquid phase adsorption [11]. IAS theory makes use of the spreading pressure ($\pi$), defined as the difference between the interfacial tension of the pure solvent–solid interface and the solution–solid interface area ($A$), given for a specific amount of solid phase. The following Gibbs relation (Eq. (3)) shows this relation [11]. The superscript $o$ denotes that the system is seen as a single-solute system. IAS calculations