Concentration effects on the selective extraction of ethanol from aqueous solution using silicalite-1 and decanol isomers

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ABSTRACT

The high-energy requirement to separate ethanol from fermentation broths by distillation is a major hurdle for the economical use of bio-renewable ethanol in a wide variety of chemical applications. Three-phase Gibbs ensemble Monte Carlo simulations have been employed to assess the performance of two promising alternatives: adsorptive separation using silicalite-1, a hydrophobic zeolite, and liquid-liquid extraction using two high-molecular-weight alcohols, namely decan-1-ol and decan-4-ol. These simulations show that in both separation processes the selectivity for ethanol over water is significantly higher at low concentrations though this trend is more pronounced in the zeolite system. The vapor-to-sorbent partition coefficient is significantly higher at low concentrations, while the organic solvent systems show only a weak dependence of the vapor-to-solvent partition coefficient on concentration. This behavior can be rationalized by the different ethanol/water aggregates (in terms of size and architecture) formed in these two environments. A key factor in these differences is the spatial confinement of the hydrogen-bonded aggregates by the alkyl tails of the solvent or by the rigid zeolite structure.

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1. Introduction

The rising cost of petroleum products and the increasingly urgent need to limit greenhouse gas emissions have focused intense research effort on the search for more sustainable and environmentally friendly sources of energy and chemical feedstocks. Ethanol in particular has received significant attention as it has already been in use in gasoline blends for several decades [1,2]. However, the production of ethanol currently requires large amounts of energy, raising its cost and compromising its environmental benefits [3–8]. One of the major sources of this high energy cost is the difficulty of separating ethanol from water by distillation. Currently, the fractional distillation of the water/ethanol mixture up to the azeotropic composition requires about 6.5 MJ/kg ethanol (i.e., about 20–30% of the energy that can be obtained from the combustion of ethanol) and the energy consumption is even higher to produce anhydrous ethanol [9]. Although it should be noted that burning feed residues can provide the energy required to drive the fractional distillation for some of the current sugar- or starch-based technologies [10].

Several alternatives means of separating ethanol from fermentation broths have been proposed and among the most promising are adsorption/pervaporation using zeolites and liquid–liquid solvent extraction. Previous simulations and experimental work [11–25] have demonstrated the ability of both approaches to selectively extract ethanol from fermentation broths, but a comprehensive understanding of how different conditions affect the separation and the microscopic origin of these effects is still lacking. In this work, Gibbs ensemble Monte Carlo simulations were used to assess the effect of ethanol concentration on the partition coefficient and selectivity of an all-silica zeolite and two different solvent extraction systems and to provide molecular level insight into the different concentration effects in the relatively rigid zeolitic system and the flexible, disordered solvent systems.

2. Methodology

For both the solvent extraction and the zeolite sorption simulations, the NpT Gibbs ensemble Monte Carlo technique [26] was used. Different phases are physically separated by using separate simulation boxes, which eliminates the contribution of interfacial effects. The phases are kept in thermodynamic contact by exchanging particles between the phases using configurational-bias Monte Carlo (CBMC) particle transfer moves [27–29]. The entire system is kept at the specified pressure by independently performing volume moves on each simulation box (except for the crystalline zeolite). The TraPPE model [29–31], including a recent extension to all-silica zeolites, was used to describe the organic molecules and the

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interactions with the zeolite framework, and water was represented by the TIP4P model [32].

In both sets of simulations, three separate simulation boxes were used: one box modeling the fermentation broth, a second box containing the extraction system (either zeolite or solvent), and a vapor phase simulation box which was included as an intermediate for particle transfers in order to improve their acceptance rates. The range of concentrations used for the first phase in the simulations with the organic extraction solvent was limited to water-rich mixtures, whereas the full composition range from water-rich to ethanol-rich was explored for the simulations with the zeolite sorbent.

Decan-1-ol and decan-4-ol were used as test cases for the solvent extraction simulations. These were chosen because decan-1-ol was found to have a high partition coefficient but a relatively low selectivity, while the decan-4-ol was found to have a relatively low partition coefficient, but a high selectivity [25]. For these simulations, the system consisted of 864 water molecules, 240 decan-1-ol or decan-4-ol molecules, 2 methanol molecules, and 25 helium atoms. The numbers of water and decanol molecules were selected to yield simulation boxes with a length of at least 30 Å, and the number of helium molecules yields a vapor phase of sufficient volume to contain on average a few water, methanol, and/or ethanol molecules. Methanol molecules were used to further enhance transfer of ethanol molecules with CBMC particle identity switch moves, which exchanges a methanol molecule for an ethanol molecule [33]. This setup is equivalent to that used in our previous work [25]. The number of ethanol molecules was adjusted to give average aqueous phase mole fractions of approximately 0.005, 0.015, 0.025, 0.045, and 0.055, which correspond to mass percentages of approximately 1%, 3%, 6%, 10%, and 13%. The ethanol concentration is sufficiently low that the solvent is assumed to be insoluble in the aqueous phase (i.e., no swap moves are attempted for solvent molecules). Helium atoms are restricted to the vapor phase.

In the solvent simulations, the moves were divided into 0.2% volume moves, 4.8% identity switch moves, 35% swap moves, 20% configurational bias regrowth moves, 20% translations, and 20% rotations. The fractions of the first three types of moves were chosen to yield about one accepted move of each type per Monte Carlo cycle which has been shown to yield high sampling efficiency [34], and the remainder was equally divided over the three types of degrees of freedom for flexible molecules. 16 independent simulations were performed for each combination of solvent and overall composition, and the statistical uncertainties are reported as the standard error of the mean for these simulations. A short series of simulations was performed to adjust the overall system composition to give the desired aqueous phase ethanol concentration. After the composition was fixed, an equilibration period for each simulation of at least 2×10^5 Monte Carlo cycles was used, where one cycle consists of N Monte Carlo moves and N is the total number of molecules in the system. The production period for each simulation was 5×10^5 cycles.

The sorbent chosen in the adsorption simulations is an all-silica zeolite, silicalite-1, whose framework type is coded as MFI [35]. The MFI zeolite has two channel systems, a sinusoidal channel that runs along the a direction in the ac plane and a straight channel pointing in the b direction. The two types of channels intersect to form a 3-dimensional channel system. The framework atoms were fixed at the positions of the ORTHO crystalline form as determined by van Koningsveld et al. [36], and were not allowed to move during the simulation [37]. The entire adsorption system consists of 1100 molecules, with water/ethanol ratios of $2^i/2^j$ ($i, j = 0, 1, . . ., 6$). Unlike the solvent extraction simulations where the solubility of the solvent in the aqueous phase can become problematic, these simulations cover the entire composition range from pure water

to pure ethanol. The equilibration period was about 2×10^5 Monte Carlo cycles and the production period was 3×10^5 Monte Carlo cycles. The simulations setup has been described in detail elsewhere [24]. Simulations for both the zeolite and the solvent systems were performed at a temperature of 298 K and atmospheric pressure and partition coefficients and selectivities are also reported for the zeolite at 323 K.

The force fields used in this work have previously been shown to yield accurate predictions for the solvent-based extraction from an aqueous solution with 10% mass percent ethanol [25] and for the unary adsorption of water, methanol, and ethanol in silicalite-1 [24].

The partition coefficient and selectivity are characterized using the quantities K_{DE} and α, respectively, which are defined as [38].

$$K_{DE} = \frac{[EtOH]_{org/zeo}}{[EtOH]_{aq}} \tag{1}$$

$$\alpha = \frac{K_{DE}}{K_{DW}} \tag{2}$$

where the concentrations are expressed as mass fractions and K_{DW} is defined as the water counterpart to K_{DE}

$$K_{DW} = \frac{[H_2O]_{org/zeo}}{[H_2O]_{aq}} \tag{3}$$

The size distribution of hydrogen-bonded aggregates was calculated and analyzed using a geometric criterion where the distance between a hydrogen atom and an acceptor oxygen is less than 2.5 Å and the O–H–O angle between the acceptor oxygen, the donor hydrogen, and the oxygen chemically bonded to the donor hydrogen has a cosine smaller than –0.1 [39].

3. Results and discussion

A plot of the partition coefficient and selectivity in the zeolite and solvent extraction systems as a function of average ethanol concentration in the aqueous phases is presented in Fig. 1. All-silica zeolites are usually believed to be very hydrophobic [40–46], and their affinity to alkanes and polyols is found to correlate well with the number of carbon atoms [47–49]. In recent simulation studies of the adsorption of alcohol/water mixtures onto the same sorbent material as studied in this work, it was found that silicalite-1 is very selective even for low-carbon-number alcohols, such as methanol and ethanol, over water [23,24]. The partition coefficient of ethanol (with the mass of silicalite-1 included) starts fairly high ($K_{DE} > 10$) for systems approaching infinite ethanol dilution ($x_{EtOH} \approx 5 \times 10^{-4}$), and quickly decreases by more than an order of magnitude at $x_{EtOH} \approx 0.1$. Upon further increase of x_{EtOH}, the partition coefficient gradually approaches a limiting value of $K_{DE} = 0.1$. Correspondingly, the selectivity starts at a value on the order of 10^4, decreases to about 10^2 at $x_{EtOH} \approx 0.1$, and finally reaches $\alpha \approx 10$ for very high ethanol concentrations ($x_{EtOH} \approx 0.98$).

A similar trend is observed in the selectivity for the solvent extraction systems, which decreases with increasing concentrations for both solvents, though the magnitude of this decrease is smaller than for silicalite-1 and smaller for decan-1-ol than for decan-4-ol. In contrast, the trends in the partition coefficient are significantly different for the solvent systems and the zeolite. The partition coefficient has a minimum for decan-1-ol at $x_{EtOH} \approx 0.025$, while the plot is nearly flat for decan-4-ol.

This behavior can be better understood by considering the Gibbs free energy of transfer (ΔG_{trans}) using the vapor phase as a reference state. The free energies for transfer from the aqueous solution to the vapor phase (vaporization) and from the vapor phase to the organic solvent/zeolite phase are shown in Fig. 2.