Supporting Information for

Alcohol and water adsorption in zeolitic imidazolate frameworks

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Disclaimer

ZIF materials and synthesis procedure

ZIF-90: 20 mmol of imidazole-2-carboxaldehyde (ImCA) was heated to 343 K in 50 mL N,N-dimethylformamide (DMF) until the ligand was fully dissolved. Next, 5 mmol of Zinc Nitrate Hexahydrate was dissolved in 50 mL of methanol. After cooling the DMF/ImCA solution to room-temperature, the methanol/Zn solution was rapidly poured into the DMF/ImCA solution and mixed for 1 hour. Submicron crystals were isolated after four cycles of centrifuging and decanting with neat methanol.

ZIF-71: A solution of zinc acetate 0.40 mmol in 15 mL of methanol and a solution of 4,5-dichloroimidizole of 1.60 mmol in 15 mL of methanol, were combined in a sealed vial and let stand at room temperature for 24 hrs. The methanol was then removed from the vial using a pipette and the remaining crystals were soaked in chloroform (3 x 20 mL) for three days. To recover the crystals, the solution was centrifuged for 5 minutes at 8000 rpm and the chloroform was decanted. The crystals were then dried under vacuum at 323 ^{K} for 24 hrs to remove any of the remaining solvents from the crystals.

ZIF-8: Purchased from Sigma-Aldrich (Basolite Z1200, BASF)

Powder X-ray Diffraction

Powder X-ray diffraction patterns were obtained on a PAnalytical X'pert diffractometer operating with Cu Kα radtion and equipped with an X'celerator detector.

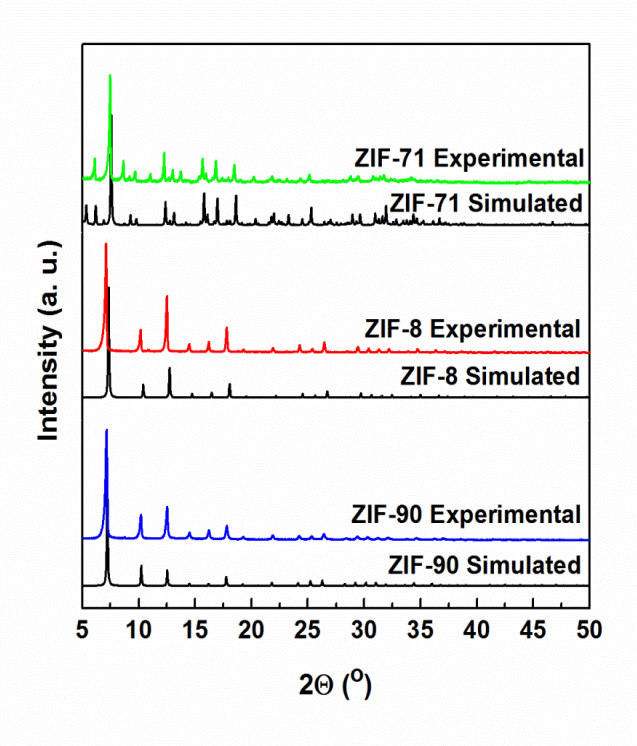


Fig.S1 PXRD pattern of ZIF-71, ZIF-8, ZIF-90 and comparison to the simulated pattern.

SEM Imaging

Scanning electron microscopy (SEM) was used to evaluate the crystal size of ZIFs. After solvent exchange and drying, the ZIF crystals were sputter-coated with a 10-20 nm thick gold coating (Model P-S1, ISI, Mountain View, CA), and transferred to a high resolution Field Emission Scanning Electron Microscope, Leo 1530 (Leo Electron Microscopy, Cambridge, UK). Figure S2 shows representative SEM images of ZIF crystals in this study.

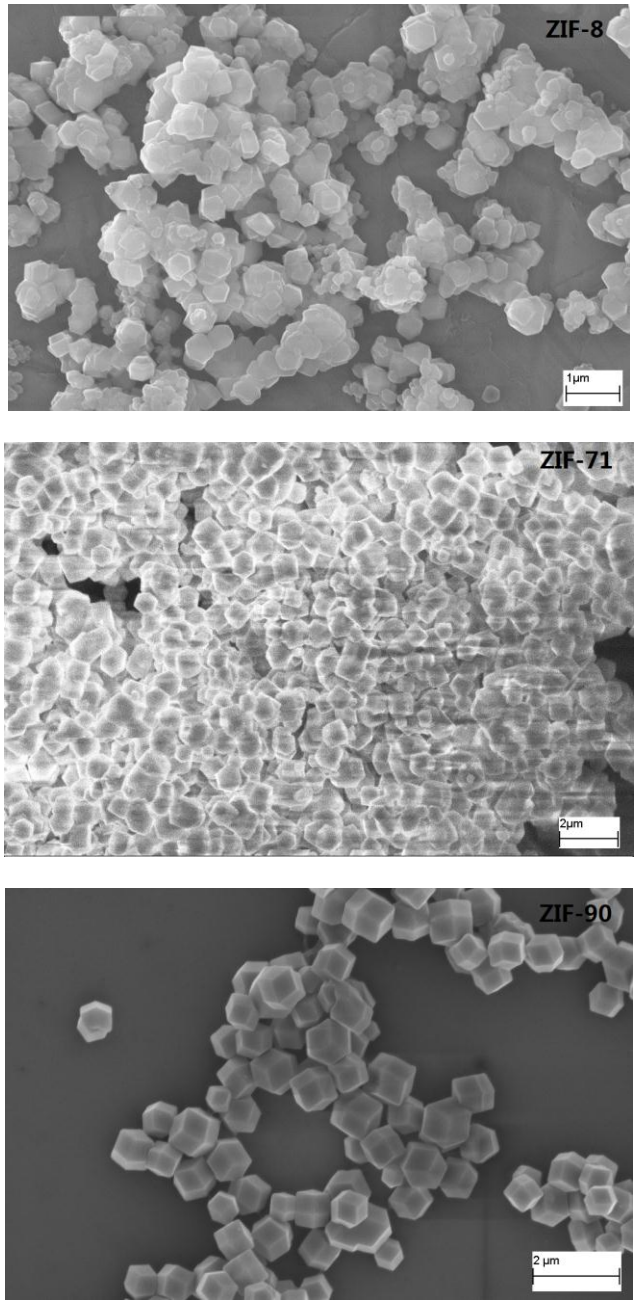


Fig. S2 SEM image of ZIF-8, ZIF-71 and ZIF-90 crystals

Pure structure information

Brunauer-Emmett-Teller (BET) surface areas and micropore volumes (t-plot method) were calculated from N_2 physisorption measurements performed on an ASAP 2020 (Micromeritics). The relative pressure range for BET calculation is up to 0.04 (P/Po) for all three ZIFs, not the standard BET pressure range (0.05-0.30).

Table S1 Pore structure information of ZIF crystals used in this study

ZIF Sample	BET (m^2/g)	Langmuir (m^2/g)	t-plot micropore volume (cm^3/g)
ZIF-8	1696	1814	0.625
ZIF-71	1183	1350	0.385
ZIF-90	1280	1466	0.485

Vapor sorption

The single-componen vapor adsorption experiments were performed on a VTI-SA vapor sorption analyzer from TA Instruments (New Castle, DE, United States) at temperatures of 308 K. The vapor activity was controlled automatically by mixing the wet vapor feed with a dry N_2 line. As such, N_2 serves as a carrier gas for the vapors. The samples "dry mass" was measured under N_2 and were at equilibrium with N_2 before introduction of the vapors to the sample chamber. The isotherms are obtained for water and ethanol adsorption at activities up to 0.98. For every adsorption test, the sample weight is ~30 mg.

The alcohol/water separation performance of ZIF-90

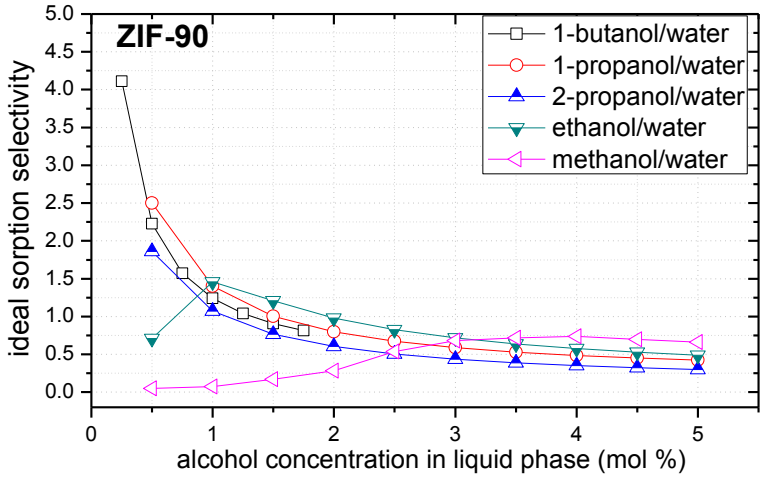


Fig. S3 Ideal alcohol/water sorption selectivity in ZIF-90 at 308K.

The calculation of saturated vapor pressure

The Antoine Equation is applied for estimation of saturated vapor pressures:

$$\log_{10} p = A - \frac{B}{C+T}$$

where p is the vapor pressure, T is temperature and A, B and C are species-specific constants.

Table S2. Antoine equation parameters for alcohols and water in this study and the saturated vapor pressures

	A	B	C	Temperature range	P_{sat} (308K/35°C, Pa)
methanol	8.08097	1582.27	239.7	15 to 100 °C	27918
ethanol	8.20417	1642.89	230.3	-57 to 80 °C	13693
1-propanol*	5.31384	1690.864	-51.804	292.4 to 370.5 K	5176
2-propanol	8.00308	1505.52	211.6	10 to 90 °C	10541
1-butanol	7.92484	1617.52	203.296	0 to 118 °C	1828
water	8.07131	1730.63	233.426	1 to 100 °C	5609

* The constants for 1-propanol are for vapor pressure in ***bar*** and temperature in ***K***. All the other constants listed in the table are for vapor pressure in ***mmHg*** and temperature in ***°C***.

References:

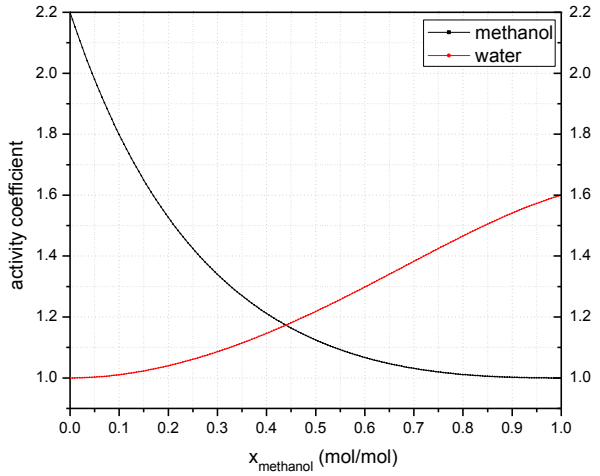
Methanol, ethanol, 1-propanol, 1-butanol:
http://ddbonline.ddbst.de/AntoineCalculation/AntoineCalculationCGI.exe

1-propanol: Kemme, H.R.; Kreps, S.I., Vapor Pressure of Primary n-Alkyl Chlorides and Alcohols, J. Chem. Eng. Data, 1969, 14, 1, 98-102.

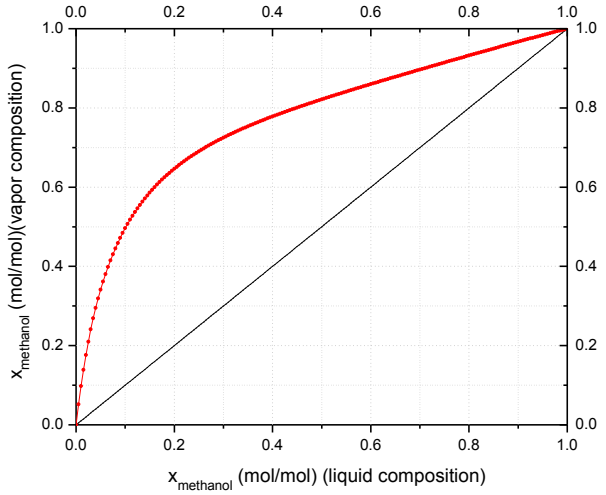
The activity coefficients and vapor-liquid equilibrium diagrams at 308K

The activity coefficients for alcohol-water mixtures are calculated from the ***infinite dilution activity coefficients*** by the Margules equation. The infinite dilution activity coefficients are provided by **Dortmund Data Bank** (www.ddbst.com). Here, we show in detail the activity coefficients for each alcohol-water mixtures at different concentrations and the corresponding vapor-liquid equilibrium (VLE) diagrams calculated by these activity coefficients.

(1) methanol-water



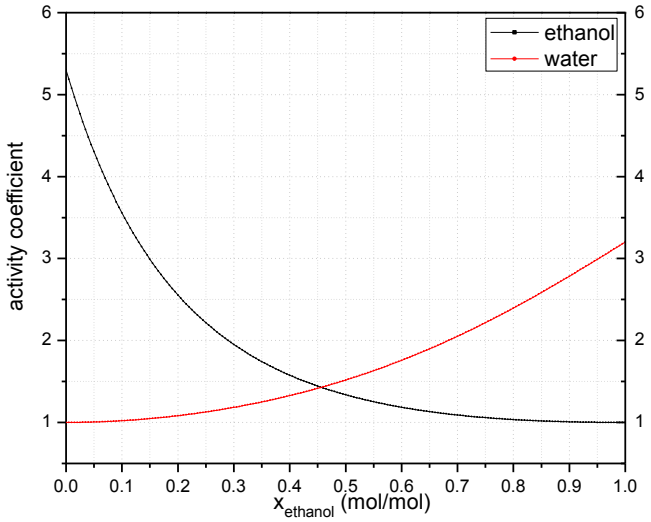
activity coefficients



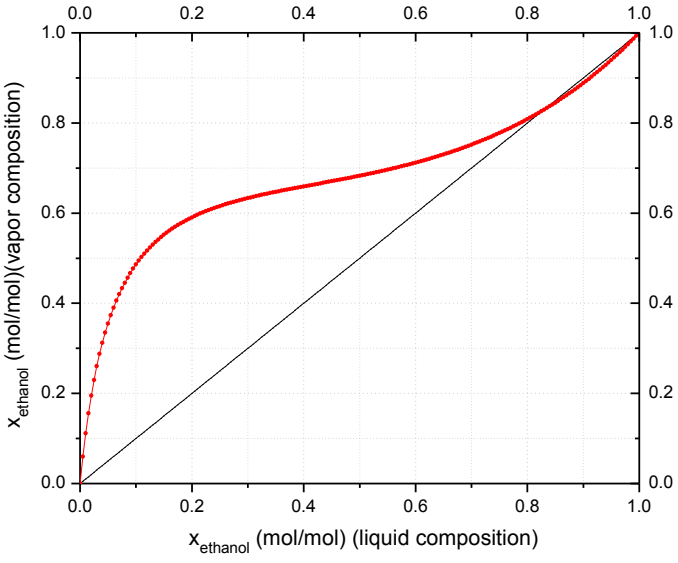
VLE diagram

(2) ethanol-water

The activity coefficients estimated by UNIFAC for ethanol-water system are also available at ddbst website. Generally, the activity coefficients by UNIFAC method are higher than the data calculated by the infinite dilution data provided by the same database bank. Since the UNIFAC data are only available for ethanol-water system publicly, here in this study, we use the data calculated by infinite dilution activity coefficients for all the alcohol-water pairs.

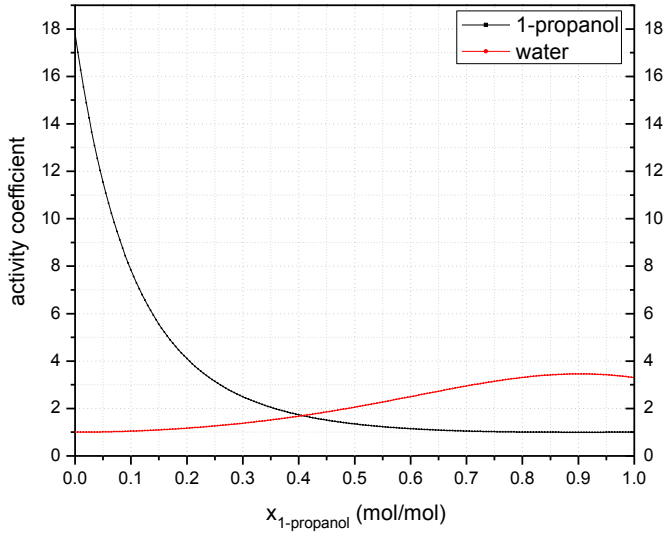


activity coefficients

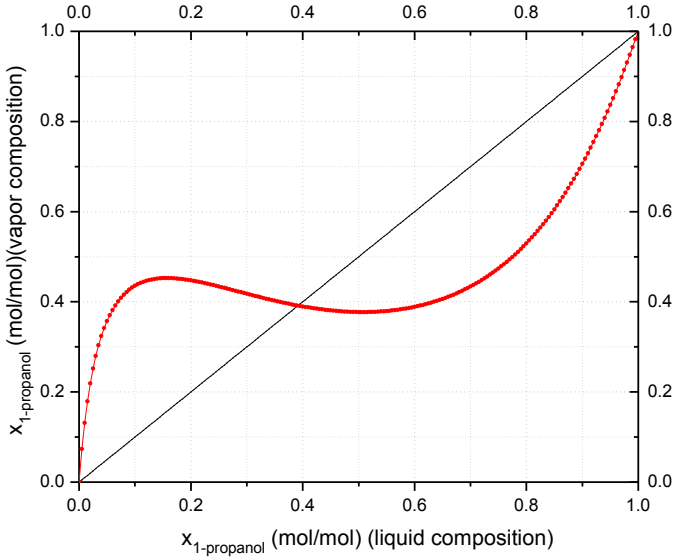


VLE diagram

(3) 1-propanol-water

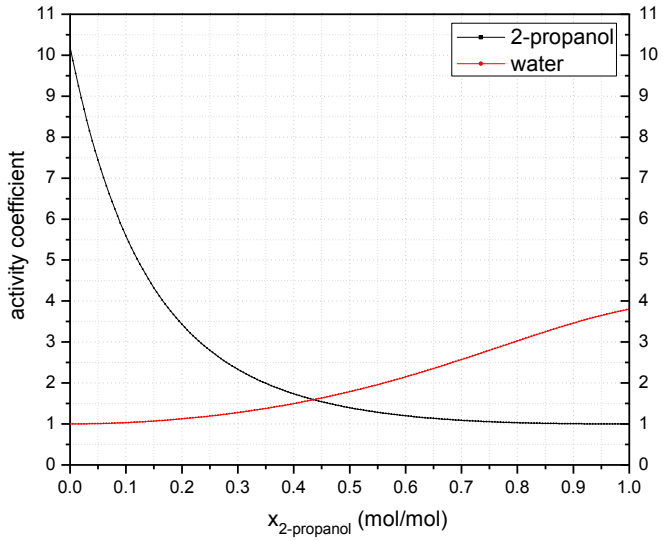


activity coefficients

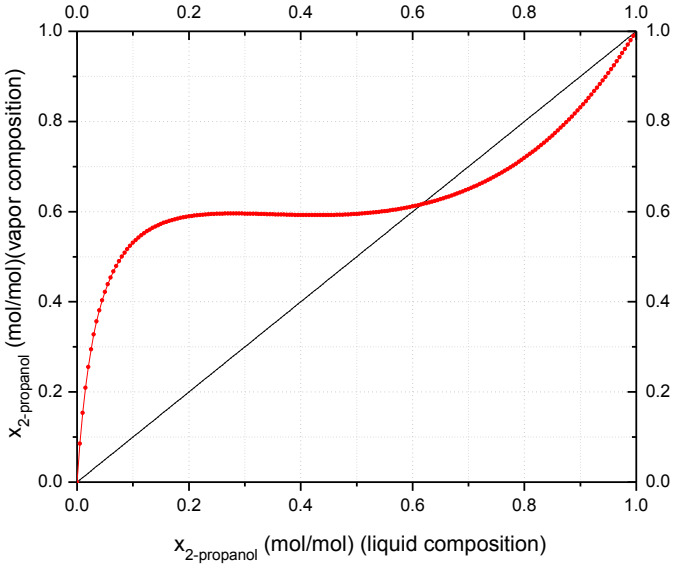


VLE diagram

(4) 2-propanol-water

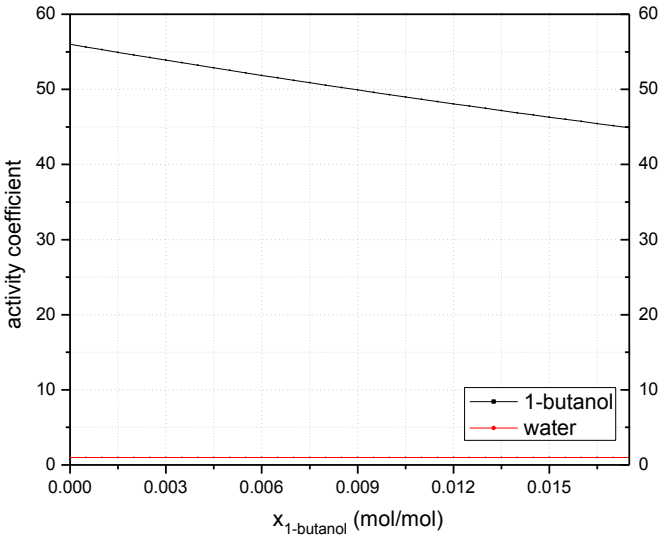


activity coefficients

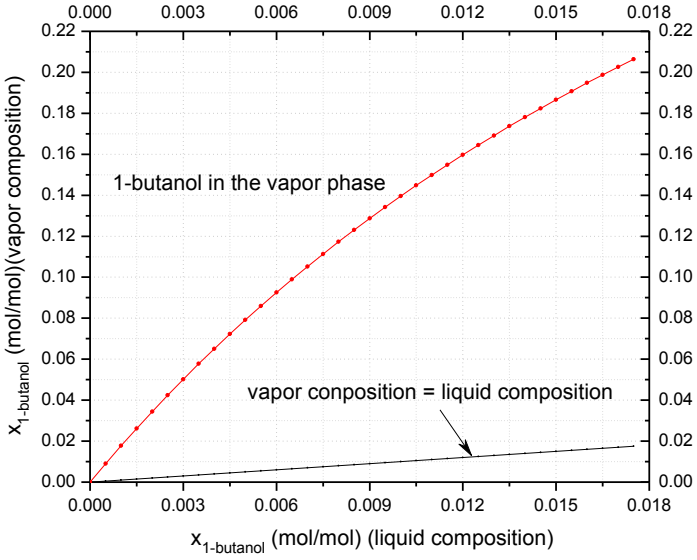


VLE diagram

(5) 1-butanol-water



activity coefficients



VLE diagram