PCCP

Accepted Manuscript

This is an *Accepted Manuscript*, which has been through the Royal Society of Chemistry peer review process and has been accepted for publication.

Accepted Manuscripts are published online shortly after acceptance, before technical editing, formatting and proof reading. Using this free service, authors can make their results available to the community, in citable form, before we publish the edited article. We will replace this *Accepted Manuscript* with the edited and formatted *Advance Article* as soon as it is available.

You can find more information about *Accepted Manuscripts* in the **Information for Authors**.

Please note that technical editing may introduce minor changes to the text and/or graphics, which may alter content. The journal's standard **Terms & Conditions** and the **Ethical guidelines** still apply. In no event shall the Royal Society of Chemistry be held responsible for any errors or omissions in this *Accepted Manuscript* or any consequences arising from the use of any information it contains.

Separation of Benzene from Mixtures with Water, Methanol, Ethanol, and Acetone: Highlighting Hydrogen Bonding and Molecular Clustering Influences in CuBTC

Juan José Gutiérrez-Sevillano,[a] Sofia Calero,[a] and Rajamani Krishna[b]

ABSTRACT

Configurational-Bias Monte Carlo (CBMC) simulations are used to establish the potential of CuBTC for separation of water/benzene, methanol/benzene, ethanol/benzene, and acetone/benzene mixtures. For operations under pore saturation conditions, the separations are in favor of molecules that partner benzene; this is due to molecular packing effects that disfavor benzene. CBMC simulations for adsorption of quaternary water/methanol/ethanol/benzene mixtures show that water can be selectively adsorbed at pore saturation, making CuBTC effective in drying applications. Ideal Adsorbed Solution Theory (IAST) calculations anticipate the right hierarchy of component loadings but the quantitative agreement with CBMC mixture simulations is poor for all investigated mixtures. The failure of the IAST to provide reasonable quantitative predictions of mixture adsorption is attributable to molecular clustering effects that are induced by hydrogen bonding between water-water, methanol-methanol, and ethanol-ethanol molecule pairs. There is, however, no detectable hydrogen bonding between benzene and partner molecules in the investigated mixtures. As a consequence of molecular clustering, the activity coefficients of benzene in the mixtures is lowered below unity by one to three orders of magnitude at pore saturation; such drastic reductions cannot be adequately captured by the Wilson model, that does not explicitly account for molecular clustering.

Molecular clustering effects are also shown to influence the loading dependence of the diffusivities of guest molecules.

1. Introduction

Several recent publications have highlighted the potential of metal-organic frameworks (MOFs) and zeolitic imidazolate frameworks (ZIFs) for separation of hexane isomers,[1, 2] xylene isomers,[3-6] styrene/ethylbenzene,[7-10] and water/alcohols.[11-13] A common distinguishing feature of these separations is that under industrially relevant operating conditions, the pores of the microporous adsorbents are invariably saturated.[14] Under pore saturation conditions, the separation hierarchy and selectivity is dictated by molecular packing effects; molecular packing effects favor the selective adsorption of molecules with the higher packing efficiencies.[9, 13-15] For example, 1,3,5 trichlorbenzene can be selectively separated from its isomers due to optimum face-to-face stacking within the triangular channels of $Fe_2(BDP)_3$.[6] Generally speaking, smaller molecules pack more efficiently and have higher saturation capacities; this implies that under pore saturation conditions smaller molecules can be selectively adsorbed from mixtures, in preference to larger-sized molecules.[12, 13, 15-19] For example, Motkuri et al.[15] have suggested that TetZB (that was synthesized using a flexible tetrahedral organic linker tetrakis[4-(carboxyphenyl)-oxamethyl]methane) has the potential of separation of variety of mixtures of polar compounds by exploiting molecular packing effects. It noteworthy that the Motkuri analysis of separations is based on the key assumption that the Ideal Adsorbed Solution Theory (IAST) theory of Myers and Prausnitz[20] affords an adequate description of mixture adsorption equilibrium. IAST calculations were also used by Zhang et al.[11] and He et al.[21] to demonstrate the potential of hydrophobic adsorbents such as ZIF-8, ZIF-71, ZIF-80, and MAF-6 for water/alcohol separations. Strictly, the applicability of the IAST is restricted to cases in which there is a homogenous distribution of adsorbate species throughout the microporous framework; IAST predictions may fail to provide quantitative predictions when segregation or clustering effects are present.[22-25]

The primary objective of this article is to demonstrate the exploitation of molecular packing effects to separate benzene from mixtures containing one or more of the following compounds: water, methanol, ethanol, and acetone. We choose hydrophilic CuBTC (= $Cu_3(BTC)_2$ with BTC = 1,3,5-

benzenetricarboxylate, also known as HKUST-1) as adsorbent, used also in our earlier study on separation of water/1-alcohol mixtures.[13] The motivation for the current study arises from the following considerations. The dehydration of ethanol/gasoline mixtures is important for avoidance of phase-separation problems during storage;[26] we may consider benzene to be representative of gasoline as regards its phase equilibrium thermodynamics. The separation of water/ethanol/benzene mixtures is also encountered in the distillation processes for water/ethanol separations using benzene as entrainer. The distillation process schemes are complicated due to the occurrence of four separate minimum boiling azeotropes: ethanol/water, ethanol/benzene, water/benzene, and water/ethanol/benzene. Acetone cannot be easily separated from benzene in high purity by distillation because of the closeness of their vapor pressures.[27]

The secondary objective of this article is to highlight the influence of molecular clustering, resulting from hydrogen bonding, on both adsorption and diffusion of guest species in CuBTC. We aim to demonstrate that molecular clustering induces strong non-ideality effects in mixture adsorption, and the IAST fails to provide quantitative predictions of separation performance.

We use Configurational-Bias Monte Carlo (CBMC) simulations to generate the required information on unary and mixture isotherms in CuBTC. The CBMC and Molecular Dynamics (MD) simulation methodologies, including details of force fields used, are provided in the ESI accompanying this manuscript.

2. Steep isotherms, and molecular clustering

The CuBTC framework is composed of copper atoms connected by benzene-1,3,5-tricarboxylate (BTC) linkers, which form a characteristic paddle-wheel structure: two copper atoms bonded to the oxygen atoms of four BTC linkers, generating four-connected square-planar vertexes. The framework contains two types of large cavities (9 Å diameter) and small cavities (of 5 Å diameter). The larger cavities (L_2 and L_3) are similar in size and shape but as a result of the paddle-wheel, the copper atoms are only accessible from the L_3 cages. L_2 and L_3 cavities are connected through triangular-shaped

windows. The small cavities (T_1) are tetrahedral pockets enclosed by the benzene rings; these are connected to L_3 cages by small triangular windows (3.5 Å size), as shown in Figure 1.

The CBMC simulated unary isotherms for water, methanol, ethanol, acetone, and benzene in CuBTC at 298 K exhibit marked inflections, requiring fitting with the multi-site Langmuir-Freundlich model; see Figure 2a. The accuracy of the fits is excellent for all five guest molecules. Particularly noteworthy are the differences in the saturation capacities of the various guest molecules: water = 54 mol kg^{-1}; methanol = 19.9 mol kg^{-1}; ethanol = 13 mol kg^{-1}; acetone = 9.9 mol kg^{-1}; benzene = 6.7 mol kg^{-1}. Let us define the fractional pore occupancy, $\theta_i = q_i/q_{i,sat}$; the variation of the pore occupancies with bulk fluid phase fugacity, f_i, is shown in Figure 2b. We note that the pore occupancies are close to unity for operation at ambient conditions of 100 kPa and 298 K.

A further characteristic feature of the unary isotherms is the steep increase in the loadings; this suggests the formation of molecular clusters, as has been argued in earlier publications.[28-30] In order to explore cluster formation in more detail, we determine the inverse thermodynamic factor, $1/\Gamma_i$, defined by $\dfrac{1}{\Gamma_i} \equiv \dfrac{\partial \ln q_i}{\partial \ln f_i} = \dfrac{f_i}{q_i}\dfrac{\partial q_i}{\partial f_i}$ by analytic differentiation of the Langmuir-Freundlich model fits. The data for $1/\Gamma_i$ are presented in Figure 2c. We prefer to plot $1/\Gamma_i$ instead of Γ_i because the latter has the undesirable property of approaching infinity as saturation loading is approached; this makes the data less easy to interpret when plotted in graphical form. For the simplest scenario in which single-site Langmuir isotherm hold, we have $1/\Gamma_i = (1-\theta_i) = (1-q_i/q_{i,sat})$, i.e. the fractional vacancy. In previous works,[28-32] we had argued that the condition $1/\Gamma_i > 1$ implies the increase of fractional vacancy beyond unity and this is physically rationalized if we allow for molecular clustering. We note from Figure 2c that $1/\Gamma_i$ exceeds unity for a certain range of pore occupancies below about 0.5 for all five guest molecules. Also noteworthy, is that clustering effects seem to be more prominent for water, methanol, and ethanol; this is evidenced by larger increases in the $1/\Gamma_i$ values above unity.

Confirmation of clustering effects of polar molecules in CuBTC is provided by the experimental data

of Tsotsalas et al.[33] Figure 2d compares the $1/\Gamma_i$ values obtained by Tsotsalas et al.[33] for methanol, by

numerical piece-wise differentiation of their experimental isotherms, with the values plotted in Figure

2c. There is reasonable agreement between the two data sets.

3. CBMC simulations of mixture adsorption, and comparisons with IAST

Figure 3, panels a, b, c, and d, present the results for CBMC simulations of the component loadings

for adsorption of equimolar water/benzene, methanol/benzene, ethanol/benzene, and acetone/benzene

mixtures in CuBTC at 298 K. For all four mixtures, we note a reversal in the hierarchy of component

loadings as conditions approach pore saturation. From the data in Figure 3 we conclude that CuBTC has

the potential of separation of separating binary mixtures of benzene with water, methanol, ethanol, and

acetone. For operation near pore saturation conditions, the selectivity is in favor of the smaller partner

molecule in the mixture with higher saturation capacity. Figure 4 presents the CBMC simulations for

equimolar quaternary water/methanol/ethanol/benzene mixtures; the data clearly indicate that water can

be selectively adsorbed from a mixture containing alcohols and benzene provided the operations are

close to pore saturation conditions. CuBTC is a good candidate for drying water/alcohol/benzene

mixtures.

We now examine whether the IAST theory provides a quantitative representation of mixture

adsorption. Figure 5a compares the IAST calculations with CBMC simulations of component loadings

of equimolar methanol/benzene mixtures. The IAST correctly anticipates that the adsorption is

favorable to the component with the higher saturation capacity as saturation conditions are approached.

However, except for $f_t < 100$ Pa in the Henry regime of adsorption, the quantitative agreement between

the IAST and CBMC simulations is poor. Similar poor agreement between CBMC and IAST is

observed for all other mixtures that have been investigated; see Figures 22 - 25 of the ESI.

The separation performance anticipated by IAST calculations is overly optimistic; this is

demonstrated by the comparisons presented in Figure 5b for adsorption selectivities determined from

CBMC mixture simulations with IAST calculations for equimolar binary mixtures. Typically, at pore

saturation, the selectivities estimated by IAST are about an order of magnitude higher than those determined from CBMC mixture simulations.

A different method of underscoring the quantitative failure of IAST is afforded by the plot presented in Figure 5c for water adsorption in CuBTC from water/methanol/ethanol/benzene mixtures. Herein, we divide the loadings of water in the mixture by the loadings of pure water, both compared at the same partial fugacity in the bulk fluid phase. The CBMC mixture simulations show that the "enhancement" factor of water reaches a value of about 8. The IAST calculations indicated by the continuous solid lines do not anticipate such a strong enhancement. Similar results are obtained for other mixtures; see Figure 25 of ESI. The most likely reason for this enhancement is H-bonding between water and partner molecules; the partner molecules "drag" water into the CuBTC framework.

Experimental evidence of the enhancement of water ingress into MFI zeolite due to H-bonding effects with partner alcohol molecules can be inferred from the experimental data of Farzaneh et al.[34] for water/butanol mixture adsorption in all-silica MFI zeolite at 308 K; see Figure 44 of ESI.

In membrane pervaporation of water/alcohol mixtures, an important consequence of enhanced water ingress into microporous adsorbents is that the water fluxes are higher than anticipated on the basis of unary isotherm data. Some experimental evidence of this is available in the work of Villegas et al.[35]

4. Radial distribution functions, and evidence of H-bonding effects

The most likely reason for the failure of IAST to accurately match CBMC mixture simulations is the phenomenon of molecular clustering; cluster formation is most likely induced by hydrogen bonding. To seek confirmation of this hypothesis, we determined the radial distribution functions (RDFs) for distances between all combinations of O and H atoms of molecule pairs; the methodology used is the same as in our previous work.[28] Figure 6, panels a, b, c, and d, presents comparisons of the RDFs for $H_{benzene}$-$O_{molecule}$ and $H_{molecule}$-$O_{molecule}$ distances for water/benzene, methanol/benzene, ethanol/benzene, and water/methanol/ethanol/benzene mixtures in CuBTC at 298 K and total fluid fugacity of 1000 Pa. We note that the RDFs for H_{water}-O_{water}, $H_{methanol}$-$O_{methanol}$, and $H_{ethanol}$-$O_{ethanol}$ pairs each exhibit a first peak at an intermolecular distance of 2 Å, that is characteristic of hydrogen bonding.[28, 36] The results

MS 7

presented in Figure 6d show that H-bonding between alcohol/alcohol pairs are stronger than the bonding between water/water pairs. It appears that the presence of adsorbed benzene molecules has a strong influence on clustering of water molecules.

Remarkably, the corresponding values for $H_{benzene}-O_{water}$, $H_{benzene}-O_{methanol}$, and $H_{benzene}-O_{ethanol}$ do not display any peaks in the RDFs. This would indicate that these partner molecules do not form clusters with benzene molecules, and clustering effects are restricted to water/water, methanol/methanol, and ethanol/ethanol pairs. In order for further verify this finding we determined the RDFs for $H_{benzene}-O_{molecule}$ distances for water/benzene, methanol/benzene, ethanol/benzene, and acetone/benzene mixtures in CuBTC at 298 K and five different total fluid fugacity values; see Figure 7. For the wide range of fugacties, f_t = 40 Pa − 10000 Pa, no peaks are observed at any molecule-benzene distance, confirming that the benzene does not form clusters with partner molecules. For ethanol/benzene mixtures in the bulk fluid phase, the molecular simulations of Požar et al. [37] have revealed micro-segregation effects.

The clustering phenomena experienced by the molecules partnering benzene provides a rationalization of the reduction in the selectivity with respect to benzene when compared to the IAST predictions as witnessed in Figure 5b. At pore saturation conditions, the separations are dictated by differences in the saturation capacities of the constituent species. The phenomenon of molecular clustering of the partner molecules water, methanol, ethanol, and acetone have the apparent effect of reducing the saturation capacity because a cluster may occupy the approximately the same site as occupied by unclustered species. This has the effect of reducing the effectiveness of adsorptive separations.

Clustering effects, resulting from H-bonding, are not catered for by IAST calculations.

5. Activity coefficients in the adsorbed phase, and modelling thereof

Using the Gibbs adsorption equation as starting point, we determined the activity coefficients in the adsorbed phase for the four binary mixtures; a detailed step-by-step calculation methodology is provided in the ESI and the results are presented in Figure 8. The small departures from unity at low pressures is a consequence of the numerical fitting procedure employed in the calculations of the

activity coefficients; the fundamentally correct limiting value of the activity coefficient $\gamma_i \to 1$; $f_t \to 0$ cannot be prescribed in the adopted methodology. For values of the total bulk fluid phase fugacity $f_t = f_1 + f_2$ lower than about 100 Pa, the activity coefficients are practically unity. Non-ideality effects come into play as the pores become increasingly occupied. For all mixtures, the activity coefficient of benzene with the lower saturation capacity, γ_2, reduces significantly below unity, by about 1 – 3 orders of magnitude, as pore saturation is approached. Concomitantly, the activity coefficient of the partner molecular with the higher saturation capacity, γ_1, increases to values slightly exceeding unity. The characteristics of the activity coefficients observed in Figure 8 are also found for water/alcohol mixtures in CuBTC,[13] and in the zeolites FAU, DDR, MFI, and CHA; see Figures 34 – 47 of the ESI.

In implementing the Real Adsorbed Solution Theory (RAST) including non-ideality effects,[13] we adopted the Wilson model for the excess Gibbs free energy (see ESI for detailed derivations and analysis)

$$\ln(\gamma_1) = \left(1 - \ln(x_1 + x_2\Lambda_{12}) - \frac{x_1}{x_1 + x_2\Lambda_{12}} - \frac{x_2\Lambda_{21}}{x_2 + x_1\Lambda_{21}}\right)\left(1 - \exp\left(-C\frac{\pi A}{RT}\right)\right)$$

$$\ln(\gamma_2) = \left(1 - \ln(x_2 + x_1\Lambda_{21}) - \frac{x_2}{x_2 + x_1\Lambda_{21}} - \frac{x_1\Lambda_{12}}{x_1 + x_2\Lambda_{12}}\right)\left(1 - \exp\left(-C\frac{\pi A}{RT}\right)\right)$$

$$(1)$$

In equation (1), π is the spreading pressure, A is the surface area per kg of framework, and $\pi A/RT$ is the adsorption potential.[38] As illustration, we present comparisons of RAST calculations following equation (1) for ethanol/benzene mixtures with the values determined numerically from CBMC mixture simulations; see Figure 9. While the correct qualitative trends in γ_i are captured by the Wilson model, a good quantitative fit was not achievable, irrespective of the choice of the three adjustable parameters Λ_{12}, Λ_{21}, and C. Similarly, the RAST model for water/benzene, methanol/benzene, and acetone/benzene mixtures did not offer any significant advantage over the IAST. There appears to be a need for development of models to describe mixture adsorption taking explicit account of molecular clustering effects.

6. Molecular clustering, and loading dependence of unary diffusivities

The separation performance is also influenced by intra-crystalline diffusivities, and how these depend on the occupancies. A molecule can jump from one adsorption site to an adjacent one, provided it is not already occupied. In the simplest scenario, we would expect the unary diffusivities to be proportional to the fractional vacancy.[39] As argued in a foregoing section, $1/\Gamma_i$ provides a quantification of the fractional vacancy when molecular clustering occurs. Consequently, the loading dependence of the unary diffusivities are strongly influenced by the loading dependence of $1/\Gamma_i$; this influence has been highlighted in the literature for a wide variety of guest/host combinations.[30, 39-41]

MD simulations were carried to determine the self-diffusivities $D_{i,self}$, of water, methanol, ethanol, and benzene. Figures 10, panels a, b, c, and d, presents plots comparing $D_{i,self}$ and $1/\Gamma_i$ vs. θ_i for each of the guest molecules. Even though there is no precise one-to-one correspondence between the two data sets, there is reasonable qualitative agreement between the two occupancy dependencies.

The tetrahedral pockets of CuBTC can accommodate about 9 molecules of water, and this explains the low water diffusivity values for occupancies below about 0.2. Compared at the same fractional pore occupancy, it is interesting to note that the diffusivities of benzene are higher than those for either methanol or ethanol. The most likely reason for this is that molecular clustering effects are practically non-existent for benzene molecules; this has been established earlier on the basis of RDFs. Methanol, and ethanol, on the other hand experience strong clustering, and this explains the lower diffusivity values as compared to benzene. The molecular clustering effects for methanol are stronger than for ethanol; for this reason, the methanol diffusivities are slightly lower than that of ethanol, when compared at the same value of pore occupancy. Video animations for diffusion of water, methanol, ethanol, and benzene in CuBTC have been provided as ESI; these provide evidence of molecular clustering, albeit qualitatively.

A further point to note is that the $D_{i,self}$ vs θ_i data for methanol displays a distinct step-wise characteristic; the diffusivity values in the range $0.6 < \theta_i < 0.8$ are practically the same. Experimental

data of Tsotsalas et al.[33] for transient desorption profiles for methanol in CuBTC at 298 K displays step-wise characteristics; see Figure 11a. The explanation for the step-wise desorption is clearly to be found in the corresponding occupancy dependence of the diffusivities. This conclusion is re-enforced in Figure 11b that presents a comparison of the experimental transient methanol desorption profile with the occupancy dependence of the self-diffusivity of methanol.

7. Conclusions

The following major conclusions emerge from our investigations.

(1) CBMC simulations establish the potential of CuBTC for separation of water/benzene, methanol/benzene, ethanol/benzene, and acetone/benzene mixtures. For separations that operate under pore saturation conditions, the selectivity is in favor of the partner molecules because of molecular packing effects that disfavors benzene. CuBTC is well suited for drying water/alcohol/benzene mixtures.

(2) IAST calculations anticipate the right hierarchy of component loadings at pore saturation but the quantitative agreement with CBMC mixture simulations is poor in all cases. At pore saturation, the selectivities predicted by IAST are about an order of magnitude higher than those determined from CBMC simulations.

(3) The RDFs demonstrate the manifestation of hydrogen bonding between water-water, methanol-methanol, and ethanol-ethanol molecule pairs. There is however no detectable hydrogen bonding between benzene and partner molecules in the investigated mixtures.

(4) Molecular clustering induced by hydrogen bonding effects result in values of activity coefficients that deviate significantly from unity. Calculations of the activity coefficients show that the activity coefficient of benzene in water/benzene, methanol/benzene, ethanol/benzene, and acetone/benzene mixtures is lowered below unity by about 1 – 3 orders of magnitude at pore saturation. Such drastic reduction in the activity coefficients cannot be adequately modelled using say the Wilson equations that do not explicitly account for molecular clustering effects; there is a need for the development of improved models for activity coefficients in this respect.

MS 11

(5) The occurrence of molecular clustering, and consequent failure of the IAST to provide quantitative predictions of mixture adsorption equilibrium serve as a cautionary note to researchers who rely on IAST calculations for evaluation of separations with MOFs and ZIFs.

(6) Molecular clustering also influence the loading dependence of the diffusivities of guest molecules. The MD simulated data for methanol diffusivities serve to rationalize the transient step-wise desorption characteristics that have been observed in experiments of Tsotsalas et al.[33]

8. Notation

A	surface area per kg of framework, $m^2\ kg^{-1}$
C	constant used in equation, $kg\ mol^{-1}$
$D_{i,self}$	self-diffusivity of species i, $m^2\ s^{-1}$
f_i	partial fugacity of species i, Pa
f_t	total fugacity of bulk fluid mixture, Pa
q_i	component molar loading of species i, $mol\ kg^{-1}$
$q_{i,sat}$	molar loading of species i at saturation, $mol\ kg^{-1}$
R	gas constant, $8.314\ J\ mol^{-1}\ K^{-1}$
T	absolute temperature, K

Greek letters

γ_i	activity coefficient of component i in adsorbed phase, dimensionless
Γ_i	thermodynamic factor, dimensionless
π	spreading pressure, $N\ m^{-1}$
Λ_{ij}	Wilson parameters, dimensionless
θ_i	fractional pore occupancy, dimensionless

Subscripts

i	referring to component i
t	referring to total mixture

9. References

1. Z. R. Herm, B. M. Wiers, J. M. Van Baten, M. R. Hudson, P. Zajdel, C. M. Brown, N. Maschiocchi, R. Krishna and J. R. Long, *Science*, 2013, **340**, 960-964.
2. R. Krishna, *Microporous Mesoporous Mater.*, 2014, **185**, 30-50.
3. S. Mukherjee, B. Joarder, B. Manna, A. V. Desai, A. K. Chaudhari and S. K. Ghosh, *Sci. Rep.*, 2014, **4**, 5761. http://dx.doi.org/10.1038/srep05761
4. A. Torres-Knoop, R. Krishna and D. Dubbeldam, *Angew. Chem. Int. Ed.*, 2014, **53**, 7774-7778.
5. R. El Osta, A. Carlin-Sinclair, N. Guillou, R. I. Walton, F. Vermoortele, M. Maes, D. De Vos and F. Millange, *Chem. Mater.*, 2012, **24**, 2781-2791.
6. A. Torres-Knoop, S. R. G. Balestra, R. Krishna, S. Calero and D. Dubbeldam, *ChemPhysChem*, 2015, **16**, 532-535.
7. M. Maes, F. Vermoortele, L. Alaerts, S. Couck, C. E. A. Kirschhock, J. F. M. Denayer and D. E. De Vos, *J. Am. Chem. Soc.*, 2010, **132**, 15277-15285.
8. T. Remy, L. Ma, M. Maes, D. E. De Vos, G. V. Baron and J. F. M. Denayer, *Ind. Eng. Chem. Res.*, 2012, **51**, 14824-14833.
9. A. Torres-Knoop, J. Heinen, R. Krishna and D. Dubbeldam, *Langmuir*, 2015, **31**, 3771-3778.
10. S. Mukherjee, B. Joarder, A. V. Desai, B. Manna, R. Krishna and S. K. Ghosh, *Inorg. Chem.*, 2015, **54**, 4403-4408.
11. K. Zhang, R. P. Lively, M. E. Dose, A. J. Brown, C. Zhang, J. Chung, S. Nair, W. J. Koros and R. R. Chance, *Chem. Commun.*, 2013, **49**, 3245-3247.
12. J. C. Saint-Remi, T. Rémy, V. van Huskeren, S. van de Perre, T. Duerinck, M. Maes, D. E. De Vos, E. Gobechiya, C. E. A. Kirschhock, G. V. Baron and J. F. M. Denayer, *ChemSusChem*, 2011, **4**, 1074-1077.
13. J. J. Gutierrez-Sevillano, S. Calero and R. Krishna, *J. Phys. Chem. C*, 2015, **119**, 3658-3666.
14. R. Krishna, *Phys. Chem. Chem. Phys.*, 2015, **17**, 39-59.
15. R. K. Motkuri, P. K. Thallapally, H. V. R. Annapureddy, L. Dang, R. Krishna, S. K. Nune, C. A. Fernandes, J. Liu and B. P. McGrail, *Chem. Commun.*, 2015, **51**, 8421-8424.
16. R. Krishna and J. M. van Baten, *Sep. Purif. Technol.*, 2011, **76**, 325-330.
17. T. Remy, J. C. Saint-Remi, R. Singh, P. A. Webley, G. V. Baron and J. F. M. Denayer, *J. Phys. Chem. C*, 2011, **115**, 8117-8125.
18. S. Van der Perre, T. Van Assche, B. Bozbiyik, J. Lannoeye, D. E. De Vos, G. V. Baron and J. F. M. Denayer, *Langmuir*, 2014, **30**, 8416-8424.
19. C. G. Efthymiou, E. J. Kyprianidou, C. J. Milios, M. J. Manos and A. J. Tasiopoulos, *J. Mater. Chem. A*, 2013, **1**, 5061-5069.
20. A. L. Myers and J. M. Prausnitz, *A.I.Ch.E.J.*, 1965, **11**, 121-130.
21. C.-T. He, L. Jiang, Z.-M. Ye, R. Krishna, Z.-S. Zhong, P.-Q. Liao, J. Xu, G. Ouyang, J.-P. Zhang and X.-M. Chen, *J. Am. Chem. Soc.*, 2015, **137**, 7217-7223.
22. R. Krishna and J. M. van Baten, *Chem. Phys. Lett.*, 2007, **446**, 344-349.
23. R. Krishna and J. M. van Baten, *Sep. Purif. Technol.*, 2008, **61**, 414-423.
24. R. Krishna and J. M. van Baten, *Chem. Eng. Sci.*, 2008, **63**, 3120-3140.
25. R. Krishna and J. M. van Baten, *Chem. Eng. J.*, 2008, **140**, 614-620.
26. G. F. Fanta, R. C. Burr, W. L. Orton and M. M. Doane, *Science*, 1980, **210**, 646-647.
27. L. Berg, Separation of benzene from acetone by azeotropic distillation, Lloyd Berg, *US Pat.*, US 4931145, 1990.
28. R. Krishna and J. M. van Baten, *Langmuir*, 2010, **26**, 10854-10867.
29. R. Krishna and J. M. van Baten, *J. Membr. Sci.*, 2010, **360**, 476-482.
30. R. Krishna and J. M. van Baten, *Phys. Chem. Chem. Phys.*, 2013, **15**, 7994-8016.
31. R. Krishna and J. M. van Baten, *Langmuir*, 2010, **26**, 3981-3992.

32. R. Krishna and J. M. van Baten, *Langmuir*, 2010, **26**, 8450-8463.
33. M. Tsotsalas, P. Hejcik, K. Sumida, Z. Kalay, S. Furukawa and S. Kitagawa, *J. Am. Chem. Soc.*, 2013, **135**, 4608-4611.
34. A. Farzaneh, M. Zhou, E. Potapova, Z. Bacsik, L. Ohlin, A. Holmgren, J. Hedlund and M. Grahn, *Langmuir*, 2015, **31**, 4887-4894.
35. M. Villegas, E. F. Castro Vidaurre and J. C. Gottifredi, *Chem. Eng. Res. Des.*, 2015, **94**, 254-265.
36. C. Zhang and X. Yang, *Fluid Phase Equilib.*, 2005, **231**, 1-10.
37. M. Požar, J.-B. Seguier, J. Guerche, R. Mazighi, L. Zoranic, M. Mijakovic, B. Kezic-Lovrincevic, F. Sokolic and A. Perera, *Phys. Chem. Chem. Phys.*, 2015, **17**, 9885-9898.
38. F. R. Siperstein and A. L. Myers, *A.I.Ch.E.J.*, 2001, **47**, 1141-1159.
39. R. Krishna, *Chem. Soc. Rev.*, 2012, **41**, 3099-3118.
40. R. Krishna and J. M. van Baten, *J. Phys. Chem. C*, 2012, **116**, 23556-23568.
41. C. Chmelik, J. Kärger, M. Wiebcke, J. Caro, J. M. van Baten and R. Krishna, *Microporous Mesoporous Mater.*, 2009, **117**, 22-32.

10. Caption for Figures

Figure 1. Pore landscape and cage connectivity of CuBTC framework.

Figure 2. (a) Comparison of the CBMC simulations for adsorption of water, methanol, ethanol, acetone, and benzene in CuBTC at 298 K with multi-site-Langmuir-Freundlich model fits. (b) Fractional pore occupancies, θ_i, versus bulk phase fluid fugacity. (c) The inverse thermodynamic factor, $1/\Gamma_i$, plotted as a function of θ_i. (d) The experimental data of Tsotsalas et al.[33] for $1/\Gamma_i$ vs. θ_i for methanol in CuBTC at 298 K, compared with corresponding data obtained in this work.

Figure 3. CBMC simulations for equimolar (a) water/benzene, (b) methanol/benzene, (c) ethanol/benzene, and (d) acetone/benzene mixtures in CuBTC at 298 K.

Figure 4. CBMC simulations for equimolar water/methanol/ethanol/benzene mixtures in CuBTC at 298 K.

Figure 5. (a) Comparison of CBMC simulations for equimolar methanol/benzene mixtures in CuBTC at 298 K with IAST calculations (b) Comparison of the adsorption selectivties for equimolar water/benzene, methanol/benzene, ethanol/benzene, and acetone/benzene mixtures in CuBTC at 298 K determined from CBMC mixture simulations with IAST calculations. (c) CBMC simulations for the enhancement of water ingress into CuBTC from water/methanol/ethanol/benzene mixtures, as compared to that of pure water. The continuous solid line represents the IAST calculations.

MS 16

Figure 6. (a, b, c) Comparing the RDFs for $H_{benzene}$-$O_{molecule}$ and $H_{molecule}$-$O_{molecule}$ distances for (a) water/benzene, (b) methanol/benzene, and (c) ethanol/benzene mixtures in CuBTC at 298 K and total fluid fugacity of 1000 Pa. (d) Comparing the RDFs for $H_{molecule}$-$O_{molecule}$ distances for quaternary watermethanol/ethanol/benzene mixtures in CuBTC at 298 K and total fluid fugacity of 1000 Pa.

Figure 7. Comparing the RDFs for $H_{benzene}$-$O_{molecule}$ distances for (a) water/benzene, (b) methanol/benzene, (c) ethanol/benzene, and (d) acetone/benzene mixtures in CuBTC at 298 K and five different total fluid fugacity values.

Figure 8. Activity coefficients of the components in the adsorbed phase for equimolar (a) water/benzene, (b) methanol/benzene, (c) ethanol/benzene, and (d) methanol/ethanol, and (e) acetone/benzene mixtures in CuBTC at 298 K.

Figure 9. RAST calculations of the activity coefficients for equimolar ethanol/benzene mixtures in CuBTC at 298 K. These calculations are based on the equation (1) taking $\Lambda_{12} = 1$; $\Lambda_{21}= 3.6$; $C = 0.12$ kg mol^{-1}. Further calculation details are provided in the ESI.

Figure 10. MD simulations of the self-diffusivities $D_{i,self}$, and the inverse thermodynamic factor $1/\Gamma_i$ in CuBTC of (a) water, (b) methanol, (c) ethanol, and (d) benzene as a function of the fractional pore occupancy, θ_i.

Figure 11. (a) Transient desorption profiles for methanol in CuBTC at 298 K. Experimental data of Tsotsalas et al.[33] (b) Comparison of the experimental transient desorption profile with the loading dependence of the self-diffusivity.

(a)

water, CBMC

benzene, CBMC

CBMC;
equimolar mixture;
CuBTC; 298 K

Component loading, q_i / mol kg^{-1}

Total fluid phase fugacity, f_t / Pa

(b)

methanol, CBMC

benzene, CBMC

CBMC;
equimolar mixture;
CuBTC; 298 K

Component loading, q_i / mol kg^{-1}

Total fluid phase fugacity, f_t / Pa

(c)

ethanol, CBMC

benzene, CBMC

CBMC;
equimolar mixture;
CuBTC; 298 K

Component loading, q_i / mol kg^{-1}

Total fluid phase fugacity, f_t / Pa

(d)

acetone, CBMC

benzene, CBMC

CBMC;
equimolar mixture;
CuBTC; 298 K

Component loading, q_i / mol kg^{-1}

Total fluid phase fugacity, f_t / Pa

(a)

(b)

(c)

(d)

The plot shows activity coefficient in adsorbed phase, γ_i, versus total fluid phase fugacity, f_t / Pa. Legend: ethanol, Wilson RAST; benzene, Wilson RAST; ethanol, numerical calculations; benzene, numerical calculations. Annotation: ethanol/benzene; $f_1 = f_2$; 298 K; CuBTC

(a)

(b)

(c)

(d)

(a)

(b)