

Molecular Simulation Studies of Separation of CO₂/N₂, CO₂/CH₄, and CH₄/N₂ by ZIFsBei Liu^{†,‡} and Berend Smit^{*,†,§}*Department of Chemical Engineering, University of California, Berkeley, California 94720-1462, and Department of Chemistry, University of California, Berkeley, California 94720-1462**Received: February 20, 2010; Revised Manuscript Received: March 24, 2010*

In this work, molecular simulations were performed to evaluate the separation performance of two typical zeolitic imidazolate frameworks (ZIFs), ZIF-68 and ZIF-69, for CO₂/N₂, CO₂/CH₄, and CH₄/N₂ mixtures. To do this, we first identified a suitable force field for describing CO₂, N₂, and CH₄ adsorption in ZIFs. On the basis of the validated force field, adsorption selectivities of the three mixtures in these ZIFs were simulated then. The results show that ZIF-69 is more beneficial for separating CO₂ from CO₂-related mixtures than ZIF-68, mainly due to the presence of chlorine atoms in cbIM linkers in the former for the pressures we have considered. The overall separation performances of these two ZIFs for separating the chosen mixtures are comparable to typical MOFs and zeolites. In addition, this work demonstrates that the electrostatic interactions produced by the frameworks are very important for achieving high adsorption separation selectivities in ZIFs, and ideal adsorbed solution theory (IAST) may be applicable to ZIFs. Furthermore, the effect of water on the separation performance of the two ZIFs was also investigated.

1. Introduction

Metal–organic frameworks (MOFs) are a family of hybrid porous materials that are formed by the coordination of metal ions with organic linkers. By varying the linkers, ligands, and metals in the materials, their synthesis can be readily adapted to control pore connectivity, structure, and dimension, featuring opportunities for a large range of differences in functionality. To date, a large number of different MOFs have been synthesized which have shown various promising applications in gas storage, separation, catalysis, etc.^{1–7} As a subclass of MOFs, zeolitic imidazolate frameworks (ZIFs) have drawn more and more attention nowadays. ZIFs are porous crystalline materials with tetrahedral networks that resemble those of zeolites with transition metals (Zn, Co, etc.) linked by imidazolate ligands.^{8–15} Among the many ZIFs synthesized, some of them have exceptional thermal and chemical stability^{8,14} and exhibit great promise for gas storage and separation.^{14–16}

At present, many studies have been carried out on the adsorption and diffusion of pure gases in ZIFs.^{8–20} Experimentally, for example, Yaghi and co-workers measured the adsorption isotherms of CO₂, CO, CH₄, N₂, and O₂ in several ZIFs.^{14–16} Wu et al.¹³ studied the H₂ adsorption sites and binding energies in ZIF-8 using a combined experimental and computational method. Among the available theoretical studies, Zhong and co-workers investigated the adsorption and diffusion characteristics of CO₂ in two typical ZIFs, ZIF-68 and ZIF-69.¹⁷ They also studied the influences of framework charges on CO₂ uptake in some ZIFs.¹⁸ Johnson and co-workers computed the adsorption and diffusion of CO₂, N₂, CH₄, and H₂ in ZIF-68 and ZIF-70 from atomistic simulations.¹⁹ Zhou et al.²⁰ employed grand canonical Monte Carlo (GCMC) simulations to study hydrogen adsorption in ZIF-8. The adsorption isotherms at 77 K were

calculated, and the adsorption sites were identified in their work. Regarding the separation of gas mixtures, Yaghi and co-workers carried out a series of experiments^{14–16} in ZIFs for separating CO₂ from CO₂-related mixtures, like CO₂/CO, CO₂/CH₄, CO₂/N₂, and CO₂/O₂. The gas separation properties of materials were derived from breakthrough experiments or single gas adsorption isotherms in their work. The results show that ZIFs are promising candidate materials for CO₂ capture. Theoretically, Babarao and Jiang investigated the separation of industrially important gas mixtures by one type of ZIFs, i.e., rho zeolite-like MOF (*rho*-ZMOF).^{21,22} Their simulation results reveal that *rho*-ZMOF is a promising candidate for the separation of syngas, natural gas, and flue gas, encouraging us to carry out a study to investigate the mixture separation performances of other ZIFs. To meet this purpose, two typical ZIFs, ZIF-68 and ZIF-69, were selected as the representatives of ZIFs. These two ZIFs have the same **GME** (hereafter, three-letter bold symbols are used to designate framework types; see <http://www.iza-structure.org/>) topology, but they differ in size and functionalized links of the cavities. Both structures are chemically and thermally stable (up to 663 K).¹⁴ The as-synthesized ZIFs are insoluble in H₂O and common organic solvents.¹⁴ This allows us to study the relative importance of the functional groups in the ZIF structures in comparison to the structural features, such as pore and aperture size. We selected CO₂/CH₄, CO₂/N₂, and CH₄/N₂ systems as the model mixtures to separate. These mixtures are important practical systems that are included in large-scale industrial applications, such as natural gas purification and CO₂ capture from flue gas. The characteristics of CO₂, N₂, and CH₄ are different: CO₂ and N₂ are two components with different quadrupolar moments, while CH₄ is a nonpolar species. Therefore, these two different mixtures give us a better understanding of the differences in separation performance of different ZIFs. In this work, we extend our previous work focusing on the adsorption selectivities of zeolites and MOFs^{23,24} to ZIFs. We focus not only on the selectivities but also on the

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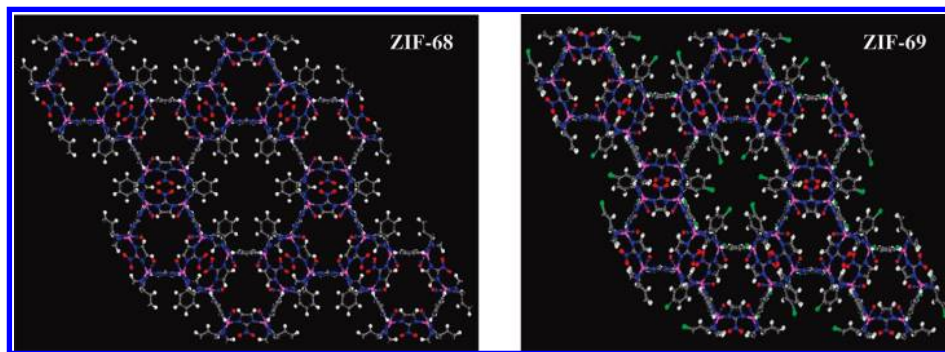


Figure 1. Crystal structures of ZIF-68 and ZIF-69 (Zn, pink; O, red; C, gray; N, blue; H, white; Cl, green (only in ZIF-69)) used in the simulations.

TABLE 1: Structural Properties for ZIF-68 and ZIF-69 Studied in This Work

material	pore size (Å)	unit cell (Å)	cell angle (deg)	ρ_{cryst}^a (g/cm ³)	S_{acc}^b (m ² /g)	V_{free}^b (cm ³ /g)
ZIF-68	10.3	$a = b = 26.6407, c = 18.4882$	$\alpha = \beta = 90, \gamma = 120$	1.033	1283	0.588
ZIF-69	7.8	$a = b = 26.0840, c = 19.4082$	$\alpha = \beta = 90, \gamma = 120$	1.146	1251	0.574

^a Obtained from the XRD crystal data.¹⁴ ^b Taken from ref 17.

microscopic mechanisms, like the effects of different functional groups and the effect of electrostatic interactions on separation selectivity.

In flue gases, besides CO₂ and N₂, water is an important component. It is therefore an important question how the presence of water is affecting the adsorption selectivity. To address this question, we performed some studies on ternary mixtures.

2. Models and Computational Method

2.1. ZIF Structures. In this work, the structures of ZIF-68 and ZIF-69 were constructed from their corresponding experimental XRD data.¹⁴ Johnson and co-workers¹⁹ found that, if a reliable, unambiguous crystal structure from experiment is available, the adsorption isotherms in ZIFs using the raw XRD structure and the DFT optimized structure were nearly identical. ZIF-68 and ZIF-69 have the same primitive GME topology (the structure has wide channels formed by rings of links) with Zn linked by different imidazolate/imidazolate-type linkers. ZIF-68 contains benzimidazole (bIM) and 2-nitroimidazole (nIM), while ZIF-69 contains 5-chlorobenzimidazole (cbIM) and 2-nitroimidazole (nIM). The guest-free crystal structures of these two ZIFs are given in Figure 1, and some details of the structures of these two ZIFs are summarized in Table 1.

2.2. Force Field. For describing the adsorption of pure components and mixtures of CH₄, CO₂, and N₂ molecules in the selected ZIFs, we used the following models for the pure components. CH₄ was modeled as a single-center Lennard-Jones molecule using the potential parameters developed by Dubbel-dam et al.^{25,26} CO₂ was modeled as a rigid linear molecule, and its intrinsic quadrupole moment was described by a partial-charge model.²⁷ The C–O bond length is 1.18 Å, and the partial point charges centered at each LJ site are $q_{\text{O}} = -0.288e$ and $q_{\text{C}} = +0.576e$. A combination of the site–site LJ and Coulombic potentials was used to calculate the CO₂–CO₂ intermolecular interactions. The LJ potential parameters for atom O and C in CO₂ were taken from the force field developed by Hiro-tani et al.,²⁷ which has been widely used for the separation of CO₂-related mixtures in MOFs.^{21,22,28,29} N₂ was modeled as a diatomic molecule with fixed bond lengths (1.1 Å). In this model, point charges are centered on each LJ site, and electric neutrality is maintained by placing a point charge of $+0.964e$ at the center

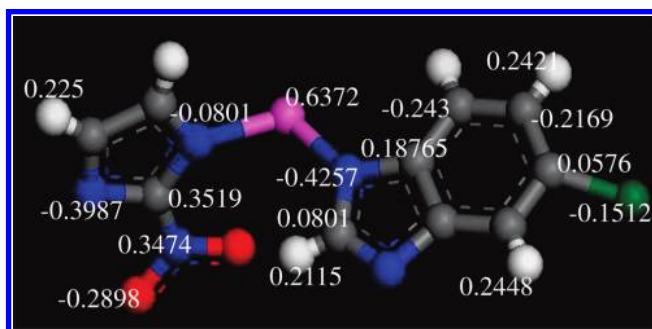


Figure 2. Atomic partial charges of ZIF-69 (Zn, pink; O, red; C, gray; N, blue; H, white; Cl, green).

of mass of the N₂ molecule. The interactions between various sites in the adsorbed molecules were also calculated by the summation of LJ interactions and the electrostatic interactions. The LJ parameters for N₂ molecule were taken from the TraPPE force field.³⁰ To examine the effect of H₂O on the separation of the chosen mixtures, H₂O molecules were included in the systems studied with H₂O represented by the TIP3P (three-point transferable interaction potential) model.³¹

For ZIF-68 and ZIF-69, a combination of the site–site LJ and Coulombic potentials was also used to calculate the interactions between adsorbate molecules and adsorbents. In our simulations, all of the LJ cross interaction parameters were determined by the Lorentz–Berthelot mixing rules. An atomistic representation was used for the ZIFs studied. For calculating the interactions between the adsorbate molecules and the atoms in the framework of the ZIF materials, we adopted the atomic partial charges of ZIFs from Liu et al.¹⁷ The dispersive interactions of all of the atoms in ZIFs are modeled by the universal force field (UFF) of Rappe et al.³² To better represent the adsorption isotherms of pure CH₄, CO₂, and N₂ in these ZIFs, part of the atomic partial charges of ZIF-69 and LJ parameters of the UFF were refined in this work. The parameters we have used are shown in Figure 2 and Table 2. A similar strategy was previously used in our work on zeolites^{25,26,33–35} and MIL-47 (V),²³ the work of Calero and co-workers for the adsorption of CO₂ in zeolites,³⁶ the work of Yang and Zhong for the adsorption of H₂ in IRMOFs and MOF-505,^{37,38} and the work of Zhong and co-workers for the adsorption of alkanes, CO₂, N₂, and O₂ in Cu-BTC and several other MOFs.^{39–42}

TABLE 2: LJ Potential Parameters for Adsorbate–Adsorbate and Adsorbate–ZIF Interactions

	CH ₄	C _{co2}	O _{co2}	N _{N2}
atom–atom σ (Å)	3.72	2.789	3.011	3.31
atom–atom ϵ/k_B (K)	158.5	29.66	82.96	36.0

atom	σ^a (Å)	ϵ/k_B^a (K)	ϵ/k_B^b (K)
ZIF_Zn	2.46	62.40	53.40
ZIF_O	3.12	30.19	21.75
ZIF_C	3.43	52.84	40.27
ZIF_N	3.26	34.72	22.72
ZIF_H	2.57	22.14	14.14
ZIF_Cl	3.52	114.23	99.23

^a Taken from the UFF of Rappe et al.³² ^b Obtained in this work.

Our computed excess adsorption isotherms as well as the experimental data¹⁶ and previous simulation results¹⁷ are shown in Figure 3. We found that the refined parameters yield a significantly better representation of the experimental data.

2.3. Simulation Method. Grand-canonical Monte Carlo (GCMC) simulations were employed to calculate the adsorption of pure components and their mixtures in the ZIFs studied. For

the calculation of the isosteric heats of adsorption at infinite dilution Q_{st}^0 , we performed Monte Carlo simulations in the *NVT* ensemble. During the simulation, we computed the internal energy ΔU , which is directly related to Q_{st}^0 .^{26,43} The Peng–Robinson equation of state was used to relate the bulk experimental pressure with chemical potential required in the GCMC simulations. The two ZIFs studied in this work were treated as rigid frameworks with atoms frozen at their crystallographic positions during the simulations. As mentioned before, the chosen ZIF-68 and ZIF-69 have high thermal and chemical stability; in addition, it has been shown that the flexibility of the framework has a negligible influence on the adsorption of gases,⁴⁴ although the effect is significant on gas diffusivity.⁴⁵ Therefore, the treatment of rigid framework is reasonable. A cutoff radius of 12.8 Å for ZIFs was applied to all of the LJ interactions. The long-range electrostatic interactions were handled using the Ewald-summation technique. For each state point, GCMC simulation consisted of 1.5×10^7 steps, to guarantee equilibration, followed by 1.5×10^7 steps to sample the desired thermodynamic properties. The statistical uncertainty was estimated by dividing each run into 10 blocks and calculating the standard deviation from the block averages. The

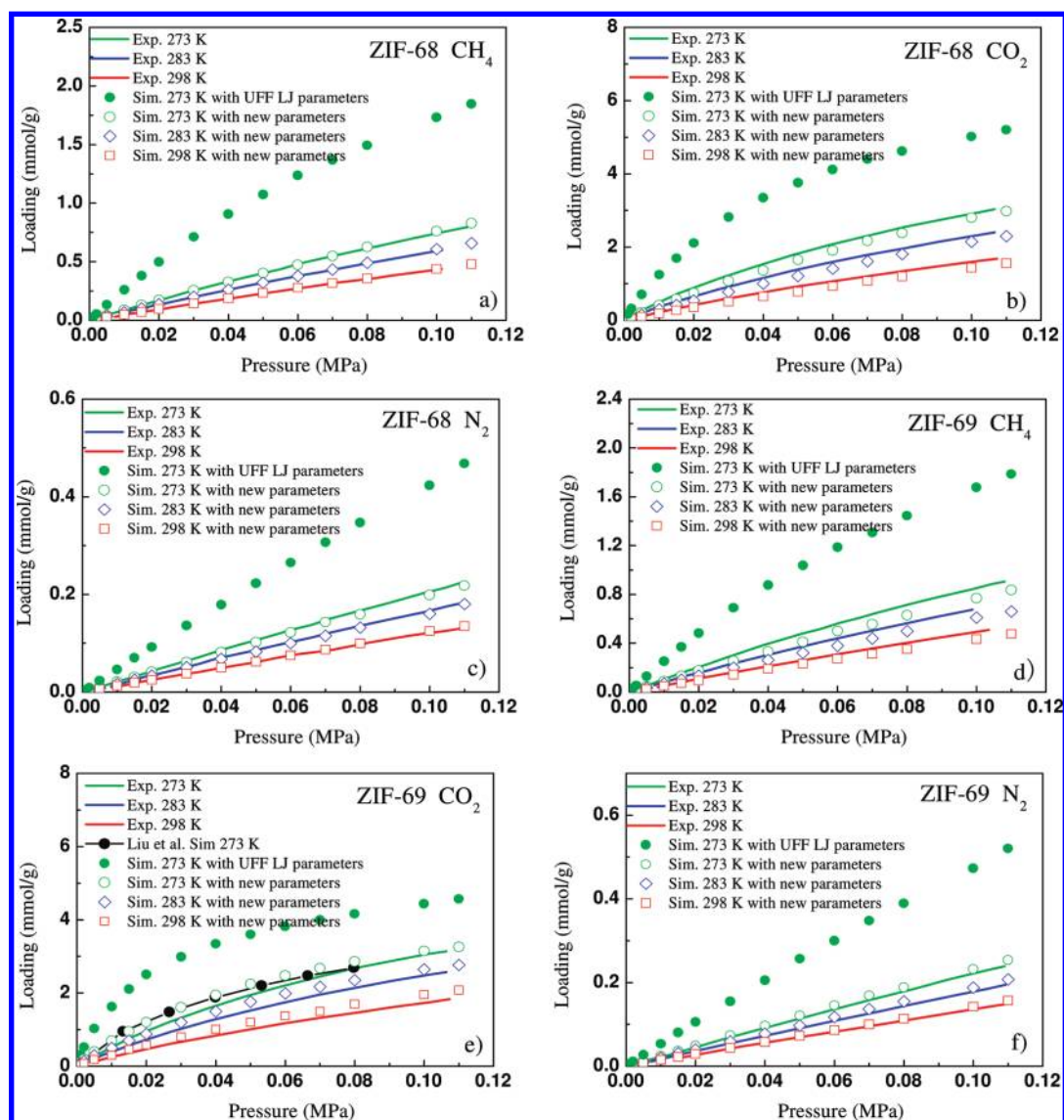


Figure 3. Comparison of the experimental and simulated adsorption isotherms of (a) CH₄, (b) CO₂, and (c) N₂ in ZIF-68 and (d) CH₄, (e) CO₂, and (f) N₂ in ZIF-69.

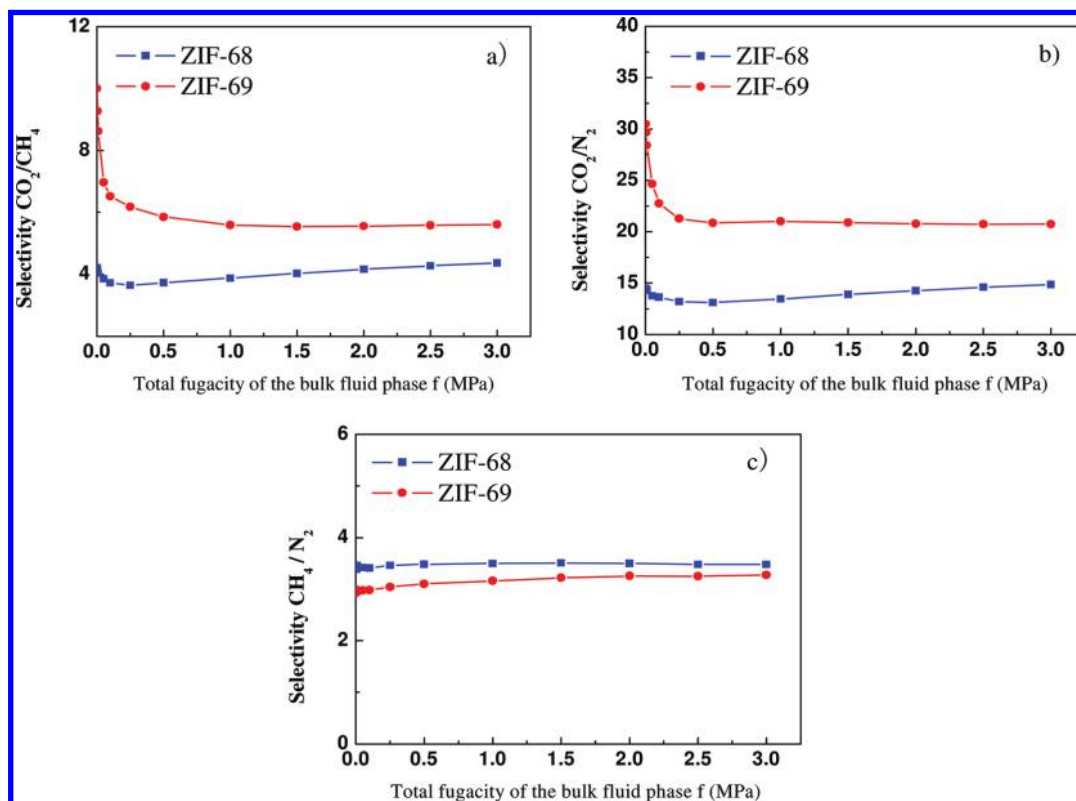


Figure 4. Selectivities for CO_2 as a function of the total bulk fugacity for (a) an equimolar binary mixture of CO_2/CH_4 , (b) 15%:85% binary mixture of CO_2/N_2 , and (c) an equimolar binary mixture of CH_4/N_2 at 298 K.

standard deviation is within $\pm 5\%$ for every simulation. A detailed description of the simulation methods can be found in ref 26.

3. Results and Discussion

3.1. Comparison of Adsorption Selectivity of Gas Mixtures in ZIF-68 and ZIF-69. In separation processes, a good indication of the ability for separation is the selectivity of a porous material for different components in mixtures. The selectivity for component A relative to component B is defined by $S = (x_A/x_B)(y_B/y_A)$, where x_A and x_B are the mole fractions of components A and B in the adsorbed phase and y_A and y_B are the mole fractions of components A and B in the bulk phase, respectively. In this work, we compared the adsorption selectivity of CO_2 for an equimolar binary mixture of CO_2/CH_4 , CO_2 for a 15%:85% binary mixture of CO_2/N_2 , and the selectivity for CH_4 for an equimolar binary mixture of CH_4/N_2 in the two ZIFs. The results of these computations are shown in Figure 4.

Figure 4a and b shows that in both ZIFs CO_2 is preferentially adsorbed over CH_4 and N_2 . For CO_2/CH_4 and CO_2/N_2 separations, ZIF-69 gives a higher selectivity compared to ZIF-68. This observation is consistent with what Yaghi and co-workers found from ratios of the initial slopes of the measured single component adsorption isotherms.¹⁶ Separation of CO_2/CH_4 and CO_2/N_2 has been performed in other porous materials, and some results are listed in Table 3 for comparison with ZIFs.

From Figure 4a,b and Table 3, we can see that the selectivities in these two ZIFs are comparable to most MOFs and zeolites. In addition, from Figure 4a and b, we can see that the selectivities in ZIF-68 and ZIF-69 initially decrease and then increase with increasing pressure. The initial decrease is attributed to the heterogeneous distribution of adsorption sites, and the later increase is due to cooperative interactions between CO_2 molecules.²¹ For CH_4/N_2 mixture separation, ZIF-68

TABLE 3: Adsorption Selectivities of CO_2/CH_4 , CO_2/N_2 , and CH_4/N_2 in Some MOFs and Zeolites

	CO_2/CH_4	CO_2/N_2	CH_4/N_2
IRMOF-1	2–3 ^{41,46,47}		2 ²³
Cu-BTC	6–9 ^{28,41,47}	35 ^{40,47}	3 ²³
MOF-508b	3–6 ⁴⁸	3–6 ⁴⁸	
MIL-47 (V)			5 ²³
<i>soc</i> -MOF	22–36 ²⁸		
<i>rho</i> -MOF	30–500 ²¹	500–19000 ²¹	
MFI	2–20 ⁴⁹	14 ⁵⁰ or 30 ⁵¹	8 ²³
DDR	3–20 ⁴⁹	22–38 ²⁴	5–7 ²⁴
FAU	4–10 ⁴⁹	20 ⁵²	

performs better, as shown in Figure 4c. Again, the selectivity in these two ZIFs is comparable to most MOFs and zeolites, as shown in Table 3.

To obtain further insight on why ZIF-69 performs better for separating CO_2 -related mixtures and why ZIF-68 is better for CH_4/N_2 mixtures, we calculated isosteric heats of adsorption at infinite dilution, Q_{st}^0 , for CO_2 , CH_4 , and N_2 in the two ZIFs. In addition, we carried out some simulations to investigate the influence of the electrostatic interactions on the adsorption selectivities. The polar functional groups are expected to favor those components having significant quadrupolar moment.^{16,17} Therefore, we expect that at low pressures the presence of the Cl functional groups in ZIF-69 should increase the amount of adsorption in the order $\text{CO}_2 > \text{N}_2 > \text{CH}_4$. This can be seen clearly in Table 4, which shows that the differences of Q_{st}^0 of CO_2 and CH_4 (10.427 kJ/mol) and those of CO_2 and N_2 (13.909 kJ/mol) in ZIF-69 are bigger than those (7.321 and 11.14 kJ/mol) in ZIF-68, while the differences of Q_{st}^0 of CH_4 and N_2 in ZIF-68 (3.819 kJ/mol) are slightly larger than that those in ZIF-69 (3.482 kJ/mol). This explains the much larger selectivities observed in ZIF-69 for separating CO_2 -related mixtures and the slightly bigger selectivity in ZIF-68 for separating CH_4/N_2 at low loadings.

TABLE 4: Isothermic Heats of Adsorption at Infinite Dilution Q_{st}^0 (kJ/mol) of CO₂, CH₄, and N₂ in ZIF-68 and ZIF-69 at 298 K as Obtained from the Simulations

	Q_{st}^0	
	ZIF-68	ZIF-69
CO ₂	23.015	26.667
CH ₄	15.694	16.240
N ₂	11.875	12.758

To investigate the importance of the electrostatic interactions on the separation of these mixtures, we carried out some simulations in which we set the various charges in our models to zero. We considered three case studies: in case 1, we switched off all of the electrostatic interactions involving the CO₂ and N₂ molecules, in case 2, only the electrostatic interactions of CO₂-adsorbents and N₂-adsorbents were switched off, and in case 3, all of the electrostatic interactions were considered. Figure 5 shows the effect of electrostatic interactions on the adsorption isotherms of (a) CO₂/CH₄, (c) CO₂/N₂, and (e) CH₄/N₂ mixtures

and the adsorption selectivities for CO₂ (b) from equimolar binary mixtures of CO₂/CH₄, (d) from 15:85 binary mixtures of CO₂/N₂, and (f) selectivities of CH₄ from equimolar binary mixtures of CH₄/N₂ at 298 K in ZIF-68 and ZIF-69.

Figure 5 shows that the electrostatic interactions have a very important effect on both the pure component adsorption and the adsorption selectivities. In fact, a significant fraction of the selectivity is lost if the material charges are set to zero. The framework charges result in a much higher selectivity for CO₂/CH₄ and CO₂/N₂ mixtures in both materials, as shown in Figure 5b and d. Regarding the CH₄/N₂ system, the electrostatic field in ZIFs can enhance the adsorption of gases with quadrupolar moment, that is, N₂ in this case, resulting in a negative contribution to the selectivity of CH₄ from the CH₄/N₂ system (Figure 5e and f). In addition, we found that without the electrostatic interactions ZIF-68 and ZIF-69 perform quite similarly. This implies that the chemistry of the materials, i.e., the presence of Cl functional groups, is an important factor for deciding the separation performances of these ZIFs.

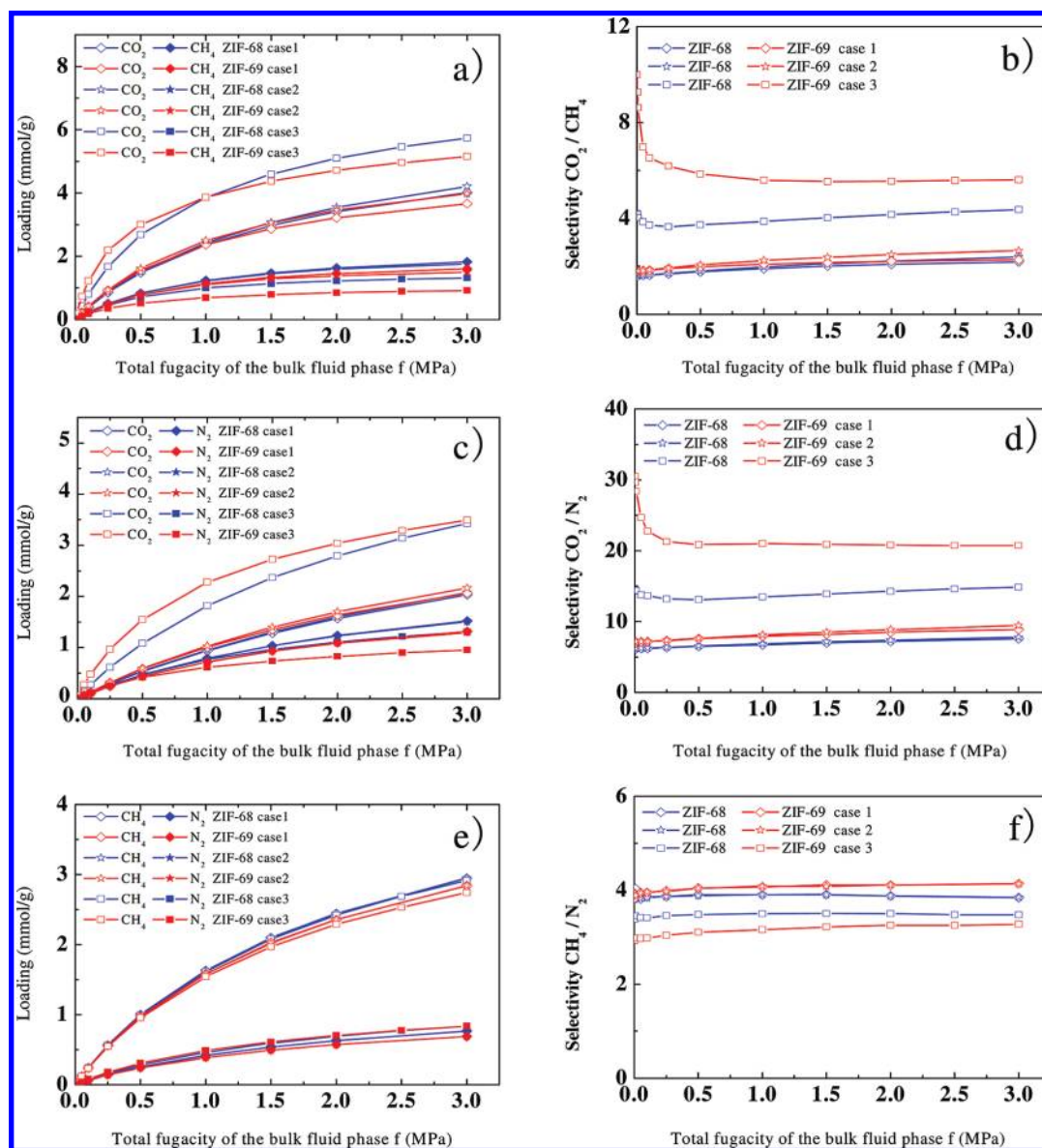


Figure 5. Effect of electrostatic interactions on the adsorption isotherms of (a) CO₂/CH₄, (c) CO₂/N₂, and (e) CH₄/N₂ mixtures and the adsorption selectivities for CO₂ from (b) equimolar binary mixtures of CO₂/CH₄, (d) from 15:85 binary mixtures of CO₂/N₂, and selectivities of CH₄ from (f) equimolar binary mixtures of CH₄/N₂ in ZIF-68 and ZIF-69 at 298 K.

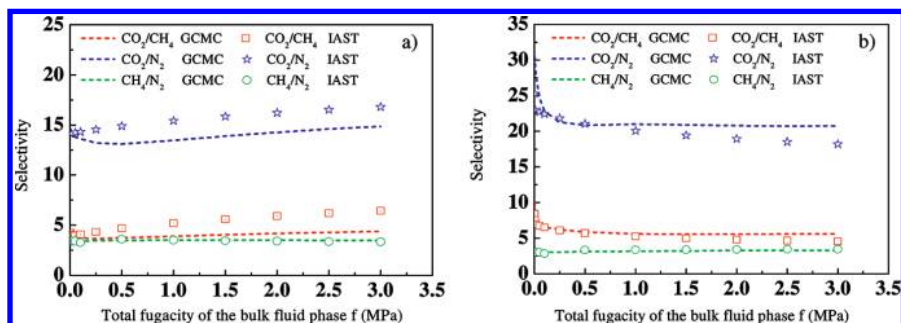


Figure 6. Comparison of IAST and GCMC for CO_2 selectivity as a function of pressure from equimolar binary mixture of CO_2/CH_4 and CO_2/N_2 , and CH_4 selectivity from equimolar binary mixture of CH_4/N_2 at 298 K in (a) ZIF-68 and (b) ZIF-69.

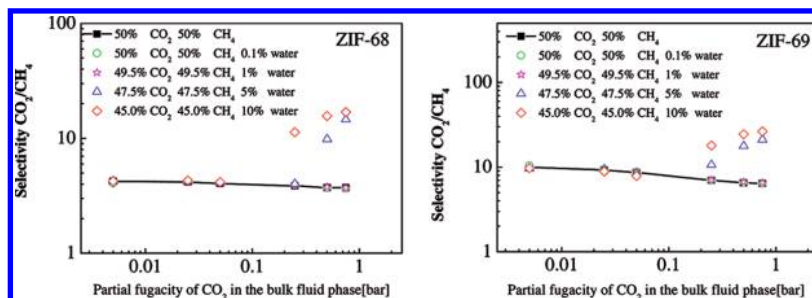


Figure 7. Selectivity of CO_2 over CH_4 in two- and three-component mixtures in ZIF-68 and ZIF-69 at 298 K.

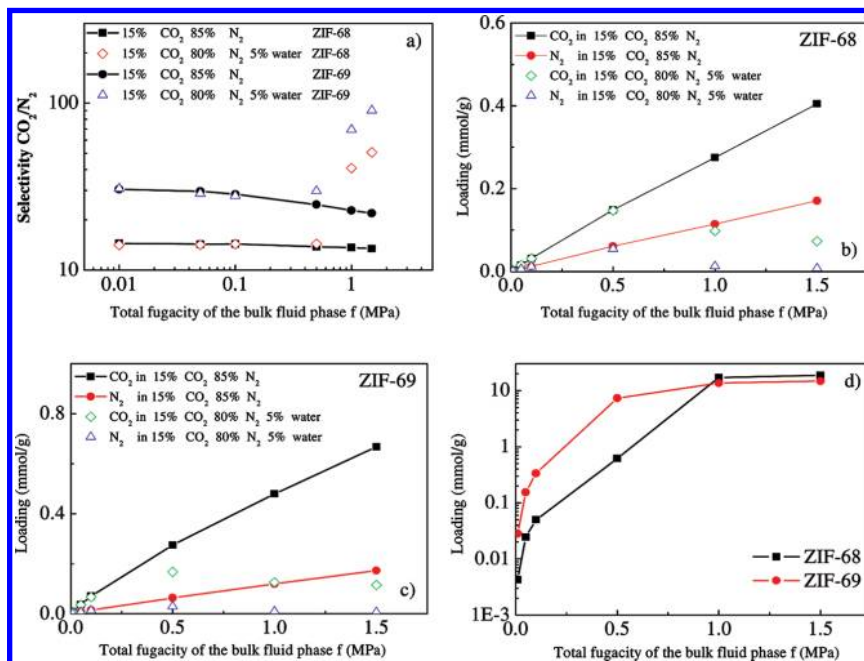


Figure 8. (a) Simulated adsorption selectivity of CO_2 over N_2 in two- and three-component mixtures in ZIF-68 and ZIF-69, (b) the adsorption isotherms of CO_2 and N_2 in two- and three-component mixtures in ZIF-68, (c) the adsorption isotherms of CO_2 and N_2 in two- and three-component mixtures in ZIF-69, and (d) simulated adsorption amount of water in $\text{CO}_2/\text{N}_2/\text{water}$ (15%:80%:5%) mixtures in ZIF-68 and ZIF-69 as a function of pressure.

At intermediate and high loadings, pore size effects (entropy effects) on adsorption are increasingly important. At very high pressure, the packing effect favors the adsorption of the smallest molecule.^{53–55} As CO_2 is the larger molecule in CO_2/N_2 and CO_2/CH_4 , we expect a decrease in the selectivity at higher pressures and a reversal of the selectivity at extremely high pressures.

3.2. IAST Predictions. It has been commonly recognized that ideal adsorbed solution theory (IAST)⁵⁶ can give good predictions of gas mixture adsorption in many porous materials, such as zeolites^{51,57} and MOFs.^{23,40,41,46,58,59} IAST is a very efficient method for calculations of adsorption selectivities. IAST

calculations were then performed in this work to check whether it is applicable for ZIFs. The calculated adsorption selectivities of CO_2 from equimolar mixtures CO_2/CH_4 and CO_2/N_2 and those of CH_4 from the equimolar mixture CH_4/N_2 in ZIF-68 and ZIF-69 are shown in Figure 6. In all cases, good agreement between GCMC simulation and IAST calculation was obtained, indicating that IAST can be a very good alternative to estimate the adsorption behavior of CO_2/N_2 , CO_2/CH_4 , and CH_4/N_2 in ZIFs.

3.3. Effect of the Presence of Water on Separation of Gas Mixtures in ZIF-68 and ZIF-69. Besides N_2 and CO_2 , flue gases contain significant amounts of water. In zeolites, it is well-known that the presence of water significantly decreases

the adsorption of CO₂ because water competitively adsorbs on the cations, blocking access for CO₂.^{60,61} In MOFs, however, the presence of water can be beneficial in some cases. For example, Yazaydin et al. reported an interesting discovery in which the CO₂ uptake and its selectivity over N₂ and CH₄ in one type of MOFs, Cu-BTC, were significantly increased by the presence of water molecules coordinated to open-metal sites in the framework.⁶¹ A very recent study of Jiang⁶² found that even the presence of a tiny amount of H₂O has a significant influence on separation of typical syngas in charged *soc*-MOF. With a trace of water, he found the selectivity of CO₂ from syngas increases at low pressure due to promoted adsorption of CO₂ by H₂O but decreases at high pressure as a consequence of competitive adsorption of H₂O over CO₂. Jiang attributed this to the strong interactions of the H₂O molecules with the positively charged exposed metal atoms and nonframework ions in charged *soc*-MOF. Since the ZIFs studied in this work do not have exposed metal atoms and nonframework ions, we expect that a trace of water would have far less effect on the selectivity for these materials. To investigate the effect of water on mixture separation in these two ZIFs, we simulated the adsorption isotherms for two three-component mixtures (CO₂/CH₄/H₂O and CO₂/N₂/H₂O).

Figure 7 shows the simulated adsorption selectivity of CO₂/CH₄ in ZIF-68 and ZIF-69 for different molar fractions of water in the bulk phase. We observe that small amounts of water (<5%) in the gas phase have little effect on the selectivity. For higher concentrations and higher total pressures, we observe an increase in the selectivity.

Furthermore, we simulated the adsorption of two-component (CO₂/N₂ = 15:85) and three-component mixtures (CO₂/N₂/H₂O = 15:80:5) in the two ZIFs. The adsorption selectivity of CO₂ from the mixtures and the corresponding adsorption isotherms are shown in Figure 8.

From Figure 8, we can see that, though the separation performances of ZIF-68 and ZIF-69 are different, the effect of water on these two ZIFs is quite similar. Figure 8a shows that at low pressure the selectivity of CO₂ over N₂ does not change with the presence of water in both ZIFs; however, at high pressures, the selectivity increases. Figure 8b–d shows that, at high pressures, there is a competitive adsorption of H₂O over CO₂ and N₂. Due to the presence of much more water, both the loadings of CO₂ and N₂ decrease, but to a different extent, resulting in an increase of the selectivity in both ZIFs.

4. Conclusions

This work shows that the selectivities of the mixtures investigated in the selected ZIFs are comparable to most zeolites and other typical MOFs. An important conclusion from this work is the role of the electrostatic interactions. The electrostatic interactions are a key factor in the selectivity; it is therefore important to ensure that these interactions are correctly taken into account in the force fields. IAST gives a reasonable prediction of the mixture adsorption selectivities on the basis of the pure component adsorption isotherms and is likely to be applicable to ZIFs. In addition, the present work shows that, only if the amount of water in the bulk phase is above 5%, the presence of water influences the adsorption selectivities in these ZIFs significantly.

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