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Thermodynamic parameters of cation exchange in MOF-5 and MFU-4*l*†

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We present a method for approximating thermodynamic parameters $\Delta G^{\circ}_{\mathrm{P,T}}$, ΔH, and ΔS for the cation exchange process in metal–organic frameworks, as exemplified by Ni^{2+} exchange into Zn_4O(1,4-benzenedicarboxylate)$_3$ (MOF-5) and Co^{2+} exchange into MOF-5 and Zn_5Cl_4-(bis(1*H*-1,2,3-triazolo-[4,5-*b*],[4′,5′-*i*])dibenzo-[1,4]-dioxin)$_3$ (MFU-4*l*). For these examples, we find that the cation exchange process is endergonic and that parameters such as solvent and cation identity impact the thermodynamics.

The process of exchanging the native metal ions in the secondary building units (SBUs) of metal–organic frameworks (MOFs) is emerging as a powerful tool for synthesizing new materials.[1–14] Because the original metal sites in a MOF are often crystallographically determined, cation exchange is a predictive tool; the new metal sites should inherit the original ligand fields and coordination geometries. Spurred on by the promise of this technique, cation exchange has been demonstrated with more than 30 distinct SBUs, uncovering interesting differences in the impact of cation identity, solvents, and MOF-types. Yet, few studies have explored the factors that govern the cation exchange process. Beyond reports of cation incorporation as a function of time,[7,10] the kinetics and thermodynamics have not been measured with precision. For cation exchange to become a rational synthetic tool, these fundamental studies must be performed. Therefore, we present a method to approximate the thermodynamic parameters of cation exchange in MOFs to explore the mechanistic role of factors such as solvent and cation identity.

As a test system, we reexamined the cation exchange of Ni^{2+} into the iconic material known as MOF-5 (Fig. 1).[15] Because we previously reported the effect of cation identity and solvent on the extent of cation exchange under pre-equilibrium conditions, we suspected they would influence the thermodynamics as well.[3,9] To measure the approximate thermodynamic parameters, we followed the thermochemical analysis applied to cation exchange in zeolites.[16–19]

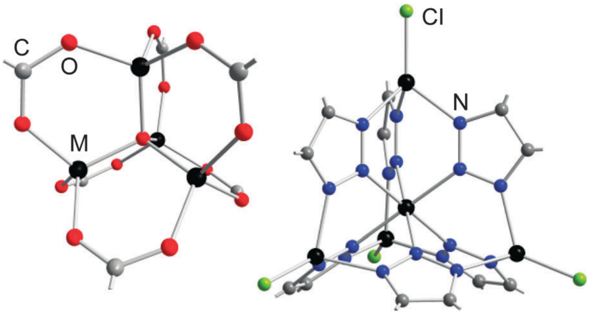

Fig. 1 Secondary building units of MOF-5 (left) and MFU-4*l* (right). Metal, chlorine, oxygen, nitrogen, and carbon atoms are depicted as black, green, red, blue, and grey spheres, respectively.

In a manner analogous to the work of Sherry,[18,19] the free energy for the exchange of Ni^{2+} in MOF-5, $\Delta G_{\mathrm{P,T}}$, of $\mathrm{Zn_{MOF}}^{2+} + \mathrm{Ni_{solution}}^{2+} \rightarrow \mathrm{Zn_{solution}}^{2+} + \mathrm{Ni_{MOF}}^{2+}$, is given by the following relation:

$$\Delta G_{\mathrm{P,T}} = -RT\ln K_{\mathrm{eq}} + RT\ln\frac{f_{\mathrm{Ni}}{}^{2} Z_{\mathrm{Ni}}{}^{2} \gamma_{\mathrm{Zn}}{}^{2} m_{\mathrm{Zn}}{}^{2}}{f_{\mathrm{Zn}}{}^{2} Z_{\mathrm{Zn}}{}^{2} \gamma_{\mathrm{Ni}}{}^{2} m_{\mathrm{Ni}}{}^{2}} \qquad (1)$$

Here, f and Z represent the activity coefficients and the molar fractions, respectively, of a given metal ion in MOF-5. Similarly, γ and m represent the mean activity coefficients and molalities, respectively, of the metal ions in solution. In all cases considered here, all terms are squared as a consequence of all ions involved being divalent.

To reach equilibrium conditions, we left MOF-5 suspended in *N*,*N*-dimethylformamide (DMF) solutions of $Ni(NO_3)_2{\cdot}6H_2O$ for 62 days (2 months) at constant temperatures of 238, 265, 296, and 313 K. During this time, the temperature was checked twice a day and was found to vary by less than 2 °C. Because the determination of accurate values for K_{eq} requires a knowledge of all of the terms in eqn (1), we employed an approximation as follows. The moles of Ni^{2+} ions inserted into MOF-5 were calculated from relative Zn/Ni ratios determined using inductively coupled plasma atomic emission spectroscopy. The activity coefficients and mean activity coefficients were assumed to be the same,

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and were therefore cancelled out. Assuming that each inserted Ni^{2+} displaces a Zn^{2+} from MOF-5 into solution, we employed the relation in eqn (2) to approximate K_{eq}.

$$K_{eq} = \frac{{Z_{Ni}}^2 {S_{Zn}}^2}{{Z_{Zn}}^2 {S_{Ni}}^2} \qquad (2)$$

Here, Z_{Ni} and Z_{Zn} represent the molar fraction of Ni and Zn ions among all metal ions in MOF-5. Similarly, S_{Ni} and S_{Zn} represent the molar fraction of Ni and Zn ions among all metal ions in solution.

Assuming that the system reached equilibrium, and using $\Delta G^\circ_{P,T} = -RT\ln K_{eq} = \Delta H - T\Delta S$, a plot of $\ln K_{eq}$ *vs.* $1/T$ yields approximate thermodynamic parameters. As shown in Fig. 2, the data for Ni^{2+} exchange into MOF-5 yield $\Delta G^\circ_{1atm,238K} = 12.9\ \text{kcal mol}^{-1}$, $\Delta G^\circ_{1atm,281K} = 13.9\ \text{kcal mol}^{-1}$, $\Delta G^\circ_{1atm,296K} = 11.3\ \text{kcal mol}^{-1}$, and $\Delta G^\circ_{1atm,313K} = 10.7\ \text{kcal mol}^{-1}$. The slope and y intercept of the resulting line imply that ΔH = 19.2 kcal mol^{-1} and ΔS = 24.7 cal mol^{-1} K^{-1}. Hence, entropy increases in the replacement of Zn^{2+} by Ni^{2+}, but the exchange is endothermic to yield an overall endergonic process. One explanation for $\Delta S > 0$ is that Ni^{2+} exchange into MOF-5 releases Zn^{2+} ions into the solution, freeing them to perform cation exchange with either Zn^{2+} or Ni^{2+} in the material. Prior to Zn^{2+} displacement from the material, no Zn^{2+} ions exist in the solution to undergo cation exchange, creating a state with fewer degrees of freedom, and hence less entropy. For the process to be endothermic, the Ni-exchanged material or the solvated Zn^{2+} species must be enthalpically unfavorable compared to the initial species. Knowing that the hydration energy of Zn^{2+} is considerably less than that of Ni^{2+}, due to its ligand field stabilization energy of zero,[20] the solvation of Zn^{2+} is the likely culprit. The relatively low absolute free energy values suggest, however, that this exchange is essentially thermoneutral, such that a large excess of inserting Ni^{2+} drives cation exchange in accordance with Le Chatelier's principle.[21]

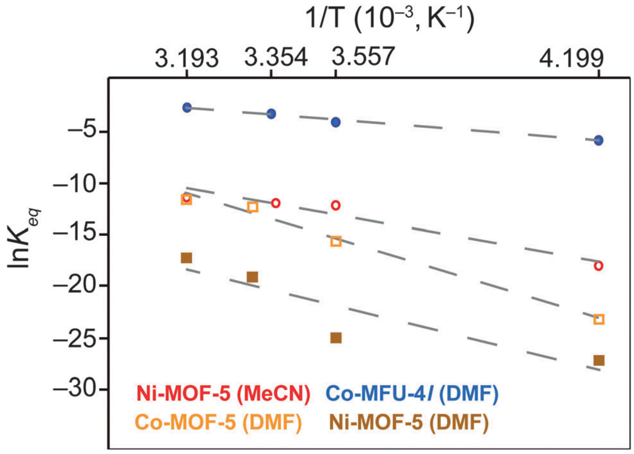

Fig. 2 $\ln K_{eq}$ *versus* $1/T$ for the K_{eq} values that were measured from the four different cation exchange reactions, as denoted by colour. Dashed grey lines denote the best-fit lines used to extract thermodynamic parameters shown in Table 1.

To explore the dependence of the thermodynamic parameters on the nature of the solvent, we repeated the procedure above for Ni^{2+} exchange in MOF-5 using acetonitrile (MeCN) under otherwise identical conditions. Using similar approximations and data analysis as before revealed enthalpy and entropy values of ΔH = 13.8 kcal mol^{-1} and ΔS = 23.0 cal mol^{-1} K^{-1}, respectively. These results suggest that in acetonitrile the exchange is less endothermic and makes available fewer degrees of freedom with respect to the same cation exchange performed in DMF. The small difference in ΔS might be caused by the inherent uncertainty of the measurements, but the large difference in ΔH might be explained by the relative stability of the solvated Ni^{2+} precursors. Based on calculations we reported previously,[3] the Ni–MeCN interaction is weaker than that of Ni–DMF so that the resulting ΔH for the exchange performed in MeCN is expected to be smaller than when performed in DMF. Meanwhile, the difference in energy between $Zn(MeCN)_6{}^{2+}$ and $Zn(DMF)_6{}^{2+}$ is likely less significant due to the negligible ligand field stabilization energy of Zn^{2+}.

Driven by these interesting results, we extended our method to study Co^{2+} exchange in MOF-5 and MFU-4*l* (Fig. 1) to examine the effect of cation and MOF identity. Using $Co(NO_3)_2 \cdot 6H_2O$ as the precursor for exchange, we obtained thermodynamic parameters of ΔH = 23.8 kcal mol^{-1} and ΔS = 54.2 cal mol^{-1} K^{-1} for MOF-5 and ΔH = 6.28 kcal mol^{-1}, ΔS = 14.6 cal mol^{-1} K^{-1} for MFU-4*l*. The thermodynamic parameters of all systems discussed here are summarized in Table 1. Although the enthalpies of exchange for Co^{2+} and Ni^{2+} substituting Zn^{2+} into MOF-5 are similar, the exchange entropy is significantly more positive for Co^{2+} when compared to Ni^{2+}. A possible explanation is that the resulting Co^{2+} center in MOF-5 is capable of releasing its bound DMF ligands into solution, whereas Ni^{2+} is more likely to remain in pseudo-O_h symmetry. The Zn^{2+} sites of the starting material may also bind and release DMF molecules, but, as proposed above, only in the final state are both Zn^{2+} and Co^{2+} or Ni^{2+} available in the solution to exchange with metal sites in the material, leading to higher entropy. Altering the MOF system offers interesting comparisons as well. The more covalent bonding provided by the nitrogen environment of MFU-4*l* may explain why Co^{2+} insertion is less endothermic in this material than in MOF-5. In other words, the favorable formation of the Co^{2+}-doped material may counterbalance the less favorable solvation of Zn^{2+}. The smaller ΔS is more puzzling. One possibility is that the coordination sphere around Co^{2+} is less disordered when in MFU-4*l* compared to the disorder imposed by Co^{2+} insertion into MOF-5.

Although the values listed in Table 1 are approximations of the thermodynamic parameters, comparing their relative magnitudes offers useful mechanistic insight. We glean from

Table 1 The enthalpy and entropy parameters extracted from the best-fit lines shown in Fig. 2. The cation exchange systems are labelled according to the solvent involved, shown in parentheses

	ΔH (kcal mol^{-1})	ΔS (cal mol^{-1} T^{-1})
Ni-MOF-5 (DMF)	19.2	24.7
Ni-MOF-5 (MeCN)	13.8	23.0
Co-MOF-5 (DMF)	23.8	54.2
Co-MFU-4*l* (DMF)	6.28	14.6

these data that solvent and cation identity do influence the equilibrium conditions of cation exchange in a given MOF-system and that the thermodynamics alter considerably between MOFs. Despite these differences, all data suggest that the processes are endergonic, requiring a large excess of inserting cation to drive the cation exchange. Prior to this report, qualitative observations intimated these findings. Using this simple method, we have a quantitative measure of systematic differences between cation exchange in MOFs.

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