



# Freundlich interpretation of pH control and ion specificity in zeolite cation exchange

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## Abstract

Zeolites are microporous metal aluminosilicates widely used to remove heavy metal cations from contaminated waters through ion exchange. Experimental observations have shown that the cation exchange capacities of zeolites can be well described by the Freundlich isotherm with fitting parameters regulated by solution pH and ion specificity; however, quantitative relationships have not been established, indicating a lack of understanding for the underlying mechanisms of zeolite cation exchange. Here, we present a novel physical model to relate proton concentration and ion energetics to the Freundlich parameters and thus elucidate the underlying mechanisms of pH control and ion specificity. The physical model is developed by considering capillarity in zeolite cation exchange, instead of the homogeneous equilibrium that has previously used to understand cation exchange, which leads to the Freundlich isotherm, instead of the Langmuir isotherm often used in data analysis. Using the Freundlich power and equilibrium constant, we further show that the pH dependence of cation exchange capacity can be quantitatively explained by the change of proton chemical potential. At pH 7 under which proton does not significantly affect the cation exchange, the comparison of Freundlich power and equilibrium constant among different metal cations reveals grouping according to their electronic structures.

**Keywords** Thermodynamics · Equilibrium · Isotherm · Adsorption · Enthalpy

## 1 Introduction

Zeolites are microporous metal aluminosilicates that are widely used to remove heavy metal cations such as lead ( $\text{Pb}^{2+}$ ), cadmium ( $\text{Cd}^{2+}$ ), zinc ( $\text{Zn}^{2+}$ ), copper ( $\text{Cu}^{2+}$ ), nickel ( $\text{Ni}^{2+}$ ), cobalt ( $\text{Co}^{2+}$ ), and manganese ( $\text{Mn}^{2+}$ ) from contaminated waters through ion exchange [1, 2]. The high cation exchange capacities of zeolites are results of their unique structures. Zeolites are made of negatively charged frameworks of aluminate and silicate tetrahedral units, forming micropores to accommodate charge-balancing structural cations such as sodium ( $\text{Na}^+$ ), potassium ( $\text{K}^+$ ), magnesium ( $\text{Mg}^{2+}$ ), and calcium ( $\text{Ca}^{2+}$ ) [3]. The separation of structural cations from the frameworks, together with the presence of water molecules in micropores, provides mobility to the

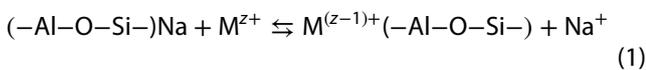
structural cations, which can be exchanged by metal cations with higher atomic weights and present in an aqueous solution [4]. Among the structural cations, monovalent sodium ions are often located in large micropores and thus can be readily exchanged [5]. The physical and chemical factors, as well as the underlying mechanisms, that control the cation exchange capacity of zeolite are still not well understood.

The cation exchange capacity of zeolite,  $q$ , can be defined for a heavy metal as the maximal amount of its cation that a unit mass of zeolite can exchange for at a specific metal concentration in the aqueous solution,  $c$ , and a given temperature,  $T$  [6]. The exchange is often considered as an equilibrium of the metal (M) cation and

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the sodium cation between two homogeneous phases, namely the zeolite and the solution [7–13]:



where  $-\text{Al}-\text{O}-\text{Si}-$  is a cation site created by adjacent aluminate/silicate tetrahedra in the framework and  $z$  is the number of charges per cation. Reaction 1 suggests that  $q$  and  $c$  should conform to the Langmuir isotherm [14]. Values of  $q$  measured at different conditions of  $c$ , however, often shows evident deviations from the Langmuir isotherm. More importantly,  $q$  is known to be influenced by pH due to the competition of proton, which cannot be explained by the Langmuir isotherm [15].

In addition to the control by pH, the exchange capacity is also known to increase generally with the increase of atomic weight of the cation, indicating an effect of ion specificity. The ion specificity is particularly important for the selective separation of multiple cations that are simultaneously present in an aqueous solution. The cation exchange capacity of clinoptilolite, a monoclinic natural zeolite, has been measured for many divalent cations. The maximal capacity modeled using the Langmuir model has been compared to a variety of cation properties, including ionic radius, electronegativity, ionization potential, dehydration energy, and ion mobility [15]. Little success has, however, been made through the comparison to provide a mechanistic explanation of ion specificity. The lack of success indicates that critical factors are missing in the current model developed to explain the cation exchange in zeolites.

Here, we present a novel physical model to elucidate the underlying mechanism for zeolite cation exchange. This model is developed by considering the capillary effect of interfacial tension between the aluminosilicate framework and water in micropores. We show that the isothermal relationships of  $q$  and  $c$  under the new physical model conform to the Freundlich isotherm [16, 17]:

$$q = K_F c^{1/n} \quad (2)$$

where  $n$  and  $K_F$  are the inverse of power and the equilibrium constant. Although the Freundlich isotherm is often considered to be empirical, it has been successfully used to describe not only the ion exchange of zeolites but also the adsorption of activated carbon, soils, and sediments [18]. We further show that the pH control and the ion specificity can be explained by the influence of proton concentration and cation-framework interaction on the interfacial enthalpy. These results provide new insights to understand zeolite cation exchange through new quantitative structure–activity relationships.

## 2 Results and discussion

Our results are presented and discussed in eight parts, which can be divided into two groups. In the first group of results, we focus on the theoretical development of the physical model for zeolite cation exchange by considering (1) capillarity at the framework–water interface, (2) equation of state for the interface, (3) Gibbs equation for adsorption, and (4) Gibbsian derivation of the Freundlich isotherm. In the second group, we present predictions of the physical model, which are then validated using experimentally measured values of  $q$  and  $c$  reported in the literature. The tested predictions include relationships of (1)  $q$  and  $c$  to the Freundlich isotherm, (2) pH and the inverse of power  $n$ , (3) pH and the equilibrium constant, and (4) ion specificity at pH 7.

### 2.1 Capillarity at the interface

According to the Gibbsian thermodynamics [19, 20], the internal energy of a system isolated from all external influences can only be varied by the absorption of heat, the reception of work, and the addition of matter. Applying this principle to the framework–water interface gives:

$$\partial U = T \partial S + \gamma \partial A + \sum \mu_i \partial m_i \quad (3)$$

where  $U$  is the internal energy,  $T$  is the absolute temperature,  $S$  is the interfacial entropy,  $\gamma$  is the interfacial tension,  $A$  is the interfacial area,  $\mu$  is the chemical potential,  $m$  is the number of moles of an interfacial constituent, and subscript  $i$  enumerates interfacial constituents, including the metal cation ( $i = \text{null}$ ), the structural cation ( $i = \text{Na}$ ), and proton ( $i = \text{H}$ ). Applying the thermodynamics to the aluminosilicate framework ( $\alpha$ ) in the absence of matter exchange, we obtain:

$$\partial U^\alpha = T^\alpha \partial S^\alpha - P^\alpha \partial V^\alpha \quad (4)$$

Similarly, we obtain:

$$\partial U^\beta = T^\beta \partial S^\beta - P^\beta \partial V^\beta + \sum \mu_i^\beta \partial m_i^\beta \quad (5)$$

where  $\mu^\beta$  is the chemical potential of  $i$  in the aqueous solution ( $\beta$ ).

According to the conservation of energy, the total internal energy ceases to change at equilibrium:

$$\partial U + \sum \partial U^j = 0 \quad (6)$$

where  $j = \alpha$  or  $\beta$ . Similarly, the conservation of entropy, volume, and matter between the phases and the interface require:

$$\sum \partial s^j = 0 \quad (7)$$

$$\sum \partial v^j = 0 \quad (8)$$

$$\sum \partial m_i^j = 0 \quad (9)$$

Taking Eqs. 4–5 into Eq. 6 and applying the conditions of Eqs. 7–9, we obtain:

$$T = T^\alpha = T^\beta \quad (10)$$

$$\gamma = (p^\alpha - p^\beta) \frac{\partial V^\alpha}{\partial A} \quad (11)$$

$$\mu_i = \mu_i^\beta \quad (12)$$

Equations 10–12 can be understood as the thermal, mechanical, and chemical balances between the two homogeneous phases and their interface.

## 2.2 Equation of state for the interface

Equation 4 can be further developed to obtain the equation of state for the interface. As a reasonable assumption, the interfacial entropy has addable contributions from all constituents, similar to the chemical potential:

$$\partial S = \sum s_i \partial m_i \quad (13)$$

where  $s_i$  is the molar entropy of  $i$ . Combining Eqs. 4 and 13, we obtain:

$$\gamma = \gamma_0 - \sum h_i \Gamma_i \quad (14)$$

where

$$h_i = Ts_i + \mu_i \quad (15)$$

is the interfacial enthalpy of  $i$ ,

$$\gamma_0 = \frac{\partial U}{\partial A} \quad (16)$$

is an initial interfacial tension, and

$$\Gamma_i = \frac{\partial m_i}{\partial A} \quad (17)$$

is the interfacial density of  $i$ .

Equation 14 indicates that the interfacial tension can be reduced by replacing a constituent having a low enthalpy with another having a high enthalpy. At the equilibrium, we can assume that proton and the sodium cation are always at equilibrium, which is not varied by

their exchange with the metal cation. The lack of exchange between proton and the sodium cation requires:

$$h_{\text{Na}} = h_{\text{H}} \quad (18)$$

In addition, the charge neutrality requires:

$$z \partial \Gamma + z_{\text{H}} \partial \Gamma_{\text{H}} + z_{\text{Na}} \partial \Gamma_{\text{Na}} = 0 \quad (19)$$

Taking Eqs. 18 and 19 into Eq. 14 with  $z_{\text{H}} = z_{\text{Na}}$ , we obtain:

$$\gamma = \gamma_0 - \Delta h \Gamma \quad (20)$$

where the change of interfacial enthalpy is:

$$\Delta h = h - \frac{z}{z_{\text{H}}} h_{\text{H}} \quad (21)$$

Equation 20 is an equation of state for the interface. It indicates that the cation exchange is driven by the reduction of interfacial tension, which is commonly observed for the adsorption of surfactants to the liquid–gas interface [21–23].

## 2.3 Gibbs equation for adsorption

The declaration of Eq. 4 in the Gibbsian thermodynamics indicates that the remaining derivatives from the complete differentiation of  $U$  should have a sum of zero:

$$S \partial T + A \partial \gamma + \sum m_i \partial \mu_i = 0 \quad (22)$$

This is the two-dimensional equivalent of the Gibbs–Duhem equation, which can be obtained from the sum of the remaining derivatives of the complete differentiation of  $U^\beta$  [24]. By considering the isothermal condition of  $\partial T = 0$ , we simplify Eq. 22 as:

$$\partial \gamma = - \sum \Gamma_i \partial \mu_i \quad (23)$$

where

$$\Gamma_i = \frac{m_i}{A} \quad (24)$$

Equations 24 and 17 are both valid under the condition that  $\Gamma_i$  is independent of  $A$ .

For the metal cation, the structural cation, and proton, the change of interfacial chemical potential equals to the change of solution chemical potential according to Eq. 12:

$$\partial \mu_i = \partial \mu_i^\beta \quad (25)$$

By considering the solution as an ideal mixture, we have:

$$\mu_i^\beta = \mu_i^\ominus + RT \ln \frac{c_i}{c_i^\ominus} \tag{26}$$

where  $R$  is the gas constant,  $T$  is the absolute temperature, and the Plimsoll symbol denotes the reference state of a pure phase for constituent  $i$ . Differentiating Eq. 26, we obtain:

$$\partial \mu_i^\beta = RT \frac{\partial c_i}{c_i} \tag{27}$$

Since the pH remains constant in the cation exchange experiments, we have  $\partial c_H = 0$  gives  $\partial \mu_H = 0$ . The chemical potential of sodium cation is usually below the concentration required to maintain the chemical balance, indicating that  $\partial \mu_{Na} = 0$ . Taking  $\partial \mu_w = \partial \mu_H = \partial \mu_{Na} = 0$  into Eq. 23, we obtain the Gibbs equation for adsorption:

$$\partial \gamma = -\Gamma \partial \mu \tag{28}$$

which indicates that the interfacial tension can be reduced by the increase of chemical potential of the metal cation as its solution concentration increases.

### 2.4 Gibbsian derivation of Freundlich isotherm

The Freundlich isotherm is obtained by differentiating Eq. 14 and combining the result of differentiation with Eq. 28:

$$\partial \mu = \Delta h \frac{\partial \Gamma}{\Gamma} \tag{29}$$

By considering that  $\Delta h$  is independent of  $\Gamma$ , we integrate Eq. 29 from the reference state to the state of equilibrium:

$$\int_{\mu^\ominus}^{\mu} \mu = \Delta h \int_{\Gamma^\ominus}^{\Gamma} \frac{\partial \Gamma}{\Gamma} \tag{30}$$

and obtain:

$$\mu = \mu^\ominus + \Delta h \ln \frac{\Gamma}{\Gamma^\ominus} \tag{31}$$

According to Eq. 25, proton has the same chemical potential at the interface and in the solution at equilibrium. The equality of Eqs. 26 and 31 gives:

$$\ln \frac{\Gamma}{\Gamma^\ominus} = \frac{RT}{\Delta h} \ln \frac{c}{c^\ominus} \tag{32}$$

Provided that  $\phi$  is the specific interfacial area of zeolite responsible for cation exchange with a unit of  $m^2 g^{-1}$ ,  $\Gamma$  is converted to the proton exchange capacity normally expressed in  $mmol g^{-1}$ :

$$q = \Gamma \phi \tag{33}$$

Taking Eq. 33 into Eq. 32, we obtain:

$$\ln \frac{q}{q^\ominus} = \frac{RT}{\Delta h} \ln \frac{c}{c^\ominus} \tag{34}$$

where  $q^\ominus$  is the exchange capacity for the metal cation at the reference state. The comparison of Eq. 34 to Eq. 3 shows that:

$$n = \frac{\Delta h}{RT} \tag{35}$$

And

$$K_F = \frac{q^\ominus}{(c^\ominus)^{1/n}} \tag{36}$$

With  $n > 0$  and thus  $\Delta h > 0$ , Eq. 35 is consistent with the understanding that the cation exchange is exothermic [25]. Equation 36 indicates that  $K_F$  are correlated with  $1/n$ , instead of being independent.

### 2.5 Regression to the Freundlich isotherm

The Freundlich isotherm shown in Eq. 2 suggests that the logarithm of cation exchange capacity is linearly correlated to the logarithm of the corresponding concentration:

$$\ln q = \frac{1}{n} \ln c + \ln K_F \tag{37}$$

The Freundlich linearity between  $\ln q$  and  $\ln c$  is illustrated in Fig. 1 for the exchange of manganese cations

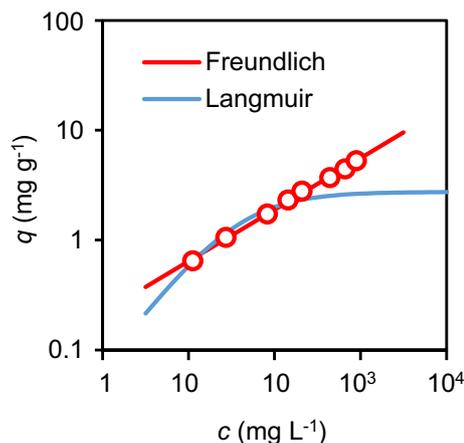


Fig. 1 Isothermal relationship of the exchange capacity ( $q$ ) of clinoptilolite for the manganese cation ( $Mn^{2+}$ ) with the solution concentration of manganese ( $c$ ) at 25 °C. Coefficients of determination ( $R^2$ ): Langmuir, 0.96; Freundlich, 0.99. Data source: Mihaly-Cozmuta et al. [15]

in clinoptilolite [15]. Regression of experimental data to Eq. 37 provides estimates for  $n$  and  $K_F$ . In comparison, regression to the Langmuir isotherm does not provide a satisfactory description of the experimental data. Similar results can be shown for cobalt, zinc, nickel, copper, cadmium, and lead [15].

## 2.6 pH and the inverse of power

The inverse of power is expected to depend on the solution pH according to Eqs. 15, 21, and 35. By combining these equations, we obtain:

$$n = \frac{Ts + \mu}{RT} - \frac{z}{z_H} \frac{Ts_H + \mu_H}{RT} \quad (38)$$

As the first approximation, we assume that the energy associated with entropy is proportional to the chemical potential:

$$Ts_i = (\chi_i - 1)\mu_i \quad (39)$$

where  $\chi_i$  is the ratio between specific enthalpy and chemical potential. Taking Eq. 39 into Eq. 38, we obtain:

$$n = \frac{\chi\mu}{RT} - \frac{z}{z_H} \frac{\chi_H\mu_H}{RT} \quad (40)$$

Using the chemical potential in the solution as a surrogate for the interfacial chemical potential according to Eq. 26, we further obtain:

$$n = \frac{z}{z_H} \frac{\chi_H}{\log(e)} \text{pH} + n_0 \quad (41)$$

where

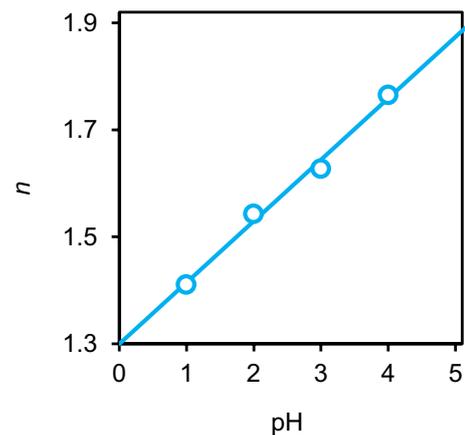
$$\text{pH} = -\log c_H \quad (42)$$

And

$$n_0 = \chi \left( \frac{\mu^\ominus}{RT} + \ln \frac{c}{c^\ominus} \right) - \frac{z}{z_H} \chi_H \left( \frac{\mu_H^\ominus}{RT} + \ln \frac{1}{c_H^\ominus} \right) \quad (43)$$

When  $\ln(c/c^\ominus)$  is negligible compared the other terms in Eq. 43, Eq. 41 predicts a linear correlation between  $n$  and pH.

Figure 2 shows the linearity between  $n$  and pH for the exchange for  $\text{Mn}^{2+}$  in clinoptilolite [15], as predicted by Eq. 41 [26]. The least-square regression gives estimates of  $\chi = 0.025(\pm 0.002)$  and  $n_0 = 1.30(\pm 0.02)$  (standard deviations in parentheses). The positive slope of  $\chi$  indicates that  $n$  increases with the increase of pH, consistent with the reduction of proton enthalpy.  $n_0$  is the value of  $n$  at pH 0.



**Fig. 2** Dependence of the inverse of power ( $n$ ) on pH for the exchange of the manganese cation ( $\text{Mn}^{2+}$ ) in clinoptilolite at 25 °C. The line is a least-square fit with a coefficient of determination of  $R^2 = 0.99$ . Data source: Mihaly-Cozmuta et al. [15]

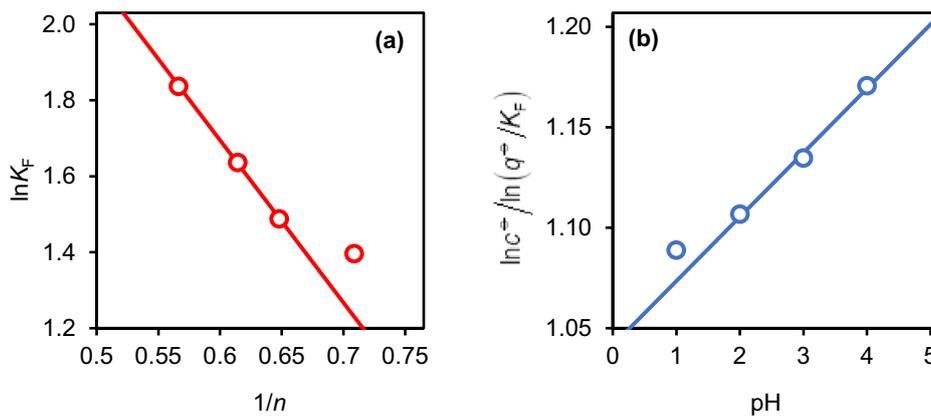
## 2.7 pH and the equilibrium constant

The Gibbsian interpretation of equilibrium constant  $K_F$ , as shown in Eq. 36, reveals that  $K_F$  correlates with power  $1/n$  through the exchange capacity and the solution concentration at the reference state. Rearranging Eq. 36, we obtain:

$$\ln K_F = \ln q^\ominus - \frac{1}{n} \ln c^\ominus \quad (44)$$

The negative correlation of  $\ln K_F$  and  $1/n$  indicates that for  $\ln c^\ominus > 0$ ,  $K_F$  cancels part of the effect of  $1/n$  on the exchange capacity. According to Eq. 3, an increase of  $1/n$  (i.e., decrease of  $n$ ) increases  $q$  for any given concentration  $c$  if  $K_F$  were kept constant. Since  $K_F$  decreases as  $1/n$  increases, the increase of  $q$  due to the increase of  $1/n$  is reduced by the simultaneous decrease of  $K_F$ , revealing a compensation effect. The compensation between  $K_F$  and  $1/n$  has been previously proposed for the adsorption of organic compounds by activated carbon and soils [27].

Figure 3a shows that for the exchange of  $\text{Mn}^{2+}$  in clinoptilolite,  $\ln K_F$  and  $1/n$  have a linear correlation, as predicted by Eq. 44, for  $\text{pH} > 1$ . This indicates that the three sets of  $\ln K_F$  and  $1/n$  share the same set of  $q^\ominus$  and  $c^\ominus$  whereas the reference-state capacity and corresponding concentration changes at pH 1, likely due the oversaturation of proton that has invalidated the chemical equilibrium for proton. Using the least-square regression, we obtain  $\ln q^\ominus = 4.27(\pm 0.06)$  and  $\ln c^\ominus = 4.28(\pm 0.09)$ , where  $q^\ominus$  and  $c^\ominus$  have units of  $\text{mg g}^{-1}$  and  $\text{mg L}^{-1}$ . Taking Eq. 44 into Eq. 41, we further obtain:



**Fig. 3** Linear correlations for the equilibrium constant ( $K_F$ ;  $\text{mg}^{1-1/n} \text{L g}^{-1}$ ). **a** The linearity between  $\ln K_F$  and  $1/n$ , as predicted by Eq. 44. **b** The linearity between the function of  $K_F$ , the reference-state capacity ( $q^\ominus$ ), and the corresponding concentration ( $c^\ominus$ ) with pH, as pre-

dicted by Eq. 45. Line are the least-square fits to three data points near the lines with coefficients of determination of  $R^2=0.99$ . Original data source: Mihaly-Cozmuta et al. [15]

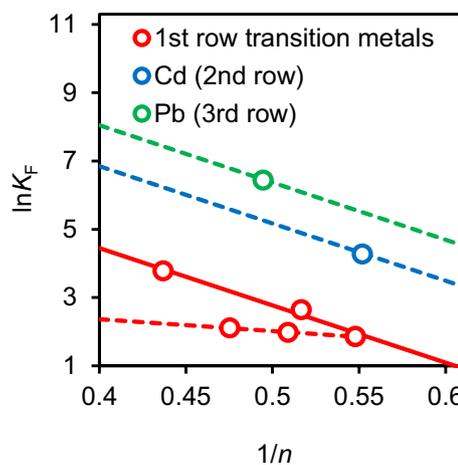
$$\frac{\ln c^\ominus}{\ln(q^\ominus/K_F)} = \frac{z}{z_H} \frac{\chi_H}{\log(e)} \text{pH} + n_0 \tag{45}$$

The linear correlation between  $\ln c^\ominus / \ln(q^\ominus / K_F)$  and pH is shown in Fig. 3b for the exchange of manganese in clinoptilolite between pH=2 and 4.

### 2.8 Ion specificity at pH 7

We analyze the ion specificity of zeolite cation exchange by considering the inverse of power and the equilibrium constant at pH 7, under which the influence of proton on the cation exchange is minimized. The values of  $1/n$  and  $K_F$  values at pH are estimated using their experimental values at pH=1–4 according to Eqs. 41 and 44.

Figure 4 compares the values of  $1/n$  and  $\ln K_F$  at pH 7 for manganese, cobalt, zinc, nickel, manganese, copper, cadmium, and lead [15]. The metal cations are separated according to their positions in the periodic table. The first row transition metals including manganese, cobalt, zinc, nickel, manganese, and copper (red circles) are aggregated at the bottom of the figure, below both cadmium (blue), a second-row transition metal, and lead (green), which is located another row below cadmium. The position-based separation indicates that the ion specificity is a result of cation electronic structure. The first row transition metals can be further divided into two groups. The first group include copper, zinc, and nickel, which share the same set of  $q^\ominus$  and  $c^\ominus$  values (solid red line). The second group include manganese, cobalt, and nickel, which share a different set of  $q^\ominus$  and  $c^\ominus$  values (dash red line). The  $n$  values of the first group are ranked as:  $\text{Cu}^{2+} > \text{Zn}^{2+} > \text{Ni}^{2+}$ , consistent with the



**Fig. 4** Linear correlation between the logarithm of equilibrium constant ( $K_F$ ;  $\text{mg}^{1-1/n} \text{L g}^{-1}$ ) and the Freundlich power ( $1/n$ ) at pH 7 for the exchange of divalent cations in clinoptilolite at 25 °C. Colors: red, the first row transition metals (from left to right: copper, manganese, cobalt, zinc, and nickel); blue, the second row transition metal cadmium; green, lead in the same row as the third row transition metals. Red lines: solid, correlation for copper, zinc, and nickel with a coefficient of determination of  $R^2=0.98$ ; dash, correlation of manganese, cobalt, and nickel with  $R^2=0.99$ . The blue and green lines are transpositions of the solid red line that go through the data points for cadmium and lead, respectively. Original data source: Mihaly-Cozmuta et al. [15]

Irving-Williams series for ligand complexation [28, 29]. In comparison, the  $n$  values of the second group are ranked as:  $\text{Ni}^{2+} < \text{Co}^{2+} < \text{Mn}^{2+}$ , which is the opposite of the Irving-Williams series. The difference between the two rankings may require further explanation through molecular orbital theories.

### 3 Conclusions

We have shown here that the consideration of capillarity in zeolite cation exchange leads to the Freundlich isotherm, instead of the Langmuir isotherm often used in data analysis. Using the Freundlich power and equilibrium constant, we further show that the pH dependence of cation exchange capacity can be quantitatively explained by the change of proton chemical potential. At pH 7 under which proton does not significantly affect the cation exchange, the comparison of Freundlich power and equilibrium constant among different metal cations reveals grouping according to their electronic structures.

The success of the Freundlich isotherm in describing the pH control and the ion specificity indicates that the cation exchange in porous materials such as zeolites is predominantly regulated by the capillary effect of interfacial tension. The interfacial tension is a physical property of liquids such as water and thus is not considered in the development of physical models such as the Langmuir isotherm in the gas phase. The interfacial tension is particularly important for porous materials such as zeolites because the large specific surface areas that these materials have.

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### Compliance with ethical standards

**Conflict of interest** The authors declare that they have no competing interests.

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