# The Interaction of Two Heavy Metal Ions at the Iron (III) Hydroxide/Solution Interface

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Summary: The interaction of the Zn^{2+} and Ni^{2+} ions at the iron (III) hydroxide/solution interface was studied as a function of the constant initial pH and over the metal ion concentration range 1-6 ppm. For each mole of heavy metal ion adsorbed, approximately two moles of H^+ ions were displaced from the interface. These results are used for expressing the adsorption data as a function of the solution concentration of both H^+ and metal ions. The results obtained permit the interfacial reaction to be described by the equation:

$$2SH + M^{2+} = S_2M + 2H^+$$
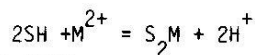
where S represents a surface site.

Introduction

Adsorption of heavy metal ions from aqueous solution onto oxide surfaces is known to be an important process affecting trace metal transport in many natural and engineering systems. Particularly important are the hydrous oxides of iron, an important class of amphoteric inorganic ion exchangers [1], which frequently form a consizable fraction of both temperate and tropical soils.

The present paper deals with the adsorption of Zn^{2+} and Ni^{2+} ions at the ferric hydroxide/aqueous solution interface and takes account of the various factors that must be considered to explain the phenomenon. In addition to the practical aspect, the present study also gives an insight to the complex process of the ion exchange adsorption which occurs at the hydrous oxide/aqueous solution interfaces.

Experimental

Preparation of ferric hydroxide, metal ion solution, background electroiyte solution and the experimental set up for the adsorption studies have been fully given elsewhere[2]. The working solutions, in this case, were in 1-6 ppm concentration range with respect to the metal cations.

For infrared absorption studies, a 10mg sample of ferric hydroxide was thoroughly ground with 0.2ml of Nujol in an agate mortar. The mixture was sandwiched between two KBr plates, and the absorption spectrum was recorded with SP3-100 Pye Unicam infrared spectrophotometer. The same procedure was repeated for ferric hydroxide sample after treating with 6 ppm Zn^{2+} ion solution in 0.1M KCl solution for 24h. The absorption spectra recorded are given in Fig.1.

Discussion

The results of the study are presented in tables (1 and 2). As can be judged, a drop in pH is observed during the adsorption of both the heavy metal ions (Zn^{2+} and Ni^{2+}). The ratio of the moles of H^+ ions released
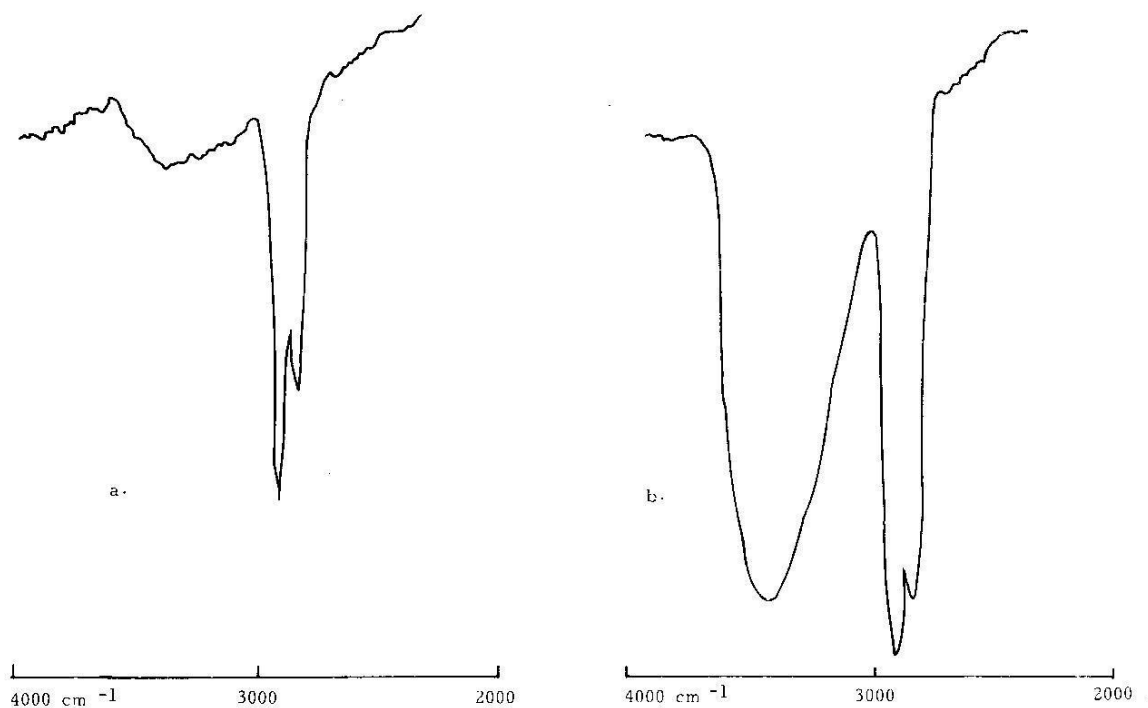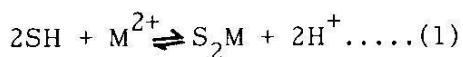
Fig.1: IR Absorption curves of the Ferric Hydroxide. a, after adsorption:-b,before adsorption.

per metal ion adsorbed is close to the values reported in the literature [3-5].

If as an approximation the values of the mole ratio are taken as 2.0, then the interfacial reaction for the adsorption of the divalent cation of Zn or Ni can be described by the reaction:

$$2SH + M^{2+} \rightleftharpoons S_2M + 2H^+ \ldots \ldots (1)$$

where SH is the uncharged adsorption site on the ferric hydroxide surface S_2M is the adsorbed form of the metal ion, M^{2+}, H^+ is the hydrogen ion released.

The fact that significant adsorption of cations occurs on ferric hydroxide even when it possesses a net positive charge indicates:

(a) that there must be a non-electrostatic contribution to the overall free energy of adsorption.

(b) that the adsorption is primarily taking place on neutral sites as implied by reaction 1.

The forces involved in this specific adsorption can be either physical or chemical in nature, though it is impossible to decide between them at the present stage. However, following the suggestion of Peri[6] and the results of tables 1 and 2, the formation of the bidentate surface complexes of the type S_2M by the reaction (1) can be portulated.

These facts are further strengthened by the IR spectra of the ferric hydroxide taken before and after the adsorption (fig.1). The OH absorption band present ($\nu = 3200-3600$ cm^{-1}) before the adsorption is missing after it. This shows the involvement of the surface OH groups in the complexation with the metal ions.

Table-1

| Initial Zn^{2+} concentration (M)	Moles Zn^{2+} ions adsorbed	Moles H^+ ions released	Molar ratio	Final pH
1.53×10^{-5}	6.04×10^{-7}	1.21×10^{-6}	2.01 ± 0.03	2.83 ± 0.02
3.06×10^{-5}	1.19×10^{-6}	2.37×10^{-6}	2.00 ± 0.03	3.13 ± 0.02
4.59×10^{-5}	1.68×10^{-6}	3.35×10^{-6}	1.99 ± 0.03	3.27 ± 0.02
6.12×10^{-5}	2.20×10^{-6}	4.36×10^{-6}	1.98 ± 0.03	3.39 ± 0.02
7.65×10^{-5}	2.68×10^{-6}	5.43×10^{-6}	2.03 ± 0.03	3.48 ± 0.02
9.18×10^{-5}	2.69×10^{-6}	5.69×10^{-6}	2.11 ± 0.03	3.51 ± 0.02

The molar ratio of hydrated protons released to Zn^{2+} ions adsorbed. Initial pH, 7.45 ± 0.04; Temperature, 31 ± 1°C; Ferric hydroxide, 0.2g; Electrolyte, (KCl), 0.1M; Solution volume, 50ml; Equilibration time, 24h.

Table-2

Initial Ni^{2+} concentration (M)	Final pH	Moles Ni^{2+} ions adsorbed	Moles H^+ ions released	Molar ratio
1.53×10^{-5}	2.69 ± 0.02	4.42×10^{-7}	8.68×10^{-7}	1.96 ± 0.02
3.06×10^{-5}	2.98 ± 0.02	8.69×10^{-7}	1.71×10^{-6}	1.97 ± 0.02
4.59×10^{-5}	3.15 ± 0.02	1.24×10^{-6}	2.49×10^{-6}	2.00 ± 0.02
6.12×10^{-5}	3.25 ± 0.02	1.63×10^{-6}	3.14×10^{-6}	1.93 ± 0.02
7.65×10^{-5}	3.34 ± 0.02	1.98×10^{-6}	3.87×10^{-6}	1.96 ± 0.02
9.18×10^{-5}	3.35 ± 0.02	1.99×10^{-6}	3.97×10^{-6}	1.99 ± 0.02

The molar ratio of hydrated protons released to Ni^{2+} ions adsorbed. Initial pH; 7.45 ± 0.04; Temperature, 31 ± 1°C; Ferric hydroxide, 0.2g; Electrolyte, (KCl), 0.1M; Solution volume, 50ml; Equilibration time, 24h.

As for the adsorption of the hydroxo/species ($ZnOH^+$, $NiOH^+$) particularly at high values of pH, the following surface reactions can be assumed in accordance with the data of tables 1 and 2;

$$M^{2+} + H_2 \rightleftharpoons MOH^+ + H^+ \ldots\ldots(2)$$

$$SH + MOH^+ \rightleftharpoons SMOH + H^+ \ldots(3)$$
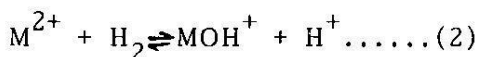
However, assuming that reaction (1) is mainly responsible for the adsorption of the metal ions, the equilibrium constant expression for it is, then;

$$K = \frac{(S_2M)\,(H^+)^2}{(M^{2+})\,(SH)^2} \quad \cdots (4)$$

Following Forbes et al.[5], equation (4) can be rearranged to the form

$$[S_2M]^{\frac{1}{2}} = \frac{K^{\prime}[M^{2+}]^{\frac{1}{2}}}{[H^+]} \quad \ldots\ldots(5)$$

where square brackets indicate concentration terms [μ mole/l for M^{2+} and H^+, and μmole/g for (S_2M)] and

$$K^{\prime} = K^{\frac{1}{2}}\,(SH)$$

By plotting the experimental data in the form $[S_2M]^{\frac{1}{2}}$ vs $[M^{2+}]^{\frac{1}{2}}/[H^+]$, the heavy metal ion adsorption can be expressed as a function of the two solution parameters, $[M^{2+}]$ and $[H^+]$. From these graphs the variation of $K^{\prime}$ with increasing metal ion adsorption can be obtained as is shown in figs.2 and 3. The values of $K^{\prime}$ were calculated from the gradient of the curves at each point.

It is apparent from figs.2 and 3 that for both Zn^{2+} and Ni^{2+} ions a decrease occurs in values of $K^{\prime}$ with the increase in adsorption. To take this into account, $K^{\prime}$ can be expressed as

$$K^{\prime} = K^{\prime}_c e^{-\alpha[S_2M]} \ldots(6)$$

where

$K^{\prime}_c$ is the affinity constant for the metal cation and α is an interaction coefficient.

Then by making proper substitution from equation(6), equation (5) becomes:

$$[S_2M]^{\frac{1}{2}} = \frac{K^{\prime}_c\,e^{-\alpha[S_2M]}[M^{2+}]^{\frac{1}{2}}}{[H^+]} \ldots(7)$$

which in the linear form is:

$$\frac{2.303}{2} \log[S_2M] = 2.303 \log K^{\prime}_c - \alpha[S_2M] + \frac{2.303}{2} \log[M^{2+}]$$

$$-2.303 \log[H^+] \ldots\ldots(8)$$

Rearranging equation (8) gives:

$$pH - \tfrac{1}{2}\,pM - \tfrac{1}{2}\log[S_2M] =$$

$$\frac{\alpha[S_2M]}{2.303} - \log K^{\prime}_c \ldots\ldots(9)$$

Thus by plotting $(pH-\tfrac{1}{2}\,pM-\tfrac{1}{2}\log[S_2M]$ vs $[S_2M]$ (fig.4), values for α and $K^{\prime}_c$ may be obtained from the slopes and intercepts respectively.

The values of α and $K^{\prime}_c$ for the Zn^{2+} and Ni^{2+} ions have been calculated by least square approximation of the best straight line through the points in fig.4, and are given in table 3. It can be seen that the affinity constant ($K^{\prime}_c$) and interaction coefficient (α) are inversely related to each other i.e. the greater the interaction
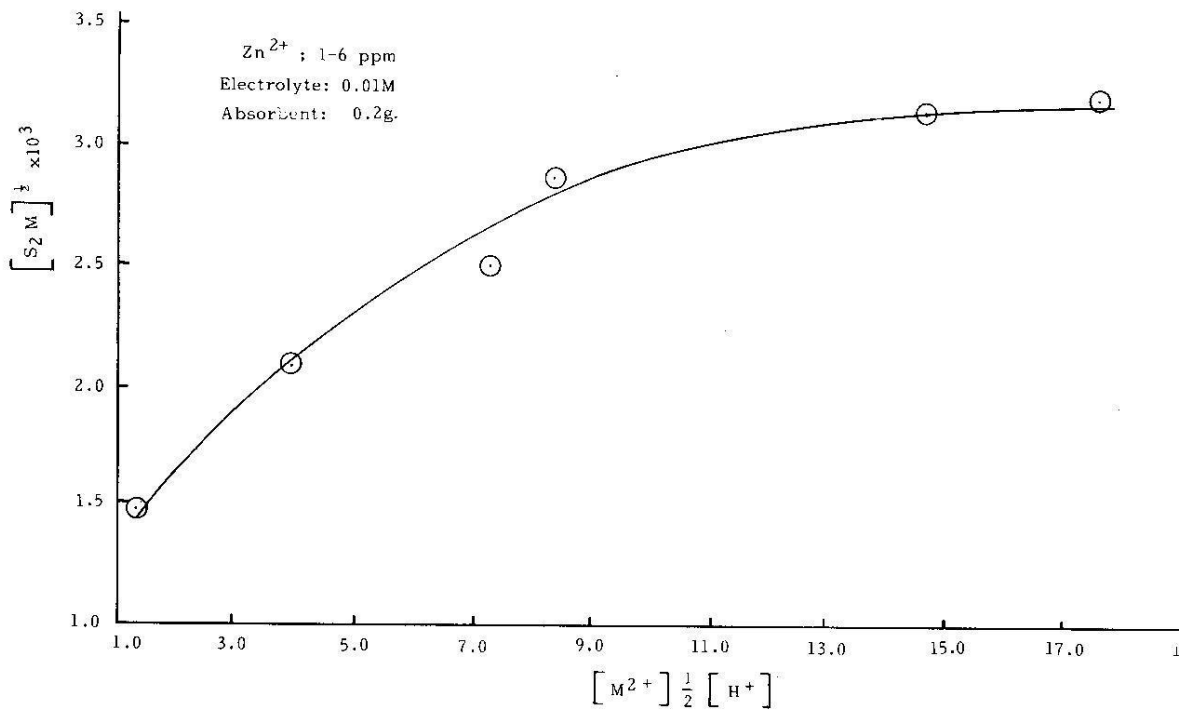
Fig.2: Zn^{2+} adsorption as a function of solution, $[M^{2+}]^{\frac{1}{2}}/[H^{+}]$, and surface $[S_2M]^{\frac{1}{2}}$, concentration.
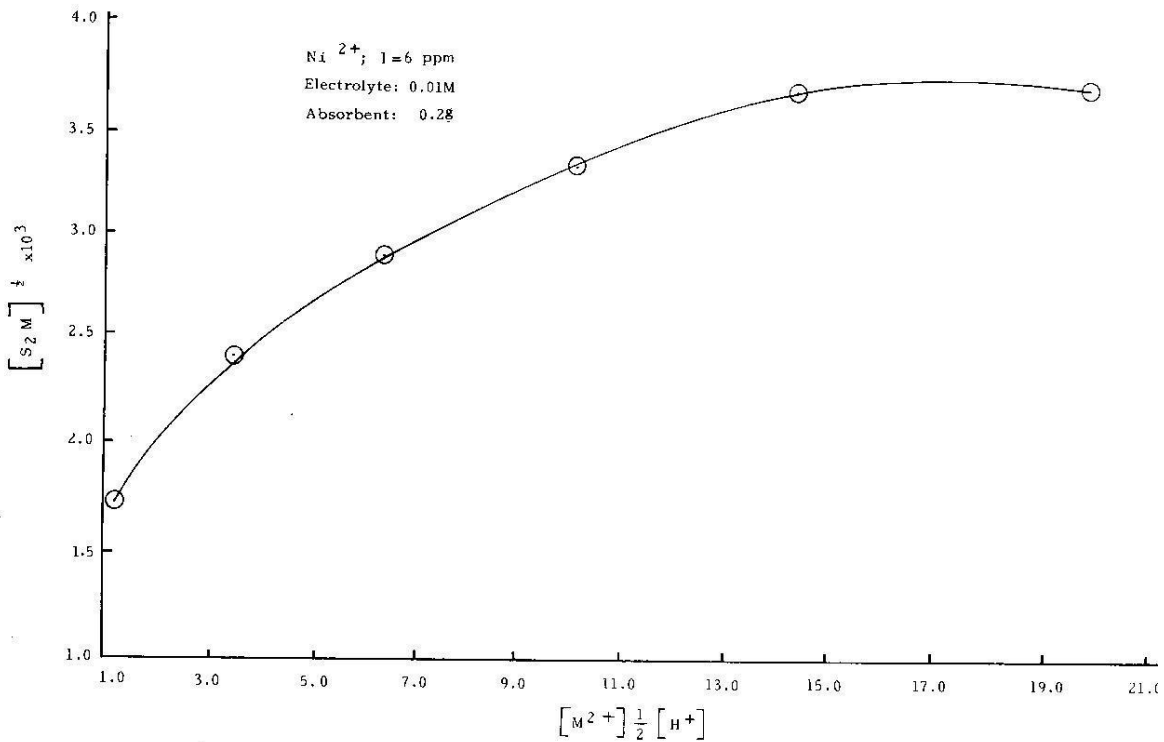

Fig.3: Ni^{2+} adsorption as a function of solution; $[M^{2+}]^{\frac{1}{2}}/[M^{+}]$, and surface, $[S_2M]^{\frac{1}{2}}$, concentration.
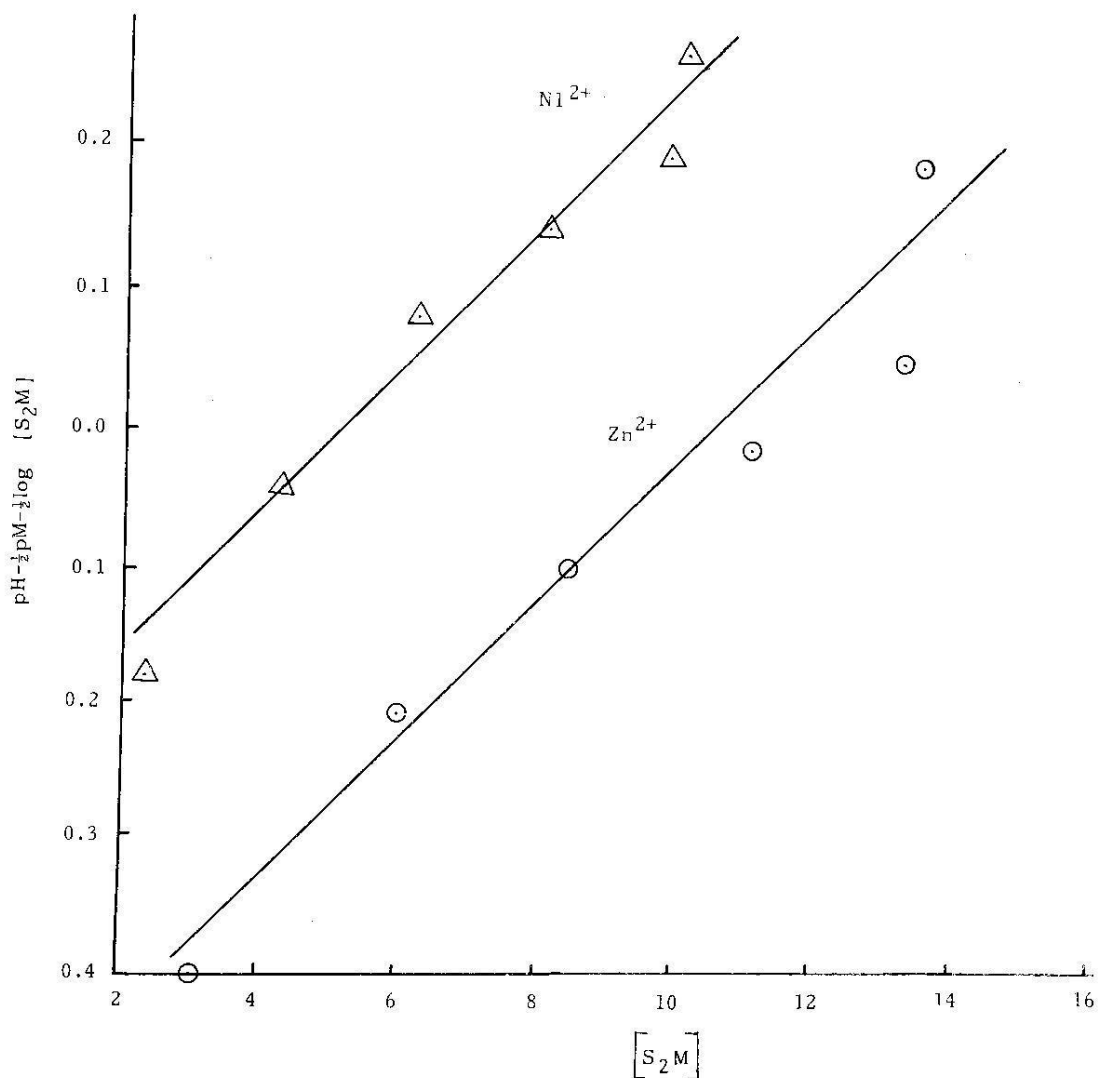
Fig.4: The variation of the function, pH-½ pM-½;log[S_2M], with the surface concent-ration, [S_2M], of heavy metal ions.

Table-3

Constants		Metal Ions	
		Zn^{2+}	Ni^{2+}
	α	0.106	0.117
	K_c	3.298	1.906
	p^{K_h}	9.700	10.600

Various constants for Zn^{2+} and Ni^{2+}; α, Interaction coefficient; K_c, Affinity constant; K_h, Hydrolysis constant.

coefficient the lesser is the affinity and hence the adsorption. It is also clear that the interaction coefficient of Zn^{2+} ion is lower compared to that of the Ni^{2+} ions and thus the affinity order is $Zn^{2+} > Ni^{2+}$.

It is also feasible to compare these results with the first hydrolysis constant of the metal ions under investigations. This is particularly necessary since at high pH values the adsorption reaction may shift from reaction 1 to 3. It is obvious from table 3 that the values of the affinity constants are related to the first hydrolysis constants of the metal cations. The higher the pK_h value of the metal ion, the smaller is the affinity constant. Thus it can be concluded that cation which is most readily hydrolysed in solution has the greater affinity for the oxide/hydroxide surfaces. The same affinity order has been reported elsewhere [7-9].

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