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Claudia V. Diniz[a]; Fiona M. Doyle[a]; Virginia S. T. Ciminelli[a]
[a] Department of Materials Science and Engineering, University of California at Berkeley, Berkeley, CA, U.S.A.

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EFFECT OF pH ON THE ADSORPTION OF SELECTED HEAVY METAL IONS FROM CONCENTRATED CHLORIDE SOLUTIONS BY THE CHELATING RESIN DOWEX M-4195

Claudia V. Diniz,[1] Fiona M. Doyle,[1,*]
and Virginia S. T. Ciminelli[2]

[1]Department of Materials Science and Engineering,
University of California at Berkeley, 577 Evans Hall #1760,
Berkeley, CA 94720-1760, USA
[2]Univ. Federal de Minas Gerais, Belo Horizonte, Brazil

ABSTRACT

The effect of pH on the adsorption of nickel (II), copper (II), cobalt (II), lead (II), manganese (II), and iron (III) from concentrated chloride solutions onto Dowex M-4195 is reported for the first time. This chelating resin has an unusual ability to adsorb many of these metals, most notably copper, even at very low pH. The selectivity for many of these metals makes this resin particularly attractive for detoxifying concentrated acidic chloride solutions generated during the processing of many manganese ores and minerals. The uptake behavior at these high-chloride concentrations differs somewhat from that at the lower chloride concentrations previously reported in the literature. The behavior

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*Corresponding author. Fax: (510) 643-6331; E-mail: fiona@socrates.berkeley.edu

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is discussed in terms of the chemistry of the bis(2-pyridylmethyl) amine (bispicolylamine) functional group.

Key Words: Chelating resins; Chloride solutions; Heavy metals; Manganese; Metal uptake; Separation/purification process

INTRODUCTION

In nature, manganese frequently occurs with other transition metals, which are accommodated within open sites in the numerous crystal forms of MnO_2. Some of these ores are worked for their manganese content. An increasing use is for production of battery grade manganese dioxide. This is prepared from some ores by leaching the primary manganese minerals, purifying the resulting solution, then precipitating pure manganese dioxide. Other ores are amenable to partial leaching, which removes nonmanganese metals to a level acceptable for direct use in batteries. The resulting leach solution can be used to produce electrolytic manganese dioxide, manganese carbonate, and fertilizers and may be used in the pharmaceutical industry. First, however, the toxic components must be removed.

Other manganese minerals are mined for the metals associated with the manganese. The copper wad deposits of Chile and the silver manganese ores of Peru are examples.[1−3] There has also been much interest in deep-sea manganese nodules. These were studied extensively during the 1970s as a source of copper, nickel, and cobalt,[4−6] and a more modest effort has continued subsequently.[7−10]

Many of the processes used to treat manganese minerals utilize concentrated chloride solutions, because of the high solubility of the metals of interest in such solutions. Such processing generates concentrated, acidic chloride solutions containing high concentrations of manganese, relatively high levels of iron (III), and traces of Cu(II), Ni(II), Co(II), and Pb(II), among others. Regardless of whether one is primarily interested in the manganese itself or the associated metals, it is necessary to separate the manganese from the other metals. Precipitation is not a viable separation method, because of the propensity of many metals to co-precipitate with manganese. We have screened several commercial resins for their suitability for this separation at low pH. The chelating resin Dowex M-4195 appears to be very promising.[11,12]

Dowex M-4195, formerly marketed as Dow XFS 4195, is a macroporous polymer, with a polystyrene-divinylbenzene matrix, onto which the weakly basic chelating bispicolylamine functional group has been attached.[13,14] Bispicolylamine or bis(2-pyridylmethyl) amine is a heterocyclic polyamine with three nitrogen donor atoms, as shown in Fig. 1. In Dowex M-4195 the resin replaces hydrogen on the aliphatic nitrogen, creating a tertiary amine.

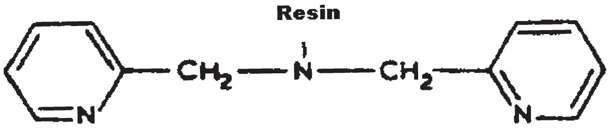

Figure 1. Bis(2-pyridylmethyl) amine functional group on Dowex M-4195.

Given the potential applications of Dowex M-4195 for separating iron and other metals from manganese in concentrated acidic chloride solutions, it is important to understand the effect of pH on metal uptake, to allow optimization of the separation. Grinstead[15] studied the effect of pH on the uptake of copper, nickel, cobalt, and iron (III) by the resin in chloride solutions containing $0.02-1\,M$ chloride. Copper showed a conditional adsorption constant (defined below) that was independent of pH over all ranges shown. In contrast, nickel, cobalt, and iron (III) all showed sharp maxima at around pH 2. Grinstead also found a sharp increase in the uptake of nickel and cobalt as the chloride concentration increased from 0.02 to $1\,M$.[15] Grinstead attributed this increase to a mass action effect wherein more chloride was available for co-sorption with metal ions onto uncharged functional groups. However, one cannot necessarily extrapolate the increases in metal uptake on increasing the chloride content reported by Grinstead to chloride concentrations of $3-4\,M$, typical of many process solutions. Grinstead noted that adsorption was unlikely to be due to an anion exchange mechanism, because of the low concentration of anionic chloro-complexes at the chloride concentrations used in his work.[15] Given this, it is likely that further increases in chloride concentration might continue to increase the uptake of metal ions that do not easily form anionic chloro-complexes, but suppress the uptake of those metals that form anionic chloro-complexes rather easily, for example lead.

In view of the uncertainty over the behavior of Dowex M-4195 at high-chloride concentrations, the present study was undertaken to examine the uptake of copper, nickel, cobalt, iron (III), lead, and manganese at different pH values from chloride solutions more concentrated than those studied hitherto. The copper, nickel, cobalt, and lead were at trace concentrations (50 mg/L), whereas iron (III) and manganese (II) were at 5 g/L, to emulate typical concentrations in solutions generated by leaching manganese materials. The study was made under conditions that provided an excess resin capacity for copper, nickel, cobalt, and lead, but an undercapacity for iron and manganese. The rationale for this was to gauge the ability of resin to scavenge trace metals from a process solution flowing through a resin column, and assess the extent of iron and manganese uptake that might be expected. The behavior of the resin is discussed in terms of the chemistry of the bis(2-pyridylmethyl) amine functional group.

EXPERIMENTAL PROCEDURE

ACS Reagent grade metal chloride salts were used ($MnCl_2 \cdot 4H_2O$, $CuCl_2 \cdot 2H_2O$, $FeCl_3 \cdot 6H_2O$, and $PbCl_2$ from Aldrich Chemical Company (Saint Louis, MO, USA), $CoCl_2 \cdot 6H_2O$, $NiCl_2 \cdot 6H_2O$, and NaCl from Fisher Chemicals (Pittsburgh, PA, USA)). ACS Certified Plus HCl was purchased from Fisher Chemicals, and Dowex M-4195 resin manufactured by Dow Chemical (Midland, MI, USA), was purchased from Supelco—Sigma Aldrich Division (Bellefonte, PA, USA).

Synthetic single metal chloride solutions were prepared by dissolving the salts in distilled water. Test solutions were prepared volumetrically from stock solutions that had been prepared gravimetrically, and standardized by atomic absorption spectrophotometry. The iron and manganese chloride solutions contained 5 g/L metal ion, while the nickel, copper, cobalt, and lead chloride solutions contained 50 mg/L metal ion. The pH was adjusted using hydrochloric acid. For the two lowest pH values, the free acidity was adjusted to 1.0 and 0.8 *M*. Assuming an activity coefficient of 1.546,[16] this corresponds to pH -0.19 and -0.09, respectively. Higher pH values were measured using an Orion pH/ISE meter with an Orion Ross combination pH electrode, after calibrating with standards of pH 1.0, 3.0, and 7.0. All pH standards were prepared using certified reagents from Fisher Chemicals. After adding HCl, the total chloride concentration was adjusted to 3.6 *M*, using sodium chloride.

The as-received resin was rinsed with water several times to remove any leached materials. It then underwent a wetting procedure[17] to ensure that it was wet, without introducing extraneous water into the test solutions.

The synthetic chloride solutions were contacted with the resin in glass bottles with plastic lids, using a resin to solution ratio of 1:50. This provided an excess resin capacity for the trace metals, but an undercapacity for iron and manganese, should they be strongly adsorbed. After contacting for 24 hr in a Lab-Line Orbit Shaker at 200 rpm, samples were filtered. The metal content of the filtrate was analyzed with a Perkin–Elmer 3100 flame atomic absorption spectrophotometer. The pH of the filtrate was also measured, as described above. All tests were run in duplicate at 25°C.

RESULTS AND DISCUSSION

Slight differences were observed between the pH of the metal chloride solutions before and after contacting with the resin. These differences were used to estimate the uptake or release of H^+ ions by the resin. It was not possible to establish any correlation between the transfer of H^+ and the uptake of metal ions. Given the additional fact that the tests were done under conditions that provided excess resin capacity, it was concluded that the pH changes reflected interaction of all the functional groups on the resin with the solution, rather than reaction of only those functional groups that chelated metal ions. Sengupta et al.[18] noted that it is difficult to maintain a constant aqueous-phase pH during batch testing with chelating resins. To address this difficulty, all pH values reported here were measured after contacting, rather than before.

Figure 2 shows the effect of equilibrium pH on the percentage of metal adsorbed by Dowex M-4195 from single metal solutions. Dowex M-4195 clearly has a strong affinity, even at very low pH, for most of the metals except manganese (II). The results indicate the ability of the resin to scavenge trace metals in the presence of high concentrations of iron, manganese, and chloride. Figures 3 and 4 show the metal adsorption profiles, in moles of metal per liter of resin. Although the percentage of iron (III) and manganese adsorbed was lower than that for the other metals tested, the loadings in mol/L resin for these two metals were much higher, because of the higher concentrations used (Fig. 4).

The total capacity of the resin has been reported to be around 0.63 mol/L for copper,[19] although some variations might be expected, depending on manufacturing conditions.

Figure 3 confirms that the resin was well undersaturated with copper (0.043 mol/L), nickel (0.045 mol/L), cobalt (0.045 mol/L), and lead (0.010 mol/L). Figure 4 suggests that the iron uptake reaches the resin capacity determined by Grinstead.[15] In contrast, the resin did not saturate with manganese, even at the highest pH tested. It is suggested that the uptake of metal ions from chloride solutions can then be represented as:

$$M^{2+} + (2-n)Cl^{-} + \overline{R(H^{+}Cl^{-})_{n}} = \overline{RMCl_{2}} + nH^{+} \qquad (1)$$

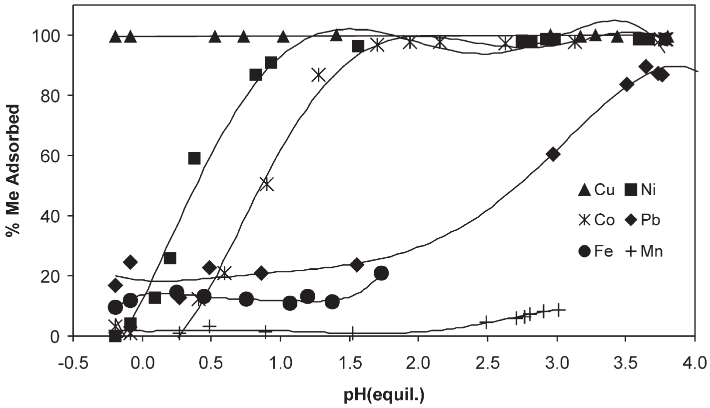

Figure 2. Effect of pH on the percentage of metals adsorbed by Dowex M-4195 from chloride solution. Initial concentrations of Cu, Co, Ni, and Pb = 50 mg/L. Initial concentration of Fe(III) and Mn(II) = 5 g/L. Resin to solution volume ratio = 1:50. Temperature = 25°C.

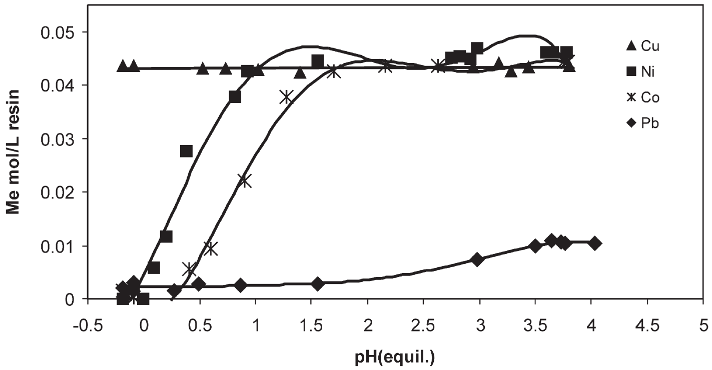

Figure 3. Effect of pH on the loading of trace metals from chloride solution onto Dowex M-4195. Initial concentrations of Cu, Co, Ni, and Pb = 50 mg/L. Resin to solution volume ratio = 1:50. Temperature = 25°C.

where overscoring denotes species present on the resin phase, and $\overline{R(H^{+}Cl^{-})_{n}}$ denotes the functional group on the resin associated with *n* hydrogen ions, and *n* chloride ions. Equation (1) is slightly different from the metal uptake reaction set forth by Grinstead,[15,19] who designated chloride ions associated with the protonated functional groups as independent species. The representation used above was adopted because cations associated with the bis(2-pyridylmethyl)

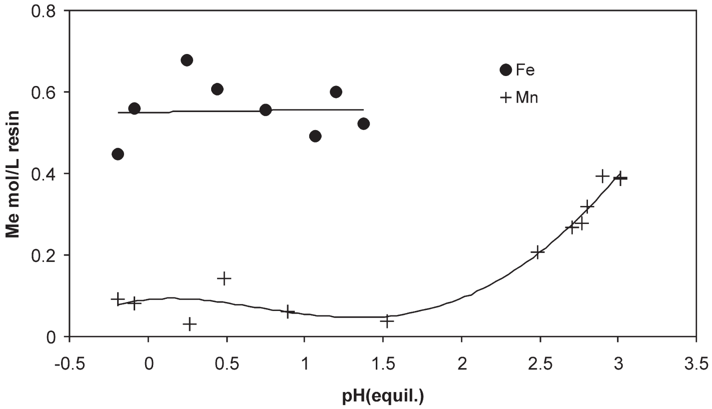

Figure 4. Effect of pH on the loading of Fe(III) and Mn(II) from chloride solution onto Dowex M-4195. Initial Fe(III) and Mn(II) concentrations = 5 g/L. Resin to solution volume ratio = 1:50.

amine functional group must always be associated with an equivalent number of anions for charge neutrality.

In order to understand the metal uptake reaction, it is necessary to determine the degree to which the functional group is protonated. Table 1 gives the pK_a values of bis(2-pyridylmethyl) amine.[20] These values suggest that all three nitrogens on the functional group of Dowex M-4195 would be protonated at the lowest pH values studied here (-0.2 to $+3.8$). They also suggest that only one of the pyridyl nitrogens is protonated in the middle range of pH values and that although, neither pyridyl nitrogen is protonated at the highest pH nor the aliphatic amine remains protonated. In fact, Grinstead obtained very smooth titration curves for Dowex M-4195 in both chloride[15] and sulfate[19] solutions, with no sharp endpoints. Table 1 also shows the “effective” pK_a’s for M-4195 in chloride and sulfate, defined as the pH at half titration for each proton. These values were interpolated from Grinstead’s titration curves for the M-4195 resin with HCl[15] and H_2SO_4.[19] The endpoint pH values, at which one, two, and three protons are taken up by each functional group, are also shown (the pK_a is less informative about the state of the functional groups when there is no sharp titration curve). It is clear that when the bis(2-pyridylmethyl) amine functional group is attached to the resin, the pyridyl nitrogens are somewhat more readily deprotonated, more so in chloride media than in sulfate (the sulfate data would also include uptake of protons by sulfate near the pK_a for HSO_4^- at pH 1.9).[19] The aliphatic amine, however, becomes much more readily deprotonated, such that in chloride solutions a fraction of these amine groups are deprotonated within the pH range studied in this work. Some shift would be expected in the dissociation constant of this amine, since attachment to the resin converts the secondary amine to a tertiary, but the magnitude of the shift is dramatic.

Figure 5 plots the number of hydrogen ions, n, associated with each bis(2-pyridylmethyl) amine group on Dowex M-4195 in chloride solutions as a

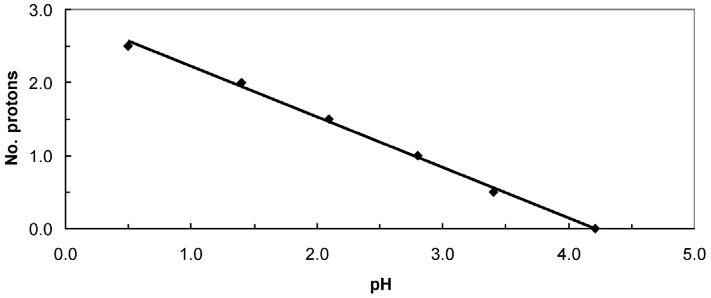

Figure 5. Number of hydrogen ions associated with each bis(2-pyridylmethyl) amine functional group in chloride solutions, as a function of pH, from data of Grinstead.[15]

Table 1. Proton Dissociation Constants for bis(2-Pyridylmethyl) Amine and Dowex M-4195 at 25°C in 0.10 *M* KNO_3

	pK_1	pK_2	pK_3	Comments	Ref.
Bis(2-pyridylmethyl) amine	1.12	2.60	7.30		[20]
M-4195, chloride[a] media, effective pK_a	~0.5	2.2	3.4	pH at half titration	[15]
M-4195, chloride media, endpoints	—	1.4	2.8	Endpoints for uptake of one and two protons per functional group	[15]
M-4195, sulfate[a] media, effective pK_a	1.5	2.7	3.5	pH at half titration	[19]
M-4195, sulfate media, endpoints	~0.9	2.3	3.1	Endpoints for uptake of one, two and three protons per functional group	[19]

[a] These values were interpolated from the Grinstead's titration curves.

function of pH, from Grinstead's titration data.[15] The data are well fitted by the regression line shown, which has the equation:

$$n = 2.9091 - 0.6907\,\mathrm{pH} \quad (\mathrm{pH} \leq 4.21) \tag{2}$$

Above pH 4.21, n would be zero. All metal uptake data should be considered in light of the decrease in the degree of protonation with increasing pH.

When the bis(2-pyridylmethyl) amine functional groups on the resin are protonated, an equivalent amount of chloride is taken up for charge neutrality, as represented by Eq. (1). The equilibrium constant, K', for Eq. (1) is:

$$K' = \frac{[\overline{\mathrm{RMCl_2}}][\mathrm{H^+}]^n}{[\mathrm{M^{2+}}][\mathrm{Cl^-}]^{2-n}[\overline{\mathrm{R(H^+Cl^-)_n}}]} \cdot \frac{\gamma_{\overline{\mathrm{RMCl_2}}}(\gamma_{\mathrm{H^+}})^n}{\gamma_{\mathrm{M^{2+}}}(\gamma_{\mathrm{Cl^-}})^{2-n}\gamma_{\overline{\mathrm{R(H^+Cl^-)_n}}}} \tag{3}$$

where γ_i denotes the activity coefficient of i. Grinstead also defined a conditional adsorption coefficient, K:

$$K = \frac{[\overline{\mathrm{RMCl_2}}]}{[\mathrm{M^{2+}}][\mathrm{R(H^+Cl^-)_n}]} \tag{4}$$

Substituting from Eq. (3), Eq. (4) is equivalent to:

$$K = K'\frac{[\mathrm{Cl^-}]^{2-n}}{[\mathrm{H^+}]^n} \cdot \frac{\gamma_{\mathrm{M^{2+}}}(\gamma_{\mathrm{Cl^-}})^{2-n}\gamma_{\overline{\mathrm{R(H^+Cl^-)_n}}}}{\gamma_{\overline{\mathrm{RMCl_2}}}(\gamma_{\mathrm{H^+}})^n} \tag{5}$$

Taking logarithms gives:

$$\log K = \log K' + \log A' + (2-n)\log[\mathrm{Cl^-}] + n\,\mathrm{pH} \tag{6}$$

or:

$$\log\frac{K}{K'A'} = (2-n)\log[\mathrm{Cl^-}] + n\mathrm{pH} \tag{7}$$

where A', a composite activity coefficient, is defined as:

$$A' = \frac{\gamma_{\mathrm{M^{2+}}}(\gamma_{\mathrm{Cl^-}})^{2-n}\gamma_{\overline{\mathrm{R(H^+Cl^-)_n}}}}{\gamma_{\overline{\mathrm{RMCl_2}}}} \tag{8}$$

It is clear that the effect of aqueous chloride concentration on the conditional adsorption coefficient will depend directly on pH, and also on the degree of protonation of the functional group, which is also pH dependent. Substituting for

n from Eq. (2) gives, at pH ≤ 4.21 :

$$\log \frac{K}{K'A'} = (0.6907\,\mathrm{pH} - 0.9091)\log[\mathrm{Cl}^-] + 2.9091\,\mathrm{pH} - 0.6907(\mathrm{pH})^2 \tag{9}$$

and at pH > 4.21 :

$$\log \frac{K}{K'A'} = 2\log[\mathrm{Cl}^-] \tag{10}$$

Figure 6 shows theoretical values of $\log K/K'A'$ (from Eqs. (9) and (10)) plotted as a function of pH for various chloride concentrations. It can be seen that if the average value of n is less than two, which occurs at pH values greater than 1.4 (point of interception of all curves), increasing the chloride concentration increases the conditional adsorption coefficient.

Grinstead[15] reported that increasing chloride concentrations promoted metal adsorption at pH 3, which is consistent with the predictions of Fig. 6. However, if the average value of n is exactly two, at pH 1.4, metal adsorption should be independent of the aqueous chloride concentration, and at pH values below 1.4, where n exceeds two, increasing aqueous chloride concentrations should impair metal uptake.

Turning to the effect of pH, Eqs. (9) and (10), and Fig. 6 show that the gradient of the plot of log $(K/K'A')$ against pH depends on the chloride

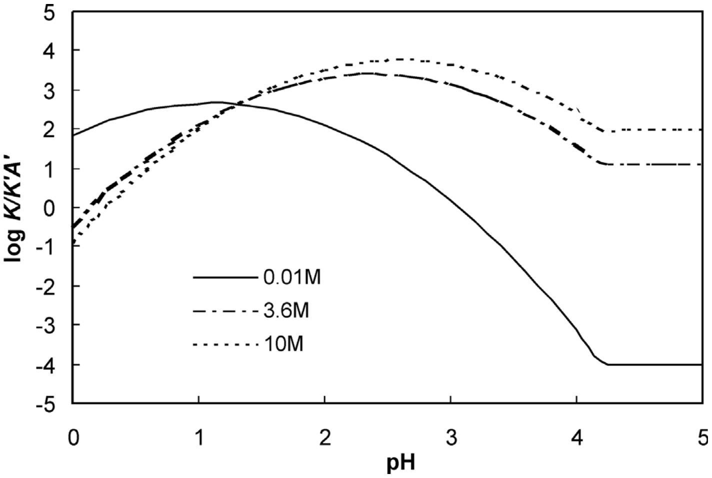

Figure 6. Plot of Eqs. (9) and (10), $\log K/K'A'$ as a function of pH for different chloride concentrations.

concentration. Grinstead[15] reported a pronounced maximum in K for the uptake of Ni(II) and Co(II) at pH 2 from solutions containing 1 g/L M^{2+}, as chloride, with no added chloride. The K was significantly lower at higher pH. This behavior is consistent with the predictions of Fig. 6, assuming that the composite activity coefficient, A', is constant over the pH range. In contrast, a plateau region was observed for Dowex M-4195 in sulfate media.[19] Grinstead attributed the decrease in K in chloride media to the strong dependence of adsorption on chloride concentration.

With the high aqueous chloride concentrations, and the large solution to resin volume ratio employed in this study, the aqueous chloride concentration would have been nearly constant. Figure 7 shows plots of the conditional adsorption constant, K, as a function of pH for the trace metal ions studied in this work. K was evaluated using Eq. (4), $[\overline{R(H^+Cl^-)_n}]$ was obtained by difference from the total capacity of the resin, taken to be 0.63 mol/L,[15] and $[\overline{RMCl_2}]$, which was determined from the difference between the metal ion concentration in the feed solution and at equilibrium. Figure 7 shows that for nickel and cobalt, adsorption is strongly dependent on pH at low pH, then is much less sensitive to pH above pH 2. Lead is adsorbed at low levels below pH 3; above this pH adsorption increases more markedly with pH. Copper is adsorbed strongly, with little sensitivity to pH, suggesting that the adsorption of copper is unaffected by the degree of protonation of the resin, while the uptake of nickel and cobalt becomes easier with de-protonation of the resin.

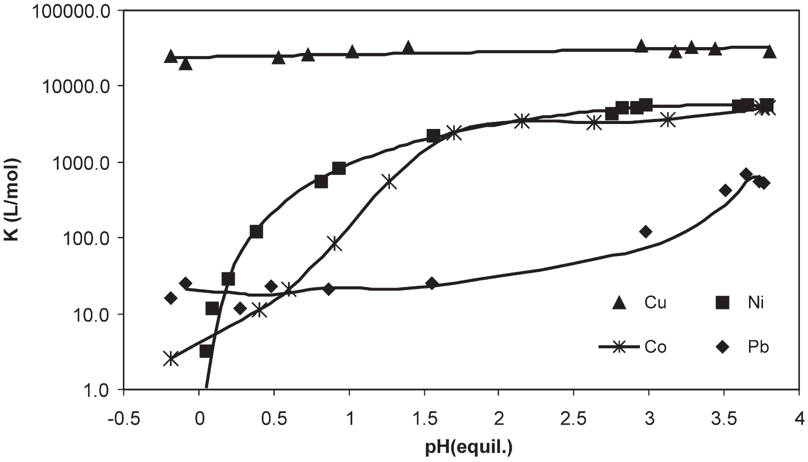

Figure 7. Conditional adsorption constant for Dowex M-4195 in chloride solutions.

In contrast with Grinstead's findings[15] and the predictions of Fig. 6, Fig. 7 shows no decrease in the adsorption constant above pH 2 for nickel and cobalt. One possible reason for the discrepancy is that in the concentrated chloride solutions used here, the composite activity coefficient, A', defined in Eq. (8) is unlikely to be independent of pH. Consequently, although $\log K/K'A'$ may show a maximum with increasing pH, $\log K$ may not. In contrast, Grinstead's solutions containing 1 g/L metal ion as chloride would have been far more ideal. It is also possible that a decrease might occur above the pH range adopted in the present study, but higher pH could not be explored experimentally, because of difficulties in controlling the equilibrium pH values above 3.8, due to spontaneous deprotonation of the resin.

The main difference between Grinstead's previous work[15] and the present study is the much higher chloride concentration in the present study. This high-chloride concentration will certainly affect the metal ion speciation, due to the formation of chloro-complexes. Species distributions were calculated using stability constants compiled by Martell and Smith.[21,22] Table 2 shows the species distributions for the metal ions in the study in a solution with a total chloride concentration of 3.6 *M*. Chloro-complexes were formed by all the metals and were the dominant species in the pH range used in this study. Hydroxo-complexes were considered, but only iron formed significant concentrations of these, at pH 3 and above. Cobalt, nickel and manganese formed significant amounts of the cationic monochloro-complex MCl^+. Iron, copper, and lead formed various chloro-complexes. Comparing the distribution of chloro-complexes with the uptake of the different metals on the resin, it is clear that the different affinities of the resin for different metals cannot be attributed exclusively to electrostatic interactions resulting from differences in speciation. The chelating effect of the bispicolylamine functional group is clearly strong enough to break up any chloro-complexes through interaction between the metal species and the nitrogen donor atoms. This is especially notable in the case of copper, which showed similarly strong uptake on the resin at low chloride concentration,[15] where copper is present as Cu^{2+}, and high-chloride concentration in the present study, where copper is present as different chloro-complexes. In both cases the uptake by the resin is independent of the degree of protonation of the functional group.

As discussed by Sengupta et al.,[18] most chelating ion exchangers have strong affinities for hydrogen ions because of weak-acid or weak-base functional groups. Consequently, metal ion uptake is drastically reduced under highly acidic conditions ($pH < 2.0$), because of competition from the hydrogen ions. They also noted that although the Dowex M-4195 resin is an exception, at least for the uptake of copper, nickel, and cobalt, no scientific explanation had been provided for its unusual properties. Examination of the literature[23] suggests that the ability to bind metal ions more efficiently than aliphatic polyamines in neutral

Table 2. Species Distribution for Synthetic Single Metal Solutions. Total Chloride Concentration = 3.6 *M*. 5 g/L Fe(III) and Mn(II). 50 mg/L Cu, Co, Ni, and Pb

System	Species	Log *K*	Percentage of Metal Present as Species
Cu(II)	$\mathrm{Cu^{2+}}$	N/A	11.6
	$\mathrm{CuCl^{+}}$	0.4[a]	61.8
	$\mathrm{CuCl_2}$	− 0.22[a]	25.2
	$\mathrm{CuCl_3^{-}}$	− 1.5[a]	1.3
	$\mathrm{CuCl_4^{2-}}$	− 2.5[a]	0.1
Ni(II)	$\mathrm{Ni^{2+}}$	N/A	52.5
	$\mathrm{NiCl^{+}}$	− 0.6[a]	47.5
Co(II)	$[\mathrm{Co^{2+}}]$	N/A	30.6
	$[\mathrm{CoCl^{+}}]$	− 0.2[a]	69.4
Pb(II)	$[\mathrm{Pb^{2+}}]$	N/A	0
	$[\mathrm{PbCl^{+}}]$	1.23[a]	0.5
	$[\mathrm{PbCl_2}]$	1.8[a]	6.5
	$[\mathrm{PbCl_3^{-}}]$	2.2[a]	59.2
	$[\mathrm{PbCl_4^{2-}}]$	1.4[a]	33.8
Mn(II)	$[\mathrm{Mn^{2+}}]$	N/A	20.5
	$[\mathrm{MnCl^{+}}]$	0.04[b]	79.5
Fe(III)	$[\mathrm{Fe^{3+}}]$	N/A	0.1
pH = 0	$[\mathrm{FeCl^{2+}}]$	1.48[a]	6.1
	$[\mathrm{FeCl_2^{+}}]$	2.13[a]	93.3
	$[\mathrm{FeCl_3}]$	− 0.7[a]	0.5
Fe(III)	$[\mathrm{Fe^{3+}}]$	N/A	0.1
pH = 3	$[\mathrm{FeCl^{2+}}]$	1.48[a]	6.0
	$[\mathrm{FeCl_2^{+}}]$	2.13[a]	92.9
	$[\mathrm{FeCl_3}]$	− 0.7[a]	0.5
	$[\mathrm{FeOH^{2+}}]$	11.81[b]	0.4
	$[\mathrm{Fe(OH)_2^{+}}]$	22.3[b]	0.1

[a] Data from Ref. [22].
[b] Data from Ref. [21].

and acidic conditions stems from both the low pK_a's of the bis(2-pyridylmethyl) amine or bispicolylamine functional group (Table 1), and steric factors. The low pK_a values ensure that even at low pH there are some deprotonated nitrogens capable of interacting directly with metal ions. The three nitrogen donor atoms allow this heterocyclic polyamine to serve as a tridentate ligand.[20] When chelation is possible, the overall favorable nature of the interaction will promote further deprotonation.

It would only be possible for all three nitrogens on the functional group to serve as donors for a single ion if the cation has a suitable ionic radius, such that the nitrogen donors can interact with available orbitals without undue strain. Many divalent, first row transition metal ions appear to satisfy these criteria.[24] However, because the functional group is attached to a polymeric matrix, which would, to a greater or lesser extent, restrict its ability to interact freely with ions,[25] one would expect the stability of the resulting complexes to be strongly sensitive to the cationic radius.

Romary et al.[20] determined that the formation constants for the bis(2-pyridylmethyl) amine complexes of selected divalent transition metal ions followed the order: Cu $>$ Ni $>$ Co $>$ Zn $>$ Mn. This order is consistent with the findings of Mellor and Maley[26] and also with the results shown in Fig. 2. Table 3[27] shows that the crystal radius of these ions increases in the order Cu $=$ Ni $<$ Co $=$ Zn $\ll$ Mn. Bis(2-pyridylmethyl) amine appeared to form tridentate complexes in the 1:1 complexes with all of these ions except Mn(II), which formed a monodentate complex.[20] It is seen that the Mn(II) ion is dramatically larger than Zn(II), which suggests that a tridentate Mn(II)–bis(2-pyridylmethyl) amine complex would be too strained to be stable. However, Cd(II), which is substantially larger than Mn(II), forms a bis(2-pyridylmethyl) amine complex, reported to be tridentate,[20] with a formation constant intermediate between that of Zn and Mn. It seems probable that the low uptake of Pb(II) by the resin stems from the fact that this ion is too large to interact with all three-donor nitrogens in the bis(2-pyridylmethyl) amine. An important observation is that copper(II) generally conforms to 4- or 6-coordinate structures and can exist in a variety of geometries, while iron (III) commonly forms 6-coordinate octahedral complexes.[28]

Table 3. Crystal Ionic Radii of Selected Ions[27]

Ion	Crystal Ionic Radius [Å]
Fe(III)	0.64
Fe(II)	0.76
Cu(II)	0.72
Ni(II)	0.72
Co(II)	0.74
Zn(II)	0.74
Mn(II)	0.80
Cd(II)	0.97
Pb(II)	1.20

CONCLUSIONS

The work reported here demonstrated that at chloride concentration of 3.6 *M*, Dowex M-4195 clearly has a strong affinity, even at very low pH, for most of the metals in the study except manganese (II), for which the resin presented a low adsorbing capacity. The adsorption of nickel and cobalt increases with pH, as the resin becomes deprotonated. Copper adsorbs strongly, even at very low pH values and adsorption is independent of the degree of protonation of the resin.

Theoretically, the adsorption of metal ions by the resin was shown to be favored by increasing chloride concentration, for pH values exceeding 1.4. Below pH 1.4, the opposite effect occurs; an increase in chloride concentration decreases the theoretical metal adsorption by the resin. The formation of chloro-complexes does not appear to inhibit metal uptake by Dowex M-4195.

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