

“Adsorption Studies of Transition Metals Manganese to Zinc over Zirconyl Silicate Resin”

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Summary: The anion exchange behaviour of first row transition elements Manganese to Zinc has been studied over Zirconyl Silicate in hydrochloric acid (0.3-3.0M) as eluent. The adsorption of these elements changes sufficiently as a function of hydrochloric acid concentration to permit their separation. The adsorption and stability of negatively charged complexes is found to be in the order of Ni(II) < Mn (II) < Cu (II) < Cr (III) < (Co (II) < Zn (II) < Fe (II). Unlike other elements studied, adsorption of Ni(II) is very small which decreases as the concentration of hydrochloric acid is increased.

Introduction

The popularity of Ion-exchange as a tool in Analytical Chemistry has been increased tremendously since last decade. The literature survey shows that great attention has been given to the cation exchange as compared to the anion exchange chromatography. The separation of base metals from chloride solution is particularly attractive.

The periodic table prepared by Kraus and Nelson [1], established the behaviour of metal chloride complexes at trace ionic concentration in the presence of a strong base anion exchange resin. They concluded that the transition metals and noble metals can form anion chloride complexes with varying affinity for an anion exchange resin. The concept of separating metals from chloride solution by continuous ion exchange has been described by Gupta and Streat [2]. Many of these elements in the proper complexing medium apparently form negatively charged complexes in sufficient concentration to permit their significant adsorption on anion exchange resins.

In our earlier studies, cation exchange properties of various inorganic ion exchanger for separation of metal ions have been reported [3-7]. The present investigations are carried out to understand the adsorption and anion exchange behaviour of negatively charged chloride complexes of first row transition metal ions, and separation of metals which form such complexes, over Zirconyl silicate.

Results and Discussion

Elimination of water from resin

Zirconyl silicate starts to loose water (Fig. 1) at 75°C and the maximum weight loss (~16%) is attained at 400°C. The weight loss between 400-800°C is relatively small with the rate 1-2% after each 100°C, the total reaching to 21% of the initial weight. The weight loss between 800-900°C is negligibly small (~ 0.5%) as no further weight loss occurs upto 1200°C. The weight loss upto 400°C may be attributed to elimination of the interstitial or free water. Further increase in the temperature (400-800°C) chemically bonded water is lost.

Effect of hydrochloric acid on adsorption

Based on the results of measurements of distribution coefficient (K_d) of Chromium, Manganese, Iron, Cobalt, Nickel, Copper and Zinc from varying concentration of hydrochloric acid and the most suitable conditions for the column separation were selected. The K_d values and the separation factor “ α ” of the transition metals are listed in Table-1. It is interesting to note that Ni(II) is the only element of the series showing negligible adsorption which further decreases as the concentration of hydrochloric acid increase. Cu(II) shows some adsorption above 1M, HCl, while Mn(II) starts adsorption above 1.4M HCl. Zn(II) shows the strongest adsorption of the series. It is considerably adsorbed in 0.2M HCl. In addition the adsorptivity of Zn(II) greatly exceeds than that of the other divalent cations. Cr(III) is the only cation in the

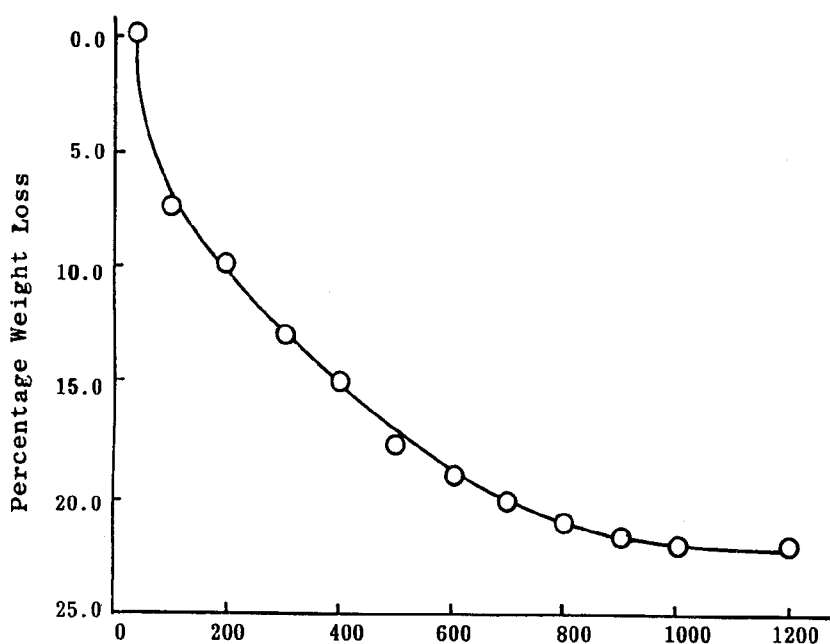


Fig. 1: Percentage Weight Loss of Zirconyl Silicate at different Temp.

Table-1: Log K_d and separation factor (α) for transition metal ions on Zirconyl silicate.

Concentration of HCl (M)	Parameter	Metal Ions						
		Ni ⁺²	Mn ⁺²	Cu ⁺²	Cr ⁺³	Co ⁺²	Zn ⁺²	Fe ⁺²
0.3	Log K_d	1.20	1.45	1.55	1.88	0.00	1.93	0.71
	α	1.21	1.17	1.21	-	-	2.72	
0.6	Log K_d	0.19	1.55	1.65	2.03	1.70	2.10	1.34
	α	8.16	1.06	1.23	1.19	1.24	1.57	
0.9	Log K_d	0.15	1.55	1.72	2.08	1.77	2.25	1.93
	α	1.03	1.10	1.21	1.18	1.27	1.66	
1.2	Log K_d	1.00	1.70	1.85	2.16	2.17	2.38	2.30
	α	1.70	1.09	1.17	1.00	1.10	1.03	
1.5	Log K_d	1.03	1.74	1.87	2.26	2.30	2.45	2.40
	α	1.69	1.07	1.21	1.02	1.07	1.02	
1.8	Log K_d	1.00	1.82	2.0	2.30	2.33	2.53	2.78
	α	1.82	1.10	1.15	1.01	1.09	1.10	
2.1	Log K_d	0.88	1.85	2.08	2.30	2.40	2.58	2.80
	α	2.10	1.12	1.11	1.04	1.08	1.09	
2.4	Log K_d	0.70	1.85	2.13	2.30	2.45	2.60	2.90
	α	2.64	1.15	1.08	1.08	1.06	1.11	
2.7	Log K_d	0.68	1.90	2.18	2.30	2.50	2.63	2.95
	α	2.80	1.15	1.06	1.09	1.05	1.12	
3.0	Log K_d	0.59	2.00	2.25	2.30	2.53	2.63	3.01
	α	3.39	1.13	1.02	1.10	1.04	1.14	

present studies which is trivalent. It shows considerable adsorption which has almost same adsorption to that of Co(II) ion but less than Fe(II) above 0.8M HCl. The observed adsorption behaviour may be due to the anion exchange property of the resin and because of the formation of negatively

charged chloride complex $[MCl_3]^-$ by metal ion. Ni(II) probably does not form negative charged complex and is therefore adsorbed on the resin as a cation. If it is assumed to be correct, then one can understand its decreasing adsorption with increase in the concentration of hydrochloric acid. From these

results it is suggested that the separation of the transition elements can easily be achieved by anion exchange chromatography. A slightly different adsorption behaviour has been observed elsewhere with quaternary amine polystyrene divinylbenzene resin Dowex-1 using hydrochloric acid with adsorption sequence $Zn^{II} > Cu^{II} > Co^{II} > Fe^{II} > Mn^{II} > Ni^{II}$ [8].

Effect of concentration of hydrochloric acid as eluent

The complexing strength of the cations depend upon the solubilities of the metal chloride MCl_2 in hydrochloric acid which increases in the order $Zn^{II} > Cu^{II} > Co^{II} > Fe^{II} > Ni^{II}$ [9]. This is because of the assumption that the undissociated compounds MCl_2 have relatively low solubility as that formation of negatively charged complexes are necessary to yield good solubility in hydrochloric acid. A comparison of the anion exchange data of the elements with those of reported soluble in hydrochloric acid indicates that $FeCl_2$ is less soluble with high anion exchange property. The adversity may be due to the use of different concentrations of hydrochloric acid (Fig. 2) shows that at low

concentration of HCl, the $Fe(II)$ adsorption is negligible which increases with increasing the concentration of hydrochloric acid. Higher adsorption of $Fe(II)$ in concentrated HCl is probably due to the oxidation of $Fe(II)$ to $Fe(III)$ in the aqueous hydrochloric acid media which is reported to be strongly adsorbed in concentrated hydrochloric acid [10] and is identified with $[FeCl_4]^-$ through resin capacity measurements [11].

Comparison of complexing strength and activity coefficients

The results of the present studies may also be compared with the complexing strength of these elements drawn from the reported values of the activity coefficients of metal chloride [12]. The increasing order of activity coefficient for metal chloride solutions is $Zn < Cu < Mn < Fe < Co \leq Ni$. In this case it may be expected that stoichiometric activity coefficients decreases with increasing complexation. The order of complexation differs greatly from that obtained from anion exchange behaviour of the respective metal chloride. It is surprising that the values of activity coefficient obtained by Harned and Owen [12] for $NiCl_2$ (0.938)

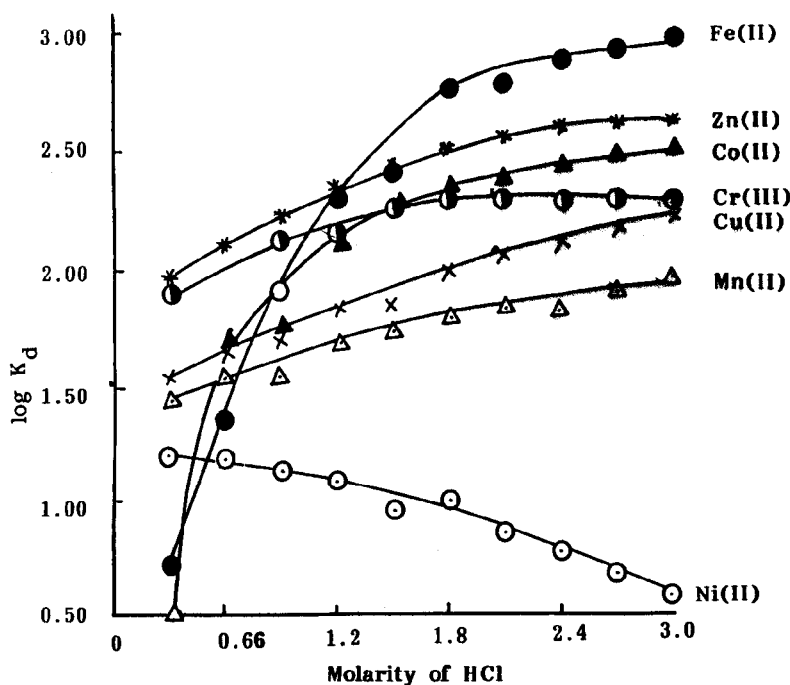


Fig.2 : Log K_d of Transition metal ions against Molarity of HCl.

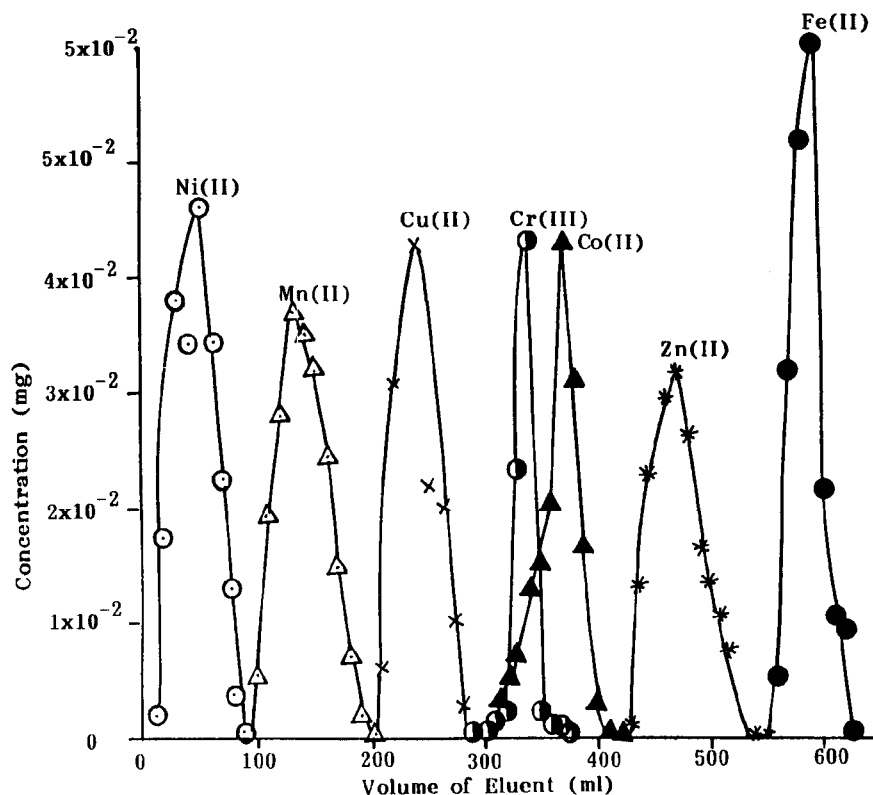


Fig. 3: Separation of Transition Elements Mn to Zn. Column: 8x0.8 cm I.D., Flow rate: 0.1 ml/min.

and CoCl_2 (0.844) are almost similar but they differ greatly with respect to the anion exchange behaviour in hydrochloric acid. It is also surprising that MnCl_2 (0.682) and FeCl_2 (0.817) have relatively lower activity coefficients than CoCl_2 (0.884). This may probably be due to reasons that the activity coefficients of the metal halides become low if the complexes MCl^+ and MCl_2 are formed. Whereas the anion exchange behaviour are related to the formation of negatively charged metal chloride complexes. The anion exchange results may also be compared with the complexation behaviour suggested by Bjerrum [13] $\text{Zn} > \text{Fe} > \text{Cu} > \text{Co}$. These studies do not include Mn(II) and Ni(II) and thus a detailed comparison is not possible. However the results are in agreement with our results and disagree the values of activity coefficients.

Separation of transition metals manganese to zinc

The considerable difference in distribution coefficient (Fig. 2) and high separation factor " α "

(Table-1) of the elements implies that their separation on anion exchange column of moderate length should be possible. To separate two substances, conditions should be selected such that the K_d values of one must be lower so that the elution is rapid. The K_d value of other substances under the same conditions should be as large as possible. So that it is tightly held with the resin. To illustrate the technique, the separation of Cr(II), Mn(II), Fe(II), Co(II), Ni(II), Cu(II) and Zn(II) was carried out and the results are shown in typical chromatogram (Fig. 3). Approximately 2 ml of a concentrated hydrochloric acid solution containing 2 mg of each metal was placed on a column containing anion exchange resin. Under these conditions Ni(II) is not adsorbed and immediately appears in eluent with concentrated hydrochloric acid. Mn(II) is not adsorbed and immediately appears in eluent with concentrated hydrochloric acid. Mn(II) is removed with 3.0M HCl, Cu(II) with 2.4M HCl, Co(II) and Cr(III) with 1.5M HCl, Zn(II) with 0.3M HCl and Fe(II) with 0.1M HCl. The eluent mixture containing

Co(II) and Cr(III) is again passed through the resin and separated with 0.3M HCl and 0.1M HCl solution respectively.

Data on percentage recovery of metal ions using hydrous chromium oxide (HCO) [4], hydrous zirconium oxide (HZO) [14], zirconium phosphate (ZP) [5], and irconyl silicate (ZS) is shown in the following table.

Table-2: Percentage recoveries of metal ions on various resins

Metal Ion	Percentage recovery			
	HCO	ZP	HZO	ZS
Mn	90	95	94	98
Co	94	94	90	78
Cu	90	95	-	83
Fe	93	85	91	95
Ni	-	88	-	99
Cr	-	-	89	79
Zn	85	-	-	87
Ca	-	95.8	-	-

In line with the earlier resins used, the efficiency or the effective separation of these metal ions using zirconyl silicate ion exchanger is quite satisfactory. This method looks to be applicable for analysis of such metal ions in ores, oils ashes, biological materials and other natural/synthetic substances.

Experimental

Hydrous Zirconyl Silicate was prepared by dissolving Zirconyl chloride (64.44g, 0.2M) in doubly distilled water followed by addition of equal volume of aqueous solution of sodium silicate (24.4 g, 0.2M). The resulting mixture was treated with 0.2M HCl until it became neutral. NH_4OH (0.2%) was then added in the neutral mixture with constant stirring until precipitation was completed and the final pH was adjusted to 8. The precipitates were allowed to settle overnight at room temperature for aging and then washed several times with distilled water until the supernatant was free from ammonium and chloride ions. The precipitates were filtered and dried at 35°C. After immersion in water, the granular material was sieved and 100 mesh fraction was collected. The water contents (determined on the basis of formation of $\text{ZrO}_2 \cdot \text{SiO}_2$ at 60°C were 22.5% and the molar ratio of $\text{ZrO}_2 \cdot \text{SiO}_2$ and SiO_2 was 1:2:96. Stock solutions of Chromium, Manganese, Iron, Cobalt, Nickel, Copper and Zinc were prepared

by dissolving appropriate weights of the reagent grade chloride or sulphate of these metal ions in distilled water. These solutions contained 1 mg metal ion/ml. Further metal ion concentrations were prepared by appropriate dilution of respective stock solutions. The concentrations of metal ions were determined using standard spectrophotometric methods [15,16]. The ion exchange column was prepared and used in an identical manner as described in the previous communication [17].

Distribution coefficients and separation factor

The distribution coefficients (K_d) of the metal ions were calculated by the batch equilibrium technique [18] at 25 °C. The K_d values were evaluated by the following standard equation:

$$K_d = \frac{\text{Ion Conc. in ref. sol.} - \text{ion conc. in measuring sol.}}{\text{Ion conc. in measuring solution}} \times \frac{\text{Vol. of sol.}}{\text{Wt. of resin}}$$

The amount of metal ions adsorbed was determined from the difference between the initial and the final concentrations in the clear supernatant solutions. The separation factor ' α ' is the ratio between the distribution coefficients of one metal (A) with that of the another metal (B). The ratio is represented as follows:

$$\alpha(A/B) = \frac{K_{dA}}{K_{dB}}$$

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