

## Study of some metallic silicates as ion-exchangers

DINESH and B BHUSHAN\*

Department of Chemistry, M D University, Rohtak 124001, India

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**Abstract.** The extraction of ammine complexes of  $\text{Cu}^{2+}$ ,  $\text{Cd}^{2+}$ ,  $\text{Ni}^{2+}$ ,  $\text{Co}^{2+}$  and  $\text{Zn}^{2+}$  by synthesised manganese, nickel and zinc silicates has been studied at different pH and ionic concentrations in the external solution. It has been found that the uptake of the metal ion  $\text{Co}^{2+}$ ,  $\text{Cu}^{2+}$  and  $\text{Zn}^{2+}$  increases with increase in pH of the external solution, attains a maximum and then decreases. However, the uptake for  $\text{Cd}^{2+}$  and  $\text{Ni}^{2+}$  increases continuously. The  $q_A$  values of all the silicates increases with the increase in the concentration of the exchanging ion and its order for the investigated metal ions is  $\text{Ni}^{2+} < \text{Co}^{2+} < \text{Cd}^{2+} < \text{Zn}^{2+} < \text{Cu}^{2+}$ .

**Keywords.** Metal silicates; ion-exchange; metal amines.

### 1. Introduction

In recent times, exchangers are well established for their potential applications (Amphlett 1964; Marinsky and Marcus 1966; Rodrigues 1986) like water softening, removal of pollutants, separation of nuclear wastes etc. One such important class of exchangers are silicates (Othmer-Kirk 1982). Both synthetic as well as natural silicates act as ion-exchangers. But the insoluble silicates, crystalline and amorphous type, are of utmost importance. The crystalline silicates, commonly called zeolites (Othmer-Kirk 1982) are used as ion-exchangers, selective sorbents, catalysts and for the controlled release of chemicals. But, still some work is possible in the field of amorphous silicates as is revealed by literature survey. So some amorphous silicates were synthesised and their ion-exchange properties were explored. The present paper describes the results of investigation on manganese silicate, nickel silicate and zinc silicate as ion-exchangers. In this investigation, the focus was on the study of the effect of pH, concentration and nature of the exchanging ion on the exchange capacity of the synthesised silicates.

### 2. Experimental

All the chemicals used were of AR grade and sodium silicate used was of Riedel-De Haen Ag Seelze, Hannover.

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\*For correspondence

### 2.1 Preparation of metal silicate

MnSO<sub>4</sub> solution (21.125 g of MnSO<sub>4</sub>·H<sub>2</sub>O) was added dropwise, with constant stirring, to a solution of sodium silicate (28.035 g of Na<sub>2</sub>SiO<sub>3</sub> in 300 ml water). The mixture was heated on a low flame for about two hours. The precipitate was washed with distilled water till free from SO<sub>4</sub><sup>2-</sup> and Cl<sup>-</sup> ions, filtered and dried in an oven at 80 ± 2°C for 36 h. The lumps formed after drying, were ground to powder form and stored.

Nickel silicate and zinc silicate were also prepared exactly in the similar manner except that nickel sulphate (32.846 g of NiSO<sub>4</sub>·7H<sub>2</sub>O in 200 ml water) and zinc sulphate (35.945 g of ZnSO<sub>4</sub>·7H<sub>2</sub>O in 200 ml water) solutions were used in place of manganese sulphate solution.

Synthesised silicates were found to be stable above pH 4. Their ion-exchange properties were confirmed by pH-metric titration (Klechkovsky 1958).

The total exchange capacity of these metallic silicates were determined (Fisher and Kunin 1955) and found to be

Manganese silicate	= 4.9 meq. per gm.
Nickel silicate	= 4.1 meq. per gm.
Zinc silicate	= 3.7 meq. per gm.

### 2.2 Preparation of solutions of metal ammine complexes

Ammine complexes of the metals were prepared by dissolving water soluble metal salts in aqueous ammonia in appropriate quantities. For the adjustment of pH, 1:4 ammonia solution and dilute acetic acid were used. All the pH measurements were carried out with the help of a Systronic pH-meter in conjunction with an Elico glass electrode.

### 2.3 Determination of $q_A$ and $K_d$ values

25.0 ml of metal ammine solution of specified composition and pH value was shaken for an hour in a stoppered conical flask containing 225 mg of the metallic silicate in a mechanical shaker (wrist action with speed controlling device). After equilibration, 5 ml of the clear supernatant was titrated complexometrically (Flaschka 1964; Vogel 1979) against EDTA with Eriochrome Black-T as the indicator for Cd<sup>2+</sup> and Zn<sup>2+</sup> and Murexide for Co<sup>2+</sup> and Ni<sup>2+</sup>. Cu<sup>2+</sup> was determined iodometrically (Vogel 1979). From this, and the known initial concentration of the metal ion, the amount taken up by the metallic silicate was calculated.

$K_d$  values were calculated using the relation (Nuffield advanced science 1970)

$$K_d = \frac{100 - X}{X} \cdot \frac{V}{m},$$

where

$K_d$  = distribution coefficient,

$X$  = % amount of the exchanging ion present in the equilibrium solution,

$V$  = volume of the solution in ml,

$m$  = quantity of the silicate in g.

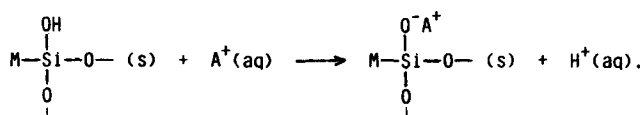
All the experimental observations were made at room temperature (25 ± 5°C).

### 3. Results and discussion

- (1) The uptake of the metal ion ( $\text{Co}^{2+}$ ,  $\text{Cu}^{2+}$  and  $\text{Zn}^{2+}$ ) increases with increase in  $\text{pH}$  of the solution, attains a maximum and then decreases. However, the uptake for  $\text{Cd}^{2+}$  and  $\text{Ni}^{2+}$  increases continuously (tables 1–3).
- (2)  $q_A$  value increases with increase in the concentration of the exchanging ions (table 4–6).
- (3) The increase in order of the uptake of investigated metal ions is as follows:  
 $\text{Ni}^{2+} < \text{Co}^{2+} < \text{Cd}^{2+} < \text{Zn}^{2+} < \text{Cu}^{2+}$ .
- (4) The increasing order of the uptake for different metallic silicates investigated is (figure 1)

zinc silicate < nickel silicate < manganese silicate

A probable mechanism for cation exchange in the metal silicates may be shown as



The increase in  $q_A$  with  $\text{pH}$  is presumably due to increase in concentration of  $\text{OH}^-$  ions, which facilitates the release of  $\text{H}^+$  ions. Decrease in the  $q_A$  value of  $\text{Cu}^{2+}$ ,  $\text{Zn}^{2+}$  and  $\text{Co}^{2+}$  after a certain  $\text{pH}$ , is probably because of the competition of excessive  $\text{NH}_4^+$  ions, as complete ammine complex formation of these ions takes place around

**Table 1.** Effect of  $\text{pH}$  on the uptake of metal ions by manganese silicate.

Amount of manganese silicate taken = 0.225 g; volume of the exchanging ion solution used = 25.0 ml; concentration of the exchanging ion solution = 0.01 M

$\text{pH}$	Amount of exchanging ion taken up ( $q_A$ ) (meq)				$K_d (\times 10^2)$			
	$\text{Cu}^{2+}$	$\text{Zn}^{2+}$	$\text{Cd}^{2+}$	$\text{Ni}^{2+}$	$\text{Cu}^{2+}$	$\text{Zn}^{2+}$	$\text{Cd}^{2+}$	$\text{Ni}^{2+}$
8.5	0.1575	0.1750	0.1125	0.0475	1.88	2.59	0.90	0.26
9.0	0.1800	0.1825	0.1300	0.0575	2.86	2.97	1.20	0.33
9.5	0.2250	0.2050	0.1500	0.0750	9.99	5.06	1.67	0.48
10.0	0.2150	0.2175	0.1675	0.0925	6.83	7.31	2.24	0.65
10.5	0.2000	0.2125	0.1825	0.1000	4.44	6.20	2.97	0.74
11.0	0.1850	0.2050	0.1925	0.1050	3.16	5.06	3.68	0.80

**Table 2.** Effect of  $\text{pH}$  on the uptake of metal ions by nickel silicate.

Amount of nickel silicate taken = 0.225 g; volume of the exchanging ion solution used = 25.0 ml; concentration of the exchanging ion solution = 0.01 M

$\text{pH}$	Amount of exchanging ion taken up ( $q_A$ ) (meq)				$K_d (\times 10^2)$			
	$\text{Cu}^{2+}$	$\text{Zn}^{2+}$	$\text{Cd}^{2+}$	$\text{Co}^{2+}$	$\text{Cu}^{2+}$	$\text{Zn}^{2+}$	$\text{Cd}^{2+}$	$\text{Co}^{2+}$
8.5	0.1750	0.1450	0.0600	0.0550	2.59	1.53	0.35	0.31
9.0	0.1925	0.1600	0.0750	0.0650	3.72	1.98	0.47	0.39
9.5	0.2050	0.1700	0.0875	0.0775	5.06	2.36	0.59	0.49
10.0	0.2000	0.1800	0.1000	0.0900	4.44	2.85	0.74	0.63
10.5	0.1875	0.1700	0.1125	0.1000	3.33	2.36	0.90	0.74
11.0	0.1750	0.1575	0.1225	0.0950	2.59	1.88	1.00	0.68

**Table 3.** Effect of pH on the uptake of metal ions by zinc silicate.

Amount of zinc silicate taken = 0.225 g; volume of the exchanging ion solution used = 25.0 ml; concentration of the exchanging ion solution = 0.01 M

pH	Amount of exchanging ion taken up ( $q_A$ ) (meq)				$Kd(\times 10^2)$			
	Cu <sup>2+</sup>	Cd <sup>2+</sup>	Co <sup>2+</sup>	Ni <sup>2+</sup>	Cu <sup>2+</sup>	Cd <sup>2+</sup>	Co <sup>2+</sup>	Ni <sup>2+</sup>
8.5	0.155	0.0300	0.0225	0.025	1.81	0.15	0.11	0.12
9.0	0.170	0.0400	0.0300	0.032	2.36	0.21	0.15	0.16
9.5	0.182	0.0500	0.0400	0.037	2.97	0.28	0.20	0.19
10.0	0.175	0.0575	0.0550	0.042	2.59	0.33	0.28	0.22
10.5	0.125	0.0675	0.0700	0.047	1.11	0.41	0.43	0.26
11.0	0.100	0.0750	0.0650	0.050	0.74	0.48	0.39	0.28

**Table 4.** Effect of concentration on the uptake of metal ions by manganese silicate.

Amount of manganese silicate used = 0.225 g; volume of the exchanging ion solution used = 25.0 ml; pH of various exchanging ion solutions Cu<sup>2+</sup> = 9.5; Zn<sup>2+</sup> = 10.0; Cd<sup>2+</sup> = 11.0 and Ni<sup>2+</sup> = 11.0

Initial concentration (mol/l)	Amount of exchanging ion taken for equilibrium (meq)	Amount of exchanging ion taken up ( $q_A$ ) (meq)				$Kd(\times 10^2)$			
		Cu <sup>2+</sup>	Zn <sup>2+</sup>	Cd <sup>2+</sup>	Ni <sup>2+</sup>	Cd <sup>2+</sup>	Zn <sup>2+</sup>	Cd <sup>2+</sup>	Ni <sup>2+</sup>
0.0025	0.062	0.060	0.0600	0.0575	0.0550	33.61	33.61	12.78	8.81
0.0050	0.125	0.120	0.1225	0.1150	0.0750	26.67	26.67	12.78	1.67
0.0100	0.250	0.225	0.2175	0.1925	0.1050	9.99	7.31	3.68	0.81
0.0125	0.322	0.270	0.2575	0.2100	0.1275	5.77	4.39	2.08	0.72
0.0167	0.417	0.305	0.2850	0.2250	0.1475	3.03	2.42	1.30	0.61
0.0250	0.625	0.330	0.3100	0.2425	0.1650	1.24	1.09	0.70	0.40
0.0500	1.250	0.350	0.3300	0.2600	0.1800	0.43	0.40	0.29	0.19

**Table 5.** Effect of concentration on the uptake of metal ions by nickel silicate.

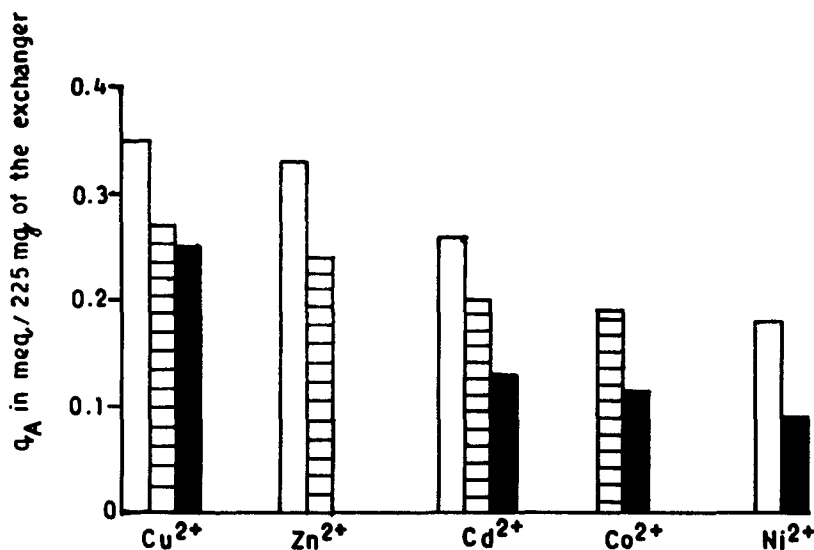
Amount of nickel silicate used = 0.225 g; volume of the exchanging ion solution used = 25.0 ml; pH of various exchanging ion solutions\*: Cu<sup>2+</sup> = 9.5; Zn<sup>2+</sup> = 10.0; Cd<sup>2+</sup> = 11.0 and Co<sup>2+</sup> = 10.5

Initial concentration (mol/l)	Amount of exchanging ion taken for equilibrium (meq)	Amount of exchanging ion taken up ( $q_A$ ) (meq)				$Kd(\times 10^2)$			
		Cu <sup>2+</sup>	Zn <sup>2+</sup>	Cd <sup>2+</sup>	Co <sup>2+</sup>	Cu <sup>2+</sup>	Zn <sup>2+</sup>	Cd <sup>2+</sup>	Co <sup>2+</sup>
0.0025	0.062	0.0575	0.0575	0.0425	0.0400	12.78	12.78	9.33	2.02
0.0050	0.125	0.1150	0.1000	0.0800	0.0725	12.78	4.44	1.98	1.51
0.0100	0.250	0.2050	0.1800	0.1225	0.1000	5.06	2.86	1.06	0.74
0.0125	0.322	0.2300	0.2000	0.1450	0.1300	2.78	1.82	0.01	0.71
0.0167	0.417	0.2450	0.2150	0.1625	0.1550	1.58	1.18	0.71	0.66
0.0250	0.625	0.2600	0.2250	0.1800	0.1775	0.79	0.63	0.45	0.44
0.0500	1.250	0.2700	0.2400	0.2000	0.1925	0.31	0.26	0.21	0.21

\*pH of exchanging ion solution is kept constant to see the effect of concentration, but it is that pH at which uptake of that exchanging ion is maximum.

**Table 6.** Effect of concentration on the uptake of metal ions by zinc silicate. Amount of zinc silicate used = 0.225 g; volume of the exchanging ion solution used = 25.0 ml; pH of various exchanging ion solutions:  $\text{Cu}^{2+} = 9.5$ ;  $\text{Cd}^{2+} = 11.9$ ;  $\text{Co}^{2+} = 10.5$  and  $\text{Ni}^{2+} = 11.0$

Initial concentration (mol/l)	Amount of exchanging ion taken for equilibrium (meq)	Amount of exchanging ion taken up ( $q_A$ ) (meq)				$K_d (\times 10^2)$			
		$\text{Cu}^{2+}$	$\text{Zn}^{2+}$	$\text{Co}^{2+}$	$\text{Ni}^{2+}$	$\text{Cu}^{2+}$	$\text{Zn}^{2+}$	$\text{Co}^{2+}$	$\text{Ni}^{2+}$
0.0025	0.062	0.0500	0.0200	0.0175	0.0150	4.63	0.53	0.42	0.35
0.005	0.125	0.0975	0.0350	0.0325	0.030	3.94	0.43	0.38	0.35
0.01	0.25	0.1820	0.0750	0.0700	0.050	2.97	0.47	0.43	0.28
0.0125	0.322	0.1950	0.0925	0.0900	0.062	1.71	0.45	0.43	0.26
0.0167	0.417	0.2050	0.1050	0.0975	0.072	1.07	0.37	0.34	0.23
0.025	0.625	0.2150	0.1175	0.1050	0.080	0.58	0.26	0.11	0.16
0.05	1.25	0.2250	0.1300	0.1150	0.090	0.24	0.13	0.11	0.09



**Figure 1.** Showing difference in maximum uptake of the investigated metal ions by manganese, nickel and zinc silicates. Concentration – 0.05 M. pH:  $\text{Cu}^{2+} = 9.5$ ;  $\text{Zn}^{2+} = 10.0$ ;  $\text{Cd}^{2+} = 11.0$ ;  $\text{Co}^{2+} = 10.5$  and  $\text{Ni}^{2+} = 11.0$  (selected pH is that at which uptake of the metal ion is maximum) manganese silicate – □, nickel silicate – ▨, zinc silicate – ■.

pH 9.5, 10.0 and 10.5, respectively. But in case of  $\text{Cd}^{2+}$  and  $\text{Ni}^{2+}$ , complete ammine complexation occurs at pH 11, so there is continuous increase in  $q_A$  value upto pH 11 (Kragten 1978).

During the study of the effect of external concentration of exchanging ion, increase in  $q_A$  with concentration was observed. However, the observed extent of rise, decreases beyond certain limit of the concentration of exchanging ion. This is presumably due to the possible lowering of the ionic activity at higher concentration. A diminution of exchange potential with decreasing ionic activity is well known (Kunin 1960).

The observed differences in  $q_A$  values for the different metal ions seems to be connected with combined effect of charge and size, i.e. ionic potential ( $\phi$ ) of the exchanging ion. The higher the value of  $\phi$ , the greater is quantity  $q_A$ .

The selected exchanging ions have identical formal charge i.e. plus two, but in the absence of definite knowledge of the structural data of the complex species in aqueous solution, it may not be unreasonable to make some qualitative estimation of the complex ionic size on the basis of the known symmetry (Bjerrus 1957) and ionic radius (Greenwood 1984) of the central metal atom [ $\text{Zn}^{2+} - 75 \text{ pm}$ ,  $\text{Cd}^+ - 95 \text{ pm}$ ,  $\text{Co}^{2+} - 74 \text{ pm}$ ,  $\text{Ni}^{2+} - 69 \text{ pm}$ ,  $\text{Cu}^{2+} - 73 \text{ pm}$ ]. Because of known differences in the symmetry of amines, the dimensions of the simple ions will not solely determine the size of the complex species. Obviously the tetrahedral symmetry involves a more compact structure than octahedral symmetry. That is the overall size of  $[\text{Zn}(\text{NH}_3)_4]^{2+}$  is less than octahedral  $[\text{Ni}(\text{NH}_3)_6]^{2+}$ . Further, it appears that  $[\text{Cu}(\text{NH}_3)_4]^{2+}$  ion has got square planar geometry thereby a laminar structure. Hence its size, if not less, may not be larger than tetrahedral  $[\text{Zn}(\text{NH}_3)_4]^{2+}$  and  $[\text{Cd}(\text{NH}_3)_4]^{2+}$  ions. Cobalt forms  $[\text{Co}(\text{NH}_3)_x]^{2+}$ , where  $x = 4$  or  $6$ . Thus the ionic radius of investigated ions would be  $\text{Cu}(\text{square planar}) < \text{Zn}(\text{tetrahedral}) < \text{Cd}(\text{tetrahedral}) < \text{Cd}(\text{tetrahedral or octahedral}) < \text{Ni}(\text{octahedral})$ .

Ionic potential of these will be therefore in the reverse order (i.e.  $\text{Cu}(\text{square planar}) > \text{Zn}(\text{tetrahedral}) > \text{Cd}(\text{tetrahedral}) > \text{Co}(\text{tetrahedral or octahedral}) > \text{Ni}(\text{octahedral})$ ).

It is in agreement with the observed order of  $q_A$  (maximum value).

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