EQUILIBRIUM UPTAKE OF CERTAIN CATIONIC METAL AMMINE COMPLEXES ON HYDROUS MANGANESE DIOXIDE

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ABSTRACT

Equilibrium uptake (q_A) of ammine complexes of Cu^{2+}, Cd^{2+}, Ni^{2+} and Zn^{2+} on hydrous manganese dioxide has been studied at different pH and ionic concentrations. It has been found that q_A and K_d value of Cu^{2+}, Cd^{2+}, Ni^{2+} and Zn^{2+} increase with increase in pH, attains a maximum and then decreases. However q_A for Ni^{2+} increase continuously with the increase in pH. q_A and K_d values also attains a maximum with increasing concentration (0.10M) beyond which a fall has been observed. The increasing order of q_A of the investigated complex ions is $- Ni^{2+} < Cd^{2+} < Zn^{2+} < Cu^{2+}$.

Key words: Ion–exchange; Metal ammines; Hydrous manganese dioxide

INTRODUCTION

The last two decades have been a clear revival in inorganic ion–exchangers studies. A major area has been in the study of hydrous oxides[1]. These exhibit special selectivities for certain ions and are radiation stable. The hydrous manganese dioxide is used as an adsorption material in cardiopulmonary angiog[2]. It has also been used for treatment of wastewater and exhaust gases to remove toxic and carcinogenic substances[3]. The properties of MnO_2 as ion exchanger have not been much explored. The present paper describes the results of investigation on hydrous manganese dioxide as an ion–exchanger. The focus in the investigation is on the study of the effect of pH, concentration and nature (i.e. stereochemical effect) of the exchanging ion on the exchange capacity of the synthesised hydrous manganese dioxide.

EXPERIMENTAL

All the chemicals used were of AR grade.

Preparation of MnO_2: It was prepared[4] by adding $KMnO_4$ solution (21.3 gL^{-1}) dropwise to a $MnSO_4$ solution (71.4 gL^{-1}) heated to about 90^0C. The resulting manganese dioxide was washed, dried at 60^0C and then sieved.

Its ion–exchange property was confirmed by pH–metric titration.[5]

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.

Determination of q_A and K_d values: 250 mL of the metal ammine solution of specified composition and pH value was shaken for one hour in a stoppered conical flask containing 250 mg of the manganese dioxide in a mechanical shaker (wrist action with speed controlling device). After equillibration 5.0 mL of clear supernatant was titrated complexometrically[6] against EDTA with Erichrome black T as the indicator for Cd^{2+} and Zn^{2+} and murexide for Ni^{2+} and Cu^{2+}.

From this and the known initial concentration of the metal ammine, the amount taken up by manganese dioxide was calculated. K_d values were calculated by using the relaiton[7].

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

All the experimental observations are done at room temperature (25.5° C).

Effect of pH on the uptake of metal ammine complexes by the manganese dioxide:

Amount of the manganese dioxide taken   = 0.250 g

Volume of the exchanging ion solution   = 25.0 mL

Concentration of the exchanging ion solution   = 0.01M

pH	Equilibrium uptake of the exchanging metal ammine, q_A (meg)				K_d (x 10^2)			
	Cu^{2+}	Zn^{2+}	Cd^{2+}	NI^{2+}	Cu^{2+}	Zn^{2+}	Cd^{2+}	NI^{2+}
8.0	0.235	0.135	0.195	0.050	15.66	1.17	3.55	0.25
8.5	0.240	0.155	0.180	0.065	24.00	1.63	2.57	0.35
9.0	0.245	0.070	0.160	0.070	49.00	0.38	1.77	0.38
9.5	0.240	0.075	0.155	0.075	24.00	0.43	1.63	0.42
10.0	0.210	0.080	0.145	0.085	5.25	0.47	1.38	0.51
10.5	0.130	0.120	0.140	0.090	1.08	0.92	1.27	0.56

Effect of concentration on the uptake of metal ammine complexes by the manganese dioxide:

Amount of the manganese dioxide taken   = 0.250 g

Volume of the exchanging ion solution   = 25.0 mL

pH of various exchanging ion solution $= Cu^{2+}$ (9.0), Zn^{2+} (8.5), Cd^{2+} (8.0), Ni^{2+} (10.5)

Initial conc. Mol L^{-1}	Equilibrium uptake of the exchanging metal ammine, q_A (meq)				K_d (x 10^2)			
	Cu^{2+}	Zn^{2+}	Cd^{2+}	NI^{2+}	Cu^{2+}	Zn^{2+}	Cd^{2+}	NI^{2+}
0.005	0.122	0.110	0.080	0.065	39.65	7.30	1.77	1.08
0.01	0.245	0.155	0.180	0.075	49.00	1.63	2.57	0.43
0.02	0.270	0.180	0.195	0.080	1.17	0.56	0.63	0.19
0.05	0.285	0.195	0.200	0.100	0.29	0.18	0.19	0.09
0.1	0.550	0.270	0.250	0.150	0.28	0.12	0.11	0.03
0.2	0.250	0.050	0.150	0.050	0.05	0.01	0.03	0.01

RESULTS AND DISCUSSION

i.   The equilibrium uptake, q_A, of Cu^{2+}, Cd^{2+} and Zn^{2+} ammine complexes initially increases with increase in the pH of the external solution, attains a maximum and then decreases, however, it increases continuously for Ni^{2+}.

ii. q_A and K_d of Cu^{2+}, Cd^{2+}, Ni^{2+} and Zn^{2+} ammine complexes increases with increasing concentration (0.01M) and then decreases.

iii. In the investigated complexes the Cu^{2+} ammine complex has the maximum q_A value, the order being Cu^{2+} (ammine) > Zn^{2+} (ammine) > Cd^{2+} (ammine) > Ni^{2+} (ammine).

The increase in q_A with pH is presumably due to increase in concentration of OH ions, which facilitates the release of H^+ ions. Decrease in the qA value of metal ions is because of the competition of excessive NH_4+ ions, as complete ammine complex formation[8] of these ions takes place around pH 9.0, 8.5, 9.0 and 10.5 for Cd^{2+}, Zn^{2+}, Cu^{2+} and Ni^{2+}, respectively.

The observed increase in q_A with the increase in the concentration of the exchanging solution is because of increase in the ionic activity[9]. However the observed extent of rise decreases beyond a certain limit, which is due to the possible lowering of the ionic activity at higher concentrations. A diminition of exchange potential with decreasing ionic activity is well known[9].

The observed difference in q_A values for the different metal ammine complexes seems to be connected with combined effect of charge and size, i.e. ionic potential (ϕ) of the exchanging ion. The higher the value of ϕ, the more is quantity q_A.

The selected exchanging ions have identical formal charge i.e.+2, 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 quantitative estimation of the complex ionic size on the basis of

the known symmetry[10] and ionic radius[11] of the central metal atom [Zn^{2+}–75 pm, Cd^{2+}–95 pm, NI^{2+}–69 pm, Cu^{2+}–73 pm]. Because of known differences in the symmetry of ammines, 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, i.e. the overall size of $[Zn(NH_3)]^{2+}$ is less than octahedral $[Ni(NH_3)_6]^{2+}$. Further it appears that $[Cu(NH_3)_4]^{2+}$ ion has got square planar geometry; thereby a laminar structure. Hence its size, if not less, may not be larger than tetrahedral $[Zn(NH_3)_4]^{2+}$ and $[Cd(NH_3)_4]^{2+}$ ions. Thus the ionic radius of investigated ions would be Cu (square planar) < Zn (tetrahedral) < CD (tetrahedral) < Ni (octahedral).

Ionic potential of these will be therefore in the reverse order i.e. Cu (square planar) > Zn (tetrahedral) > Cd (tetrahedral) > Ni (octahedral).

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

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