Int. J. Chem. Sci. : 2 (3), 2004, 355–360

KINETICS OF THE EXCHANGE OF SOME METAL AMMINE COMPLEXES BY HYDROUS MANGANESE DIOXIDE

BRIJ BHUSHAN and MANJU RANI

Department of Chemistry, Maharshi Dayanand University, ROHTAK (Haryana) INDIA

ABSTRACT

The rate of exchange of metal ammine complexes of Cu (II), Zn (II), Cd (II) and Ni (II) in hydrous manganese dioxide has been studied at different concentration of the exchanging ions. The rate of exchange is controlled by both types of the diffusion mechanisms i.e. diffusion and particle diffusion. Up to 0.10 M concentration, both; film and particle diffusion controls the rate process, however, particle diffusion controls the rate process above 0.10 M^1. It has been found that the exchange of the selected cations Cu (II), Zn (II), Cd (II) and Ni (II) is characteristically dependent upon the nature of the exchanging ions.

Key words : Metal amine complex, Exchange, Hydrous manganese dioxide

INTRODUCTION

Inorganic ion exchangers have established[2–4] their place in analytical chemistry due to their differential selectivity for metal ions. The rate factor in the ion exchange process is of great importance for economically viable industrial use of these materials and in understanding the mechanism of exchange process. A kinetic study has been performed in hydrous manganese dioxide for the exchange of some metal cations namely Cu (II), Zn (II), Cd (II) and Ni (II) etc. applying the Helfferich Plleset Equation[5].

EXPERIMENTAL

All the chemicals used were of AR grade.

Preparation of hydrous manganese dioxide

It was prepared[6] by adding a $KMnO_4$ solution (21.3g L^{-1}) dropwise to a $MnSO_4$ solution (71.4g L^{-1}) heated to about 90°C. The resulting manganese dioxide was washed, dried at 60°C and then sieved. Its ion exchange property was confirmed by pH– metric titrations[7].

Preparation of solution of metal ammine complexes

Ammine complexes of the metals were prepared by dissolving water–soluble salts in aqueous ammonia in appropriate amounts. 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 Systronic pH–meter in conjunction with an Elico–glass electrode.

Kinetic measurements

25 mL of the metal ammine solutions of specified concentration and pH was shaken with 250 mg of the manganese dioxide for specified time interval in a stoppered conical flask. The solution is immediately centrifuged, and aliquots of the supernatant solution are titrated complexometrically[8] to determine the amount of exchanging ions remaining in the solution.

A series of similar determinations were carried out at different intervals of time using separate sample mixtures of identical composition. The fractional attainment of equilibrium F at any time is then calculated by the relation –

$$F = \frac{\text{Amount of the metal ion complex taken up at time 't'}}{\text{Total amount of the metal ion complex taken up at equilibrium}}$$

The Bt (time co–ordinate) values corresponding to experimentally determined 'F' values were obtained from the Reichenberg's table[9].

The effective diffusion coefficient D^i ($cm^2\ sec^{-1}$) were calculated using the relation –

$$B = \Pi^2 D^i / r^2 \text{ or } \Pi^2 D^i / r^2 = Bt/t \text{ or } D^i = Bt \times r^2 / t \times \Pi^2$$

Exchange rate of metal ammines

Volume of the exchanging ion solution used = 25 mL

pH of various exchanging ion solutions: Cu (II) –9.0, Zn (II)–8.5, Cd (II)–8.0, Ni (II)–10.5

Table 1. Concentration of the exchanging ion solution = 0.01 M

Time	AMOUNT TAKEN UP IN MEO				F				Bt			
	Cu (II)	Zn (II)	Cd (II)	Ni (II)	Cu (II)	Zn (II)	Cd (II)	Ni (II)	Cu (II)	Zn (II)	Cd (II)	Ni (II)
30 sec	0.080	0.070	0.090	0.045	0.69	0.70	0.75	0.64	0.703	0.734	0.905	0.569
1 min	0.090	0.075	0.100	0.055	0.78	0.75	0.83	0.71	1.028	0.905	1.28	0.765
2 min	0.095	0.080	0.105	0.060	0.82	0.80	0.87	0.78	1.224	1.12	1.543	1.028
5 min	0.105	0.085	0.110	0.065	0.91	0.85	0.91	0.85	1.91	1.404	1.91	1.404
10 min	0.110	0.090	0.115	0.070	0.96	0.90	0.96	0.92	2.72	1.8	2.72	2.03
20 min	0.115	0.100	0.120	0.070	1.00	1.00	1.00	1.00	–	–	–	–
30 min	0.115	0.100	0.120	0.070	1.00	1.00	1.00	1.00	–	–	–	–
45 min	0.115	0.100	0.120	0.070	1.00	1.00	1.00	1.00	–	–	–	–
60 min	0.115	0.100	0.120	0.070	1.00	1.00	1.00	1.00	–	–	–	–

Table 2. Concentration of the exchanging ion solution = 0.02 M

Time	AMOUNT TAKEN UP IN MEO				F				Bt			
	Cu (II)	Zn (II)	Cd (II)	Ni (II)	Cu (II)	Zn (II)	Cd (II)	Ni (II)	Cu (II)	Zn (II)	Cd (II)	Ni (II)
30 sec	0.155	0.100	0.115	0.080	0.72	0.74	0.79	0.76	0.798	0.868	1.073	0.944
1 min	0.170	0.110	0.125	0.085	0.79	0.81	0.86	0.80	1.073	1.171	1.468	1.120
2 min	0.185	0.120	0.130	0.090	0.86	0.88	0.89	0.85	1.368	1.623	1.71	1.404
5 min	0.200	0.125	0.135	0.095	0.93	0.92	0.93	0.90	2.16	2.030	2.16	1.404
10 min	0.210	0.130	0.140	0.100	0.97	0.96	0.96	0.95	3.01	2.720	2.72	1.80
20 min	0.215	0.135	0.145	0.105	1.00	1.00	1.00	1.00	–	–	–	–
30 min	0.215	0.135	0.145	0.105	1.00	1.00	1.00	1.00	–	–	–	–
45 min	0.215	0.135	0.145	0.105	1.00	1.00	1.00	1.00	–	–	–	–
60 min	0.215	0.135	0.145	0.105	1.00	1.00	1.00	1.00	–	–	–	–

Table 3. Concentration of the exchanging ion solution = 0.01 M

Time	F				BT				$D^i/D^{-i} \times 10^{-12}$ ($cm^2\ sec^{-1}$)			
30 sec	0.65	0.75	0.81	0.78	0.594	0.905	1.171	0.028	2.86 (2.83)	5.00 (5.74)	5.00 (4.45)	2.66 (2.76)
1 min	0.75	0.84	0.86	0.83	0.905	1.340	1.468	1.280	2.86 (2.83)	5.00 (5.74)	5.00 (4.45)	2.66 (2.76)
2 min	0.78	0.89	0.90	0.89	1.028	1.71	1.80	1.71	2.86 (2.83)	5.00 (5.74)	5.00 (4.45)	2.66 (2.76)
5 min	0.93	0.93	0.95	0.94	2.16	2.16	2.50	2.32	2.86 (2.83)	5.00 (5.74)	5.00 (4.45)	2.66 (2.76)
10 min	0.96	0.97	0.98	0.97	2.73	3.01	2.41	3.01	2.86 (2.83)	5.00 (5.74)	5.00 (4.45)	2.66 (2.76)
20 min	1.00	1.00	1.00	1.00	–	–	–	–	2.86 (2.83)	5.00 (5.74)	5.00 (4.45)	2.66 (2.76)
30 min	1.00	1.00	1.00	1.00	–	–	–	–	2.86 (2.83)	5.00 (5.74)	5.00 (4.45)	2.66 (2.76)
45 min	1.00	1.00	1.00	1.00	–	–	–	–	2.86 (2.83)	5.00 (5.74)	5.00 (4.45)	2.66 (2.76)
60 min	1.00	1.00	1.00	1.00	–	–	–	–	2.86 (2.83)	5.00 (5.74)	5.00 (4.45)	2.66 (2.76)

Table 4. Concentration of the exchanging ion solution = 0.2 M

Time	F				BT				$D^i/D^{-i} \times 10^{-12}$ (cm^2 sec^{-1})			
30 sec	0.67	0.78	0.82	0.81	0.647	1.028	1.224	1.171	3.33 (3.50)	4.87 (5.75)	4.57 (4.45)	3.71 (3.80)
1 min	0.76	0.85	0.87	0.88	0.944	1.404	1.543	1.623	3.33 (3.50)	4.87 (5.75)	4.57 (4.45)	3.71 (3.80)
2 min	0.83	0.90	0.89	0.90	1.280	1.80	1.71	1.80	3.33 (3.50)	4.87 (5.75)	4.57 (4.45)	3.71 (3.80)
5 min	0.93	0.93	0.95	0.94	2.160	2.16	2.50	2.32	3.33 (3.50)	4.87 (5.75)	4.57 (4.45)	3.71 (3.80)
10 min	0.96	0.97	0.98	0.97	2.72	3.01	3.41	3.01	3.33 (3.50)	4.87 (5.75)	4.57 (4.45)	3.71 (3.80)
20 min	1.00	1.00	1.00	1.00	–	–	–	–	3.33 (3.50)	4.87 (5.75)	4.57 (4.45)	3.71 (3.80)
30 min	1.00	1.00	1.00	1.00	–	–	–	–	3.33 (3.50)	4.87 (5.75)	4.57 (4.45)	3.71 (3.80)
45 min	1.00	1.00	1.00	1.00	–	–	–	–	3.33 (3.50)	4.87 (5.75)	4.57 (4.45)	3.71 (3.80)
60 min	1.00	1.00	1.00	1.00	–	–	–	–	3.33 (3.50)	4.87 (5.75)	4.57 (4.45)	3.71 (3.80)

RESULTS AND DISCUSSION

The results presented in the Tables 1, 2, 3 and 4 bring out the following facts:

(i) The overall exchange takes place in two distinct phases, relatively quick process in the initial stage and which is followed by a slower one, till equilibrium is reached.

(ii) Average radius of the exchanger particle and pH of the external solution remaining the same 'F' increases with the external concentration of the exchanging ion solution and becomes almost independent of the concentration above 0.10 M concentration.

(iii) The rate of exchange of the metal ammine complexes decreases in the following order.

Cu^{2+} –ammine > Zn^{2+} – ammine > Cd^{2+} – ammine > Ni^{2+} – ammine

From the results given here, it appears that up to 0.10 M concentrations, both film and particle diffusion controls the rate process, however, particle diffusion controls the rate process above 0.10 M concentrations. A quantitative estimation of the contribution of particle diffusion may possibly be made by a graphic analysis of Bt vs. t curves, a reference to these curves shows that the plots corresponding to the later part of the sorption lies on a straight line, on extrapolation of which intersects the Bt–axis (Fig. 1). However, the ideal curve[10] in terms of Helffrich Plleset equation[5], for complete particle diffusion for which diffusion coefficient 'D^i' becomes independent of F (fractional attainment of equilibrium) is a straight line passing

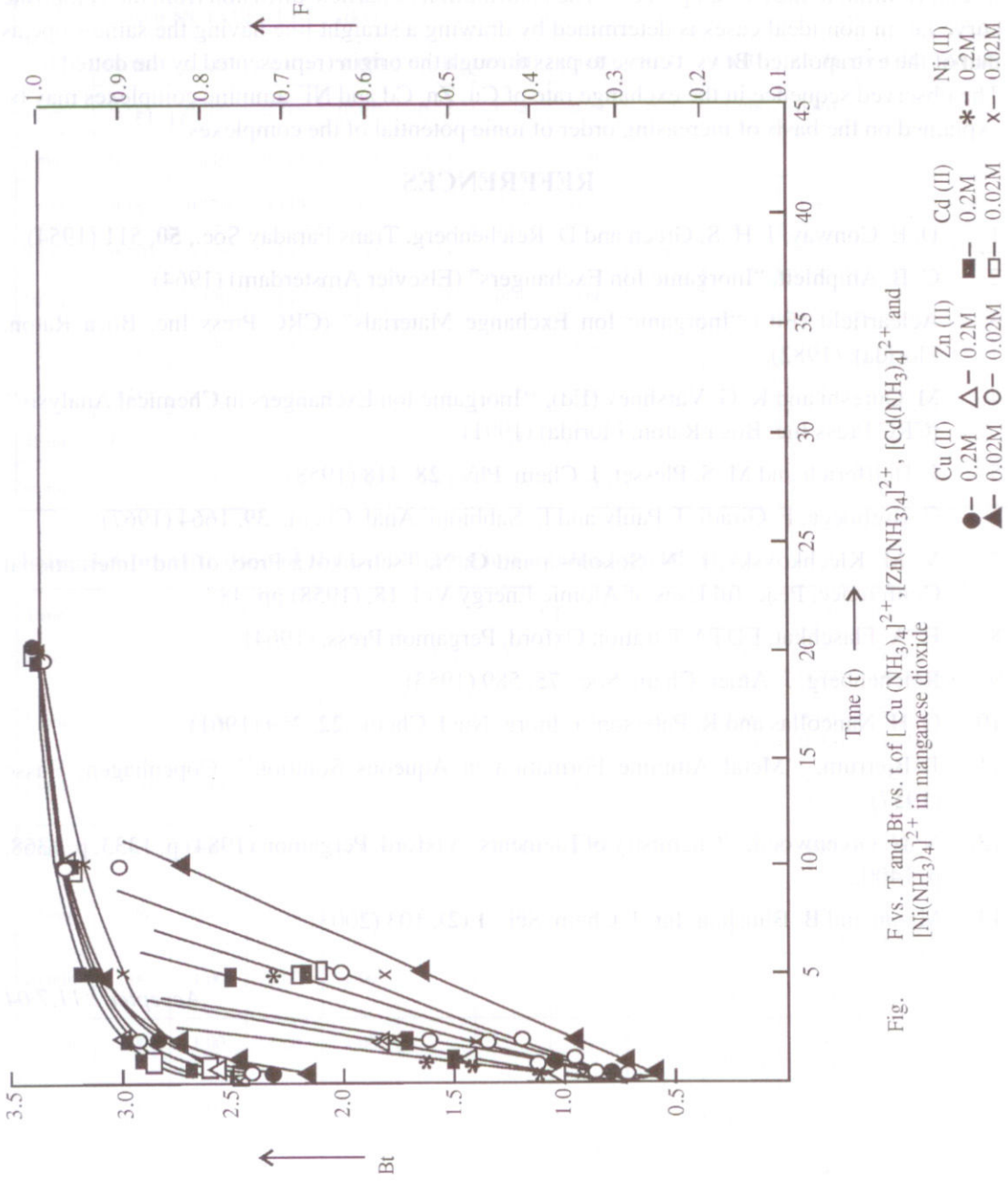

Fig. F vs. T and Bt vs. t of $[Cu(NH_3)_4]^{2+}$, $[Zn(NH_3)_4]^{2+}$, $[Cd(NH_3)_4]^{2+}$ and $[Ni(NH_3)_4]^{2+}$ in manganese dioxide

through the origin. Non–ideal behavior of the plots indicates that film diffusion is still making its contribution to the overall process. The contribution of particle diffusion from the composite curve i.e. in non ideal cases is determined by drawing a straight line having the same slope as that of the extrapolated Bt vs. t curve to pass through the origin (represented by the dotted line). The observed sequence in the exchange rate of Cu, Zn, Cd and Ni^{-} ammine complexes may be explained on the basis of increasing order of ionic potential of the complexes[11–13]

REFERENCES

1. D. E. Conway, J. H. S. Green and D. Reichenberg, Trans Faraday Soc., **50**, 511 (1954).
2. C. B. Amphlett, "Inorganic Ion Exchangers" (Elsevier Amsterdam) (1964).
3. Aclearfield (Ed.) "Inorganic Ion Exchange Materials" (CRC Press Inc, Boca Raton, Florida), (1982).
4. M. Qureshi and K. G. Varshney (Ed), ''Inorganic Ion Exchangers in Chemical Analysis'' (CRC Press Inc, Boca Raton, Florida) (1991).
5. F. Helfferich and M. S. Plesset, J. Chem. Phy., **28**, 418 (1958).
6. C. Bigliocca, F. Giradi, J. Pauly and E. Sabbioni, Anal. Chem., **39**, 1664 (1967).
7. V. M. Klechkovsky, L. N. Sokolova and G. N. Tselishkova Proc. of Ind. International Conference, Peaceful Uses of Atomic Energy Vol. 18, (1958) pp. 487.
8. H. A. Flaschkat, EDTA Titration Oxford, Pergamon Press, (1964).
9. Reichenberg, J. Amer. Chem. Soc., **75**, 589 (1953).
10. G. H. Nancollas and R. Paterson, J. Inorg. Nucl. Chem., **22**, 259 (1961).
11. J. Bjerrum, ''Metal Ammine Formation in Aqueous Solution'', Copenhagen, Hasse (1957).
12. N. N. Greenwood, ''Chemistry of Elements'' Oxford. Pergamon (1984) p. 1333, p. 1368, p. 1400.
13. Manju and B. Bhushan, Int. J. Chem. Sci., **1 (2)**, 103 (2003).

Accepted : 11.7.04