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Study of the Extent of Dynamic Interaction of Certain Cationic Metal Ammine Complexes with Magnesium Molybdosilicate

SEEMA and B. BHUSHAN*
Department of Chemistry, Maharshi Dayanand University, Rohtak-124 001, India
E-mail: ssbb1515@yahoo.co.in

The rate of exchange of ammine complexes of Cu(II), Zn(II), Cd(II), Ni(II) and Co(II) in magnesium molybdosilicate has been studied at different concentrations of the exchanging ions. The rate of exchange is controlled by both the mechanisms, *i.e.*, film diffusion and particle diffusion. The rate is controlled by film diffusion at lower concentration, whereas particle diffusion controls the rate process predominantly at and above 0.10 M concentration. It has been found that the rate of exchange of the above selected ammine complexes is characteristically dependent upon the ionic potential of the exchanging ion.

Key Words: Metal ammine complexes, Rate of exchange, Magnesium molybdosilicate.

In analytical chemistry, inorganic ion exchangers have established an important place due to differential selectivity for metal ions[1–3]. The rate factor in the ion exchange process finds importance for economical and industrial uses of these materials. A kinetic study has been undertaken in the magnesium molybdosilicate to find out the rate controlling mechanism for the exchange of some metal ammines namely Cu(II), Zn(II), Cd(II), Ni(II) and Co(II). The particle diffusion coefficient can be calculated quantitatively by Helfferich Plesset equation[4] in an ideal system. However, we have calculated the same in non-ideal system from the slope of the straight line drawn parallel to the Bt (time coordinate) curve passing through the origin.

EXPERIMENTAL

All the chemicals used were of AR grade. Deionized water was used throughout the work. All the observations were recorded at room temperature (30 ± 5°C).

Synthesis of magnesium molybdosilicate

Magnesium molybdosilicate was prepared by mixing the aqueous solution of magnesium sulphate, ammonium molybdate and sodium metasilicate in the mole ratio of 7 : 1 : 4, respectively with constant stirring. Addition of the solutions was in the following order: sodium metasilicate, ammonium molybdate and then magnesium sulphate. The pH of the mixture solution was adjusted to 10 with 1 : 1 ammonia. The precipitates appearing were gel like, left for 24 h, filtered, washed with deionized water 3-4 times and dried at 50°C and finally sieved (0.235×10^5 cm). Its ion exchange behaviour was confirmed by pH-metric titrations.

Preparation of metal ammine complexes

Stock solutions of Cu(II), Zn(II), Cd(II), Ni(II) and Co(II) metal ions of concentration 0.40 M were prepared by dissolving the requisite quantities of AR grade metal sulphates in deionized water. Ammine complexes of the metals of different ionic strengths were obtained by taking appropriate volumes of the stock solutions, adding ammonia solution and adjusting the pH with dilute ammonia (1 : 2) and dilute acetic acid (1 : 2) solution. All the pH measurements were carried out with the help of Systronics pH-meter 335 in conjunction with an Elico glass electrode.

Dynamic interaction measurement

25 mL of the metal ammine solution of specified concentration and specified pH was shaken with 250 mg of the magnesium molybdosilicate for specified time intervals in a stoppered conical flask by a mechanical shaker (wrist action with speed controlling device). The solution was immediately centrifuged and aliquots of the supernatant solution were titrated complexometrically[6] with EDTA solution using eriochrome black T as indicator for Zn(II) and Cd(II), murexide for Co(II) and Ni(II) and iodometrically[7] for Cu(II) to determine the amount of exchanging ions remaining in the solution. Hence, the amount taken up by the exchanger was calculated by knowing initial concentration and final concentration at time t.

A series of similar determinations were carried out at different time intervals using separate sample mixtures of identical composition. The fractional attainment of equilibrium F at any time t 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 coordinate) values corresponding to experimentally determined 'F' values were obtained from the Reichenberg's table[8].

The effective diffusion coefficients D^i ($cm^2\ s^{-1}$) were calculated using the relation:

$$B = \frac{\pi^2 D^i}{r^2}$$

or

$$\frac{Bt}{t} = \frac{\pi^2 D^i}{r^2}$$

or

$$D^i = \frac{Bt}{t} \times \frac{r^2}{\pi^2}$$

RESULTS AND DISCUSSION

The results presented in Tables 1, 2, 3, 4 and 5 bring out the following facts:

1. The overall exchange takes place in two distinct phases: a relatively quick process in the initial stage, *i.e.*, film diffusion, followed by a slower one, *i.e.*, particle diffusion, till equilibrium is reached.
2. Average radius of the exchanger particle and pH of the exchanging solution remaining the same, 'F' increases with the increase in external concentration of the exchanging ion solution and becomes almost independent of the concentration above 0.10 M concentration.
3. The rate of exchange of the metal ammine complexes shows the following order:

$$Cu(II) > Zn(II) > Cd(II) > Co(II) > Ni(II)$$

TABLE-1

Volume of the exchanging ion solution used every time = 25 mL; pH of the exchanging ion [Cu(II)] solution = 9.5

Time (min)	Concentration								$D^i/\bar{D}^i \times 10^{-15}$ ($cm^2 s^{-1}$)
	0.01 M		0.05 M		0.10 M		0.20 M		
	F	Bt	F	Bt	F	Bt	F	Bt	
1	0.75	0.905	0.81	1.171	0.84	1.340	0.85	1.404	13.083 (0.647)
2	0.79	1.073	0.84	1.340	0.86	1.468	0.87	1.543	7.189 (0.647)
5	0.82	1.340	0.87	1.543	0.89	1.710	0.90	1.800	3.354 (0.647)
10	0.86	1.468	0.91	1.910	0.92	2.030	0.93	2.160	2.013 (0.647)
15	0.89	1.710	0.94	2.320	0.95	2.500	0.95	2.500	1.553 (0.647)
20	0.92	2.030	0.95	2.500	0.96	2.720	0.97	3.010	1.402 (0.647)
25	0.94	2.320	0.97	3.010	0.97	3.010	0.98	3.410	1.271 (0.647)
30	0.96	2.720	0.98	3.410	0.98	3.410	0.98	3.410	1.060 (0.647)
45	1.00	—	1.00	—	1.00	—	1.00	—	—
60	1.00	—	1.00	—	1.00	—	1.00	—	—
90	1.00	—	1.00	—	1.00	—	1.00	—	—

TABLE-2

Volume of the exchanging ion solution used every time = 25 mL; pH of the exchanging ion [Zn(II)] solution = 10

Time (min)	Concentration								$D^i/\overline{D}^i \times 10^{-15}$ ($cm^2 s^{-1}$)
	0.01 M		0.05 M		0.10 M		0.20 M		
	F	Bt	F	Bt	F	Bt	F	Bt	
1	0.66	0.620	0.73	0.832	0.75	0.905	0.76	0.944	8.796 (0.751)
2	0.69	0.703	0.75	0.905	0.77	0.985	0.78	1.020	4.752 (0.751)
5	0.75	0.905	0.81	1.171	0.82	1.224	0.83	1.280	2.385 (0.751)
10	0.82	1.224	0.87	1.543	0.88	1.623	0.89	1.710	1.593 (0.751)
15	0.87	1.543	0.91	1.910	0.93	2.160	0.93	2.160	1.342 (0.751)
20	0.90	1.800	0.94	2.320	0.95	2.500	0.95	2.500	1.165 (0.751)
25	0.93	2.160	0.96	2.720	0.96	2.720	0.97	3.010	1.122 (0.751)
30	0.95	2.500	0.97	3.010	0.98	3.410	0.98	3.410	1.059 (0.751)
45	1.00	—	1.00	—	1.00	—	1.00	—	—
60	1.00	—	1.00	—	1.00	—	1.00	—	—
90	1.00	—	1.00	—	1.00	—	1.00	—	—

From these results, it appears that at up to 0.05 M concentrations the rate of exchange is mainly controlled by film diffusion, whereas the particle diffusion predominantly controls the rate process at and above 0.10 M concentration.

A quantitative estimation of the contribution of each mechanism, film and particle diffusion, to the overall exchange may possibly be made by a graphic analysis of the Bt *vs.* t curves as shown in Fig. 1. A reference to these curves shows that the plots corresponding to the later part of the exchange lies on a straight line, an extrapolation of which intersects the Bt-axis. However, the ideal curve[9] in terms of Helfferich Plesset equation, for complete particle diffusion for which diffusion coefficient D^i becomes independent of fractional attainment of equilibrium (F), is a straight line passing through the origin. Non-ideal behaviour of the plots indicates that film diffusion is still making its contribution to the overall process.

TABLE-3

Volume of the exchanging ion solution used every time = 25 mL; pH of the exchanging ion [Cd(II)] solution = 10.5

Time (min)	Concentration								$D^i/\overline{D^i} \times 10^{-15}$ ($cm^2 s^{-1}$)
	0.01 M		0.05 M		0.10 M		0.20 M		
	F	Bt	F	Bt	F	Bt	F	Bt	
1	0.64	0.564	0.74	0.868	0.77	0.985	0.78	1.028	9.579 (0.582)
2	0.70	0.734	0.78	1.028	0.80	1.120	0.81	1.171	5.456 (0.582)
5	0.76	0.944	0.83	1.280	0.84	1.340	0.84	1.340	2.497 (0.582)
10	0.78	1.028	0.86	1.468	0.87	1.543	0.88	1.623	1.512 (0.582)
15	0.83	1.280	0.89	1.710	0.91	1.910	0.92	2.030	1.261 (0.582)
20	0.87	1.543	0.91	1.910	0.94	2.320	0.95	2.500	1.165 (0.582)
25	0.90	1.800	0.93	2.160	0.96	2.720	0.96	2.720	1.014 (0.582)
30	0.92	2.030	0.95	2.500	0.97	3.010	0.97	3.010	0.935 (0.582)
45	1.00	—	1.00	—	1.00	—	1.00	—	—
60	1.00	—	1.00	—	1.00	—	1.00	—	—
90	1.00	—	1.00	—	1.00	—	1.00	—	—

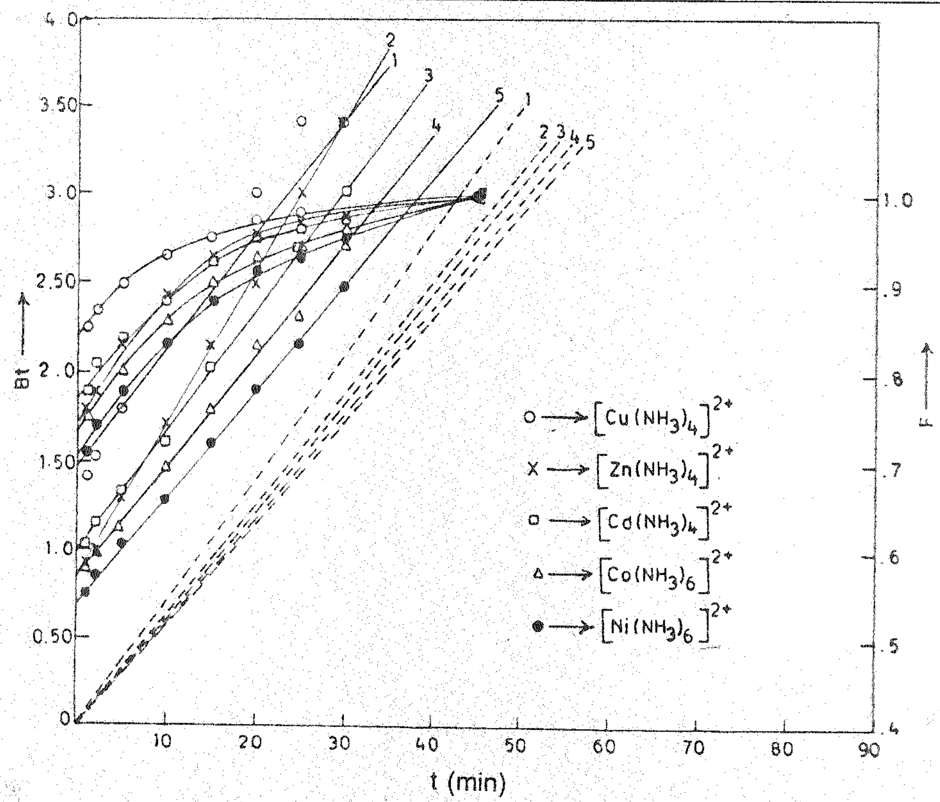

Fig. 1. F *vs.* t and Bt *vs.* t at 0.20 M concentration in magnesium molybdosilicate

TABLE-4

Volume of the exchanging ion solution used every time = 25 mL; pH of the exchanging ion [Co(II)] solution = 10.5

Time (min)	Concentration								$D^i/\overline{D}^i \times 10^{-15}$ ($cm^2 s^{-1}$)
	0.01 M		0.05 M		0.10 M		0.20 M		
	F	Bt	F	Bt	F	Bt	F	Bt	
1	0.65	0.594	0.72	0.798	0.74	0.868	0.75	0.905	8.433 (0.473)
2	0.68	0.675	0.74	0.868	0.76	0.944	0.77	0.985	4.589 (0.473)
5	0.71	0.765	0.76	0.944	0.79	1.073	0.80	1.120	2.087 (0.473)
10	0.75	0.905	0.81	1.171	0.84	1.340	0.86	1.468	1.368 (0.473)
15	0.80	1.120	0.85	1.404	0.88	1.623	0.90	1.800	1.118 (0.473)
20	0.83	1.280	0.88	1.623	0.91	1.910	0.93	2.160	1.006 (0.473)
25	0.86	1.468	0.91	1.910	0.93	2.160	0.94	2.320	0.865 (0.473)
30	0.88	1.623	0.93	2.160	0.95	2.500	0.96	2.720	0.845 (0.473)
45	1.00	—	1.00	—	1.00	—	1.00	—	—
60	1.00	—	1.00	—	1.00	—	1.00	—	—
90	1.00	—	1.00	—	1.00	—	1.00	—	—

With a view to isolate the contribution of particle diffusion from the composite curve, we may possibly represent this rate process in the Bt *vs.* t curve by allowing a straight line, having the same slope as that of the extrapolated curve, to pass through the origin. The particle diffusion curves drawn, wherever possible on the basis of this approach, are represented by dashed (----) lines. This analytical approach has also been adopted for calculating the values of the diffusion coefficient, represented as $\overline{D}^1$ (idealized). The observed order of the exchange rates of Cu(II), Zn(II), Cd(II), Ni(II) and Co(II) ammine complexes may be explained on the basis of increasing ionic potential of the complexes[10-12].

TABLE-5

Volume of the exchanging ion solution used every time = 25 mL; pH of the exchanging ion [Ni(II)] solution = 10.5

Time (min)	Concentration								$D^i/\overline{D}^i \times 10^{-15}$ ($cm^2 s^{-1}$)
	0.01 M		0.05 M		0.10 M		0.20 M		
	F	Bt	F	Bt	F	Bt	F	Bt	
1	0.59	0.458	0.67	0.647	0.70	0.734	0.75	0.765	7.128 (0.466)
2	0.63	0.545	0.70	0.734	0.73	0.832	0.74	0.868	4.044 (0.466)
5	0.67	0.647	0.73	0.832	0.76	0.944	0.78	1.028	1.916 (0.466)
10	0.74	0.868	0.80	1.120	0.82	1.224	0.83	1.280	1.193 (0.466)
15	0.80	1.120	0.84	1.340	0.86	1.468	0.88	1.623	1.008 (0.466)
20	0.84	1.340	0.88	1.623	0.90	1.800	0.91	1.910	0.890 (0.466)
25	0.87	1.543	0.91	1.190	0.92	2.030	0.93	2.160	0.805 (0.466)
30	0.90	1.500	0.93	2.160	0.94	2.320	0.95	2.500	0.776 (0.466)
45	1.00	—	1.00	—	1.00	—	1.00	—	—
60	1.00	—	1.00	—	1.00	—	1.00	—	—
90	1.00	—	1.00	—	1.00	—	1.00	—	—

REFERENCES

1. C.B. Amphlett, Inorganic Ion Exchangers, Elsevier, Amsterdam (1964).
2. A. Clearfield, Inorganic Ion Exchange Materials, CRC Press Inc., Boca Raton, Florida (1982).
3. M. Qureshi and K.G. Varshney, Inorganic Ion Exchangers in Chemical Analysis, CRC Press Inc., Boca Raton, Florida (1991).
4. F. Helfferich and M.S. Plesset, *J. Chem. Phys.*, **28**, 418 (1958).
5. N.E. Topp and K.W. Pepper, *J. Chem. Soc.*, 3299 (1949).
6. H.A. Flaschka, EDTA Titrations, Pergamon Press, Oxford (1964).
7. G.H. Jeffery, J. Bassett, J. Mendham and R.C. Denney, A.I. Vogel's Text Book of Quantitative Chemical Analysis, 5th Edn., Longman Group Ltd., London, p. 384 (1997).
8. D. Reichenberg, *J. Am. Chem. Soc.*, **75**, 589 (1953).
9. G.H. Nancollas and R. Paterson, *J. Inorg. Nucl. Chem.*, **22**, 259 (1961).
10. J. Bjerrus, Metal Ammine Formation in Aqueous Solution, Haase, Copenhagen (1957).
11. N.N. Greenwood and A. Earnshaw, Chemistry of the Elements, 2nd Edn., Butterworth-Heinemann, Linacre House, Jordan Hill, Oxford, pp. 1115, 1148, 1176, 1205 (1997).
12. Seema and B. Bhushan, *Asian J. Chem.*, **18**, 581 (2006).

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