

KINETICS OF SORPTION OF CERTAIN DIVALENT COMPLEX CATIONS IN CERIC PHOSPHATE, AN ION-EXCHANGER

A. K. BHADURI AND K. R. KAR

Department of Chemistry, University of Delhi, Delhi 110 007

ABSTRACT

Kinetics of sorption of the ammine and ethylenediamine complexes of Cu^{2+} , Zn^{2+} , Ni^{2+} and Cd^{2+} in ceric phosphate have been studied. It is found that the overall exchange process takes place in two distinct phases; a relatively quick process in the first stage is followed by a slower one, till the equilibrium is reached. Average size of the exchanger particles remaining the same, 'F' increases with the external concentration of the exchanging ion until it becomes independent of concentration. Under otherwise identical experimental conditions, the observed decreasing order of the rate of exchange of the ammine complexes is: $\text{Cu} > \text{Zn} > \text{Ni} > \text{Cd}$; and that of en-complexes is, $\text{Cu} > \text{Zn}$. It is further observed that the rate of sorption of the en-complexes of Ni^{2+} and Cd^{2+} takes place superficially only.

INTRODUCTION

THE speed of ion exchange reaction is an important practical consideration¹. Apart from the immense practical utility of the ion-exchange kinetics study, for the purpose of chemical separations, an understanding of the factors contributing to the rate of ion exchange reactions is of considerable theoretical interest². The present paper describes an investigation of the kinetics of the exchange reactions in ceric phosphate using ammine and ethylenediamine complexes of Cu^{2+} , Zn^{2+} , Ni^{2+} and Cd^{2+} as exchanging ions. The study includes: (A) dependence of the sorption rate on the concentration of the exchanging ion; (B) the effect of size and shape of the exchanging ion on the rate of exchange.

ammonia or 0.01 M ethylenediamine solution. The sample of CeO_2 with an average particle radius 9.2×10^{-3} cm was obtained with the help of standard sieves.

PROCEDURE FOR THE RATE-STUDY

Samples of 25 ml of the metal amines and ethylenediamines were added to a series of stoppered conical flasks, each containing 100 mg of the exchanger. The resulting mixtures were shaken mechanically up to equilibrium. The solutions were centrifuged and the supernatants (5 ml) were analysed for Cu^{2+} iodometrically⁵ and Cd^{2+} , Zn^{2+} and Ni^{2+} complexometrically⁶; and the amount of metal ions sorbed, hence their 'F' values were found out from the relation⁷

$$F = \frac{\text{Amount of the metal ion sorbed at time } t}{\text{Total amount of the metal ion sorbed at equilibrium}}$$

MATERIALS AND METHOD

All the reagents used were of A.R. quality. Ceric phosphate was prepared by the dropwise addition of one volume of a saturated ceric ammonium sulphate solution in 0.5 M H_2SO_4 , to one volume of a well stirred solution of 6 M H_3PO_4 , at room temperature. The precipitate obtained was further stirred for an hour and washed free of sulphate ion and was finally dried at $25 \pm 2^\circ \text{C}$. The ratio of PO_4/Ce in the sample, when analysed quantitatively³, was found to be equal to 1.68. Ceric phosphate (CeP) prepared in this way behaves as a cation exchanger in basic medium, as confirmed by means of pH-titration⁴. Ammine and ethylenediamine complexes of Cu^{2+} , Zn^{2+} , Ni^{2+} and Cd^{2+} were prepared by dissolving appropriate quantities of their water soluble salts in aqueous ammonia and ethylenediamine solutions. The pH of the solutions was adjusted with either (1:4)

RESULTS AND DISCUSSION

The results presented in Tables I-III, indicate that:

- (i) The ion exchange kinetics exhibit two distinctly separate stages, relatively quick process in the first stage followed by a slower one, till the equilibrium is reached (Tables I and II).
- (ii) Average size of the exchanger particles remaining the same 'F' increases with the external concentration of the exchanging ion until it becomes independent of concentration (Tables I and II).
- (iii) Under otherwise identical experimental conditions, the observed decreasing order of the rate of exchange of the ammine complexes is (Table I)



and that of en-complexes (Table II): $\text{Cu} > \text{Zn}$.

TABLE I

Dependence of 'F' values on the concentration of different ammine complexes

Amount of the exchanger (CeP) = 100 mg. Total volume = 25 ml; pH = 10.5. Particle radius = 9.2×10^{-3} cm.

Time	Fractional attainment of equilibrium (F)											
	Cu(NH ₃) ₄ ²⁺			Zn(NH ₃) ₄ ²⁺			Ni(NH ₃) ₆ ²⁺			Cd(NH ₃) ₄ ²⁺		
	0.01M	0.05M	0.10M	0.01M	0.05M	0.10M	0.01M	0.05M	0.10M	0.01M	0.05M	0.10M
30 secs	0.26	0.35	0.40	0.27	0.325	0.38	0.26	0.30	0.46	0.25	0.25	0.375
1 min	0.53	0.55	0.575	0.45	0.40	0.475	0.375	0.39	0.50	0.35	0.30	0.46
2 min	0.62	0.575	0.635	0.48	0.48	0.53	0.45	0.425	0.55	0.425	0.40	0.51
5 min	0.69	0.65	0.71	0.575	0.595	0.625	0.55	0.575	0.62	0.50	0.525	0.63
10 min	0.735	0.75	0.76	0.644	0.66	0.70	0.64	0.65	0.69	0.583	0.625	0.68
20 min	0.82	0.80	0.83	0.75	0.74	0.78	0.74	0.73	0.76	0.73	0.73	0.75
30 min	0.86	0.87	0.86	0.81	0.82	0.82	0.80	0.79	0.80	0.79	0.80	0.79
45 min	0.91	0.91	0.91	0.873	0.875	0.88	0.85	0.80	0.86	0.84	0.83	0.84
60 min	0.95	0.94	0.93	0.934	0.92	0.93	0.89	0.89	0.91	0.89	0.88	0.885
75 min	0.98	0.98	0.97	0.95	0.95	0.95	0.93	0.91	0.92	0.92	0.92	0.92
90 min	1.00	1.00	1.00	0.978	0.978	0.978	0.96	0.97	0.96	0.96	0.95	0.94
100 min	1.00	1.00	1.00	0.985	0.985	0.98	0.98	0.98	0.975	0.97	0.97	0.96
110 min	1.00	1.00	1.00	0.995	0.995	0.995	0.99	0.99	0.99	0.985	0.985	0.98
120 min	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00

TABLE II

Dependence of 'F' values on the concentration of Cu²⁺ and Zn²⁺ en-complexesAmount of the exchanger (CeP) = 100 mg. Total volume = 25 ml; pH = 10.5. Particle radius = 9.2×10^{-3} cm.

Time	Fractional attainment of equilibrium (F)			
	Cu(en) ₃ ²⁺		Zn(en) ₃ ²⁺	
	0.05M	0.10M	0.05M	0.10M
5 min	0.50	0.72	0.40	0.575
10 min	0.60	0.80	0.55	0.675
15 min	0.72	0.86	0.66	0.70
20 min	0.80	0.89	0.71	0.75
30 min	0.88	0.92	0.79	0.79
45 min	0.95	0.95	0.84	0.84
60 min	0.97	0.97	0.88	0.90
75 min	0.975	0.98	0.90	0.91
90 min	0.98	0.985	0.93	0.93
120 min	0.995	0.995	0.96	0.96
150 min	1.00	1.00	1.00	1.00

TABLE III

Dependence of 'F' values on the concentration of Ni²⁺ and Cd²⁺ en-complexes

Amount of the exchanger (CeP) = 100 mg. Total volume = 25 ml, pH = 10.5. Particle radius = 9.2 × 10⁻³ cm.

Time	Fractional attainment of equilibrium (F)					
	Ni(en) ₃ ²⁺			Cd(en) ₃ ²⁺		
	0.01M	0.05M	0.10M	0.01M	0.05M	0.10M
30 secs	0.01	0.025	0.075	0.01	0.03	0.05
1 min	0.025	0.05	0.15	0.025	0.05	0.07
2 min	0.06	0.10	0.25	0.05	0.08	0.15
5 min	0.15	0.25	0.50	0.125	0.20	0.33
10 min	0.30	0.50	1.00	0.275	0.40	0.63
15 min	0.44	0.70	1.00	0.38	0.55	0.87
20 min	0.65	0.845	1.00	0.52	0.68	1.00
30 min	0.70	1.00	1.00	0.73	0.86	1.00
45 min	1.00	1.00	1.00	0.91	1.00	1.00
60 min	1.00	1.00	1.00	1.00	1.00	1.00

It has been further observed that the rate of sorption of the en-complexes of Ni²⁺ Cd²⁺ increase continuously with the external concentration (Table III).

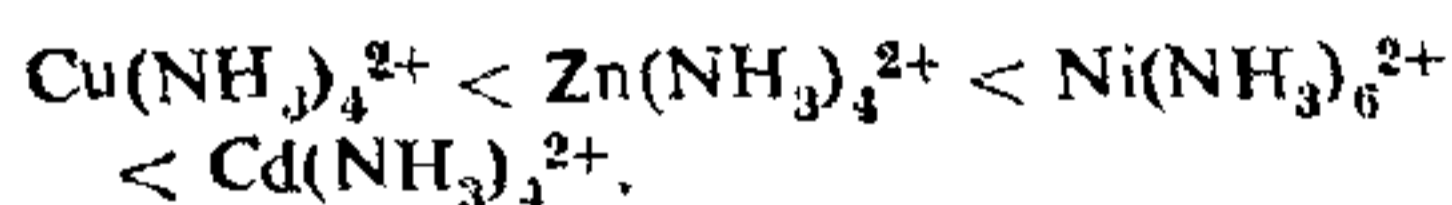
(iv) The rate of sorption of the ammine complexes of Cu²⁺ and Zn²⁺ is higher than the corresponding en-complexes (Tables I and II).

Overall exchange process consists of two types of diffusion processes⁸. The first one involves diffusion across a liquid film about the solid particle and the second involves diffusion of ions inside the solid particle.

Our results (Tables I-III) show both film and particle diffusion are responsible for the overall exchange process. Since, 'F' values initially increase with the increase of exchanging ion concentration from 0.01 M to 0.10 M, followed by a more or less identical 'F' values towards the end. However, the observed fact that 'F' values of en-complexes of Ni²⁺ and Cd²⁺ increase continuously even at the concentration ranges where the corresponding ammine complexes attain concentration independence, indicates that the sorption of these complexes occurs by film diffusion only to the practically complete exclusion of particle diffusion. This may be possible if it is considered that ionic dimensions of the en-complexes

of Cd²⁺ and Ni²⁺ are too large to enter into the exchanger particles. This possibility is in agreement with the accepted view⁹.

The observed sequence in the order of rates of sorption of the ammine seems to be intimately connected with the stereo-chemical characteristics of the exchanging ions and may be explained in the light of the decreasing order of their stereo-chemical covalent radii¹⁰⁻¹²; square planar Cu(II), 1.28 Å; tetrahedral Zn(II), 1.31 Å and Cd(II), 1.48 Å; octahedral Ni(II), 1.39 Å. Therefore their sizes follow the order:



The en-complexes of the metal ions under study are all known to have octahedral symmetry¹³. The order of the covalent radii is, therefore, likely to parallel the order of ionic radius of the simple metal ions¹⁴, viz., Cu²⁺, 0.69 Å and Zn²⁺, 0.74 Å. Therefore their sizes will follow the order:



From our experimental observations, it appears that, ionic charge remaining the same, the smaller the size of the exchanging ion, the faster is the rate of sorption. Further, considering the relative rates of the ammine and en-complexes of Cu²⁺ and Zn²⁺, the lower rate

of sorption of the en-complexes is attributed to their larger dimensions as compared to that of the corresponding ammine complexes.

ACKNOWLEDGEMENT

The author (A. K. B.) is grateful to U.G.C., India, for providing financial help.

1. Kunin, R., *Elements of Ion Exchange*, Reinhold, New York, 1960, p. 15.
2. Amphlett, C. B., *Inorganic Ion Exchangers*, Elsevier, Amsterdam, 1964, p. 126.
3. Alberti, G., Constantine, U., Gregorio, P. G. and Torracca, E., *J. inorg. Nucl. Chem.*, 1968, 30, 295.
4. Kunin, R., *Elements of Ion Exchange*, Reinhold, New York, p. 14.
5. Vogel, A. I., *A Text Book of Quantitative Inorganic Analysis*, Third ed. ELBS, 1968, p. 358.
6. Flaschka, H. A., *EDTA Titrations*, Pergamon Press, Oxford, Second ed., 1964, pp. 80, 83.
7. Kunin, R., *Element of Ion Exchange*, Reinhold, New York, 1960, p. 12.
8. —, *Ibid.*, p. 16.
9. —, *Ibid.*, p. 17.
10. Pauling, L., *The Nature of the Chemical Bond*, Third ed., Cornell University Press, New York, 1963, pp. 249, 252.
11. Heslop, R. B. and Robinson, P. L., *Inorganic Chemistry*, Third ed., Elsevier, New York, 1967, p. 743.
12. — and —, *Ibid.*, pp. 702, 705, 741, 756.
13. — and —, *Ibid.*, pp. 695, 756.
14. Cotton, F. A. and Wilkinson, G., *Advanced Inorganic Chemistry*, Wiley Eastern Private Ltd., New Delhi, 1970.

CONTROL OF SEED DETERIORATION IN COTTON (*GOSSYPIUM HIRSUTUM* L.)

C. DHARMALINGAM* AND R. N. BASU

University College of Agriculture, Calcutta University, 35, Ballygunge Circular Road, Calcutta 700 019

ABSTRACT

The deterioration of cotton seeds under warm-humid conditions can be controlled by hydration-dehydration pretreatment of stored (5-6-month-old) seeds. A soaking duration of 2-3 hours for the fuzzy seeds and about one hour for the delinted seeds, followed by drying back to the original weight, would greatly reduce the loss of viability of seeds during subsequent storage. The treated seeds not only maintained a high germination percentage but also showed a significantly greater vigour of seedlings in comparison to the untreated control seeds. Although hydration itself gave the major effect, dilute solutions (2×10^{-4} M) of disodium phosphate and *p*-hydroxybenzoic acid showed further improvement in germination percentage of seeds.

INTRODUCTION

IN the major cotton belts of South India, cotton is grown in two seasons. But the seed of a particular harvest cannot be used immediately for sowing the following crop because of the time required for ginning and processing and for seed certification prior to marketing of seeds. Therefore the current seed has to be stored for 6-8 months after harvest. Further, many seed producers frequently have large surplus carry-over stocks which remain unsold and need to be stored till the next season. Under ordinary uncontrolled storage, cotton seeds lose vigour and viability at a fairly rapid rate. Temperature and humidity controlled storage facilities would greatly solve the problem of seed deterioration but at present very few growers and seed merchants have such facilities. Relatively inexpensive and easily practicable methods should

therefore be standardised to maintain cotton seeds at a high level of germinability. Studies in this laboratory have led to the development of a hydration-dehydration method of seed treatment¹ for the stored seeds of a wide range of crop plants and in the present paper, the standardisation of seed treatment for controlling the deterioration of stored cotton seeds is described.

MATERIALS AND METHODS

Two-month-old seeds of the popular cotton cultivar MCUS, obtained from the Cotton Breeding Station of the Tamil Nadu Agricultural University, Coimbatore, were stored in unsealed polyvinyl bags at $27^\circ \pm 5^\circ$ C and a relative mean humidity of $73 \pm 7\%$ for three months. The 5-month-old fuzzy seeds were then given the hydration treatment by soaking in double the volume of distilled water for 0.5 to 5 hours. After soaking, the seeds were taken out and the excess water removed by blotting and dried back to the original weight in a current of hot air at $36^\circ \pm 1^\circ$ C. The

* Assistant Professor of Seed Technology (on study leave), Tamil Nadu Agricultural University, Coimbatore 641 003.