Forward and Reverse Ion Exchange Equilibria on Antimony(V) Phosphate-I: Evaluation of Various Thermodynamic Parameters for the Exchange of Alkali and Alkaline Earth Metal Ions on its Surface

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Forward and reverse ion exchange equilibrium studies have been performed on antimony(V) phosphate cation exchanger. The various thermodynamic parameters like equilibrium constants and energy, entropy and enthalpy changes during the exchange of alkali and alkaline earth metal ions have been determined and a correlation has been made of these parameters with the ion exchange characteristics of the material. The study gives an insight to the ion exchange process going on in the exchanger phase.

INTRODUCTION

Ion exchange equilibrium studies on an inorganic ion exchanger help us in the elucidation of its ion exchange potential and utility under various conditions of use. Such studies are fundamental in understanding the exchange phenomenon taking place on the surface of an ion exchanger and thus corroborating the results achieved with theory. However, only a few ion exchange materials have been studied so far[1-10]. Further, only a little attention has been paid for the reverse ion exchange process on such materials. The present study is, therefore, an extension of such a work and deals with the forward and reverse ion exchange equilibria on antimony(V) phosphate, a new and amorphous ion exchanger, for alkali and alkaline earth metal ions.

MATERIALS AND METHODS

Reagents and Chemicals

Antimony(V) chloride used in this study was of approximately 98% purity obtained from Fluka, Switzerland and tri-sodium orthophosphate was a B.D.H. Poole (England) product. All other reagents and chemicals were 'Analytical Reagent' grade.

Apparatus

A waterbath incubator shaker having a temperature variation of

±0.5°C was used for the equilibrium studies. Determination of alkali metal ions was done on a flame photometer.

Synthesis of the Ion Exchange Material

Antimony(V) phosphate (SbP) was prepared by mixing the solution of antimony(V) chloride (0.1M) prepared in 4M HCl and that of the tri-sodium ortho-phosphate (0.05M) in demineralized water (D.M.W.) in the same volume ratio. The pH of the resultant mixture was adjusted to 0–1. The gel thus obtained was digested at room temperature (*ca.* 30°C) for 24 hrs., filtered by suction, washed with D.M.W. and dried in an air oven at 45°C. The dried gel cracked into small granules when put in D.M.W., which were converted into the H⁺-form by treating with approximately 1M HNO₃ for 24 hrs. with occasional shaking and intermittently replacing the supernatant liquid. The material thus obtained was finally washed to a pH 6–7 and dried at 45°C as above before sieving to a uniform size (60–100 mesh). The Na⁺-ion exchange capacity obtained by column process was found to be 1.75-meq/dry g.

Equilibrium Experiments

0.2 g portions of the exchanger in H⁺ form were shaken in various stoppered conical flasks at desired temperatures (30° and 50°C) for 4 hrs. with the metal ion solutions (20 ml) having a constant ionic strength (0.03M), adjusted with the appropriate amounts of HNO₃. Amounts of the alkali metal ions in the solution were determined by flame photometer. Alkaline earth metal ions and hydrogen ions were determined titrimetrically using EDTA and NaOH solutions respectively as titrants.

Evaluation of the Thermodynamic Parameters

The ion exchange process occurring on the exchanger can be represented by the equation

$$n\bar{H}^+ + M^{n+} \rightleftharpoons \bar{M}^{n+} + nH^+ \tag{1}$$
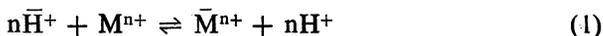
where M^{n+} represents the metal ion, n its valency and bar means the ion in the exchanger phase. The equilibrium between the ionic concentrations in the exchanger and solution phases is expressed as

$$\bar{C}_H + C_M \rightleftharpoons \bar{C}_M + C_H \tag{2}$$

while the equivalent ionic fractions of the metal and hydrogen ions in the two phases are calculated from the expressions:

$$\bar{X}_M = \frac{\bar{C}_M}{\bar{C}}, \; X_M = \frac{C_M}{C}, \; \bar{X}_H = \frac{\bar{C}_H}{\bar{C}} \text{ and } X_H = \frac{C_H}{C}$$

where $\bar{C}$ and C are the total electrolyte concentration in the exchanger and solution phases respectively.

The separation factors (α) and the selectivity coefficients (K_c) for the forward and reverse exchanges were calculated from the following equations, assuming the ratio of the activity coefficients in dilute solutions as unity[11,12]

$$\alpha_H^M = \bar{X}_M \cdot X_H / \bar{X}_{Hx} X_M, \quad K_c^F = \bar{X}_M \cdot [X_H]^n / [\bar{X}_H]^n \cdot X_M$$

for the forward exchange and

$$\alpha_M^H = \bar{X}_H \cdot X_M / \bar{X}_M \cdot X_H, \quad K_c^R = [\bar{X}_H]^n \cdot X_M / [X_H]^n \cdot \bar{X}_M$$

for the reverse exchange.

The thermodynamic constants were then obtained[13] from the equation:

$$\ln K = Z_A - Z_B + \int_0^1 \ln C_c \, d\bar{X}_M \qquad (3)$$

where Z_A and Z_B are the valencies of the competing ions.

Having known the value of $\ln K$, the standard free energy of exchange ($\Delta G°$)[14], standard enthalpy changes ($\Delta H°$) and standard entropy changes ($\Delta S°$) were calculated by the following equations

$$\Delta G° = -RT \ln K \qquad (4)$$

$$\ln \frac{K_{T_2}}{K_{T_1}} = -\frac{\Delta H°}{R} \left[\frac{1}{T_2} - \frac{1}{T_1} \right] \qquad (5)$$

and

$$\Delta G° = \Delta H° - T \, \Delta S° \qquad (6)$$

where R is the universal gas constant and T is the temperature in Kelvin.

RESULTS AND DISCUSSION

Figure 1 shows the results of the equilibrium versus time experiments
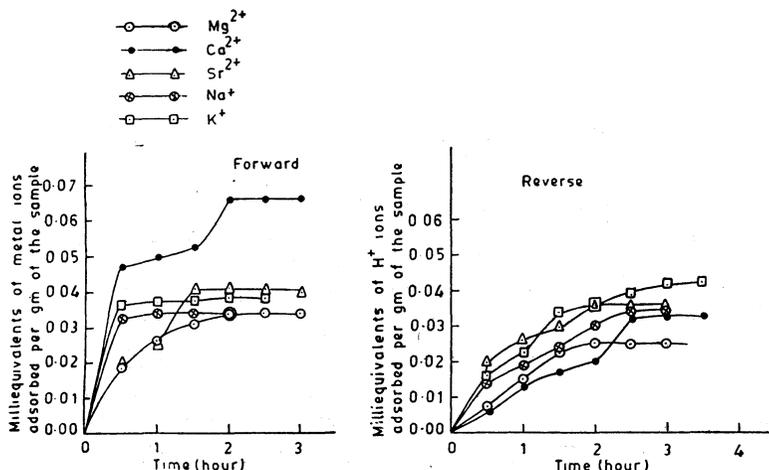

Fig. 1. Forward and reverse ion exchange as a function of time on antimony (V) phosphate.

done in both the forward and reverse directions. For the forward exchange the material was taken in the H$^+$-form (HSbP) while in the reverse one it was taken in the metal form (MSbP). As these figures indicate an equilibrium is attained within 2 hrs in the forward direction while within 3 hrs in the reverse direction. Four hrs were, therefore, chosen in all the studies in order to ascertain the achievement of equilibrium.

The separation factors (α_H^M, α_M^H) and selectivity coefficients (K_c^F, K_c^R) for all metal ions at 30 and 50°C are summarized in Tables 1 to 3 for the forward and reverse exchanges. Figures 2 to 5 show their exchange
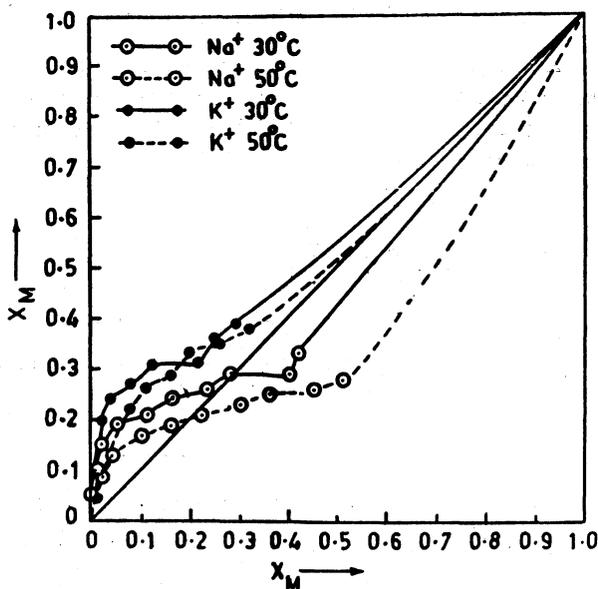

Fig. 2. Forward exchange isotherms (Na$^+$–H$^+$, K$^+$–H$^+$) on antimony (V) phosphate at 30°C and 50°C.

isotherms. As it is clear from these figures the exchanger has a preference for all the metal ions except Mg^{2+}, during the forward exchange at both temperatures, Ca^{2+} and Sr^{2+} being the most strongly adsorbed ions. Adsorption studies on this material have also indicated this trend earlier[15]. A reversal in the preference is, however, observed for Na$^+$ and K$^+$ ions after a certain value of ionic fraction i.e. 0.3. The exchange isotherm for the Mg^{2+}–H$^+$ exchange is entirely different. It shows a preference for H$^+$ ions in comparison to the Mg^{2+} ions at both the temperatures studied. This behaviour of SbP is similar to the antimony(V) silicate (SbSi) prepared earlier in these laboratories[7]. However, it is different from Zr(IV) phosphosilicate[9,10]. In the reverse process the exchanger shows, in

TABLE 1

VALUES OF SEPARATION FACTORS AND SELECTIVITY COEFFICIENTS OF SODIUM-HYDROGEN AND POTASSIUM-HYDROGEN IONS AT 30° AND 50°C FOR FORWARD AND REVERSE EXCHANGE ON ANTIMONY(V) PHOSPHATES

For Forward Exchange

Sl. No.	α_H^{Na}		$\log K_c$		α_H^{K}		$\log K_c$	
	30°C	50°C	30°C	50°C	30°C	50°C	30°C	50°C
1.	0.67	0.37	−0.16	−0.43	1.56	1.32	0.19	0.12
2.	0.61	0.43	−0.21	−0.36	1.67	1.52	0.22	0.18
3.	1.09	0.59	0.03	−0.00	1.66	1.96	0.22	0.29
4.	1.24	0.68	0.11	−0.16	3.32	2.19	0.52	0.34
5.	1.66	0.95	0.22	−0.02	4.16	0.82	0.62	0.45
6.	2.21	1.19	0.34	−0.07	6.89	3.33	0.83	0.53
7.	4.36	1.80	0.64	0.25	11.49	4.48	1.06	0.65
8.	6.21	3.06	0.79	0.48	16.21	7.58	1.21	0.88
9.	9.46	5.20	0.97	0.71	31.52	13.96	1.49	1.14
10.	107.43	13.19	2.03	1.13	97.08	29.72	1.98	1.47
11.	∞	∞	∞	∞	∞	∞	∞	∞

For Reverse Exchange

Sl. No.	α_{Na}^{H}		$\log K_c$		α_K^{H}		$\log K_c$	
	30°C	50°C	30°C	50°C	30°C	50°C	30°C	50°C
1.	∞	∞	∞	∞	∞	∞	∞	∞
2.	0.85	1.07	−0.06	0.03	0.84	1.07	−0.07	−0.03
3.	0.45	0.62	−0.34	−0.20	0.66	0.67	0.17·	−0.17
4.	0.39	0.26	−0.40	−0.57	0.42	0.60	−0.37	−0.20
5.	0.30	0.21	−0.52	−0.66	0.22	0.15	−0.66	−0.80
6.	0.27	0.12	−0.56	−0.90	0.09	0.13	−1.03	−0.88
7.	0.15	0.06	−0.81	−1.19	0.03	0.12	−1.40	−0.89
8.	0.03	0.03	−1.44	−1.50	0.03	0.01	−1.48	−1.75
9.	0.03	0.02	−1.45	−1.57	0.01	0.01	−1.48	−1.81
10.	0.01	0.04	−1.93	−1.33	0.02	0.04	−1.54	−1.39
11.	0.05	0.06	−1.23	−1.18	0.05	0.04	−1.27	−1.30

TABLE 2

VALUES OF SEPARATION FACTORS AND SELECTIVITY COEFFICIENTS
OF MAGNESIUM-HYDROGEN AND CALCIUM-HYDROGEN IONS
AT 30° AND 50°C FOR FORWARD AND REVERSE EXCHANGES
ON ANTIMONY (V) PHOSPHATE

For Forward Exchanges

S. No.	α_H^{Mg}		$\log K_c$		α_H^{Ca}		$\log K_c$	
	30°C	50°C	30°C	50°C	30°C	50°C	30°C	50°C
1.	0.03	0.07	−2.23	−1.56	2.15	15.47	0.44	1.59
2.	0.08	0.09	−1.41	−1.39	2.71	18.62	0.56	1.63
3.	0.08	0.15	−1.38	−1.06	4.16	53.63	0.70	2.07
4.	0.12	0.22	−1.15	−0.81	4.17	59.91	0.74	2.05
5.	0.13	0.28	−1.05	−0.67	11.37	72.70	1.22	2.08
6.	0.13	0.34	−1.03	−0.56	18.32	59.09	1.47	1.85
7.	0.22	0.42	−0.74	−0.46	32.96	32.30	1.63	1.62
8.	0.23	0.98	−0.72	−0.01	21.08	19.56	1.39	1.36
9.	0.33	5.33	−0.52	0.76	10.89	∞	1.08	∞
10.	0.97	∞	−0.01	∞	3.94	∞	0.60	∞
11.	∞	∞	∞	∞	∞	∞	∞	∞

For Reverse Exchange

Sl. No.	α_{Mg}^{H}		$\log K_c$		α_{Ca}^{H}		$\log K_e$	
	30°C	50°C	30°C	50°C	30°C	50 C	30°C	50°C
1.	∞	∞	∞	∞	∞	∞	∞	∞
2.	0.16	0.05	−0.83	−1.35	0.65	0.04	−0.20	−1.40
3.	0.12	0.28	−1.00	−0.62	0.66	0.03	−0.20	−1.58
4.	0.12	0.26	−1.05	−0.69	0.42	0.29	−0.45	−0.62
5.	0.23	0.28	−0.77	−0.68	0.36	0.20	−0.54	−0.84
6.	0.30	0.35	−0.66	−0.58	0.48	0.19	−0.41	−0.91
7.	0.20	0.29	−0.94	−0.70	0.33	0.12	−0.64	−1.19
8.	0.13	0.18	−1.21	−1.04	0.33	0.20	−0.66	−0.97
9.	0.10	0.14	−1.49	−1.27	0.34	0.26	−0.68	−0.86
10.	0.09	0.11	−1.55	−1.50	0.21	0.21	−1.03	−1.04
11.	0.06	0.07	−2.03	−1.85	0.18	0.12	−1.16	−1.51

TABLE 3

VALUES OF SEPARATION FACTORS AND SELECTIVITY COEFFICIENTS OF STRONTIUM-HYDROGEN IONS AT 30° AND 50°C FOR FORWARD AND REVERSE EXCHANGES ON ANTIMONY (V) PHOSPHATE

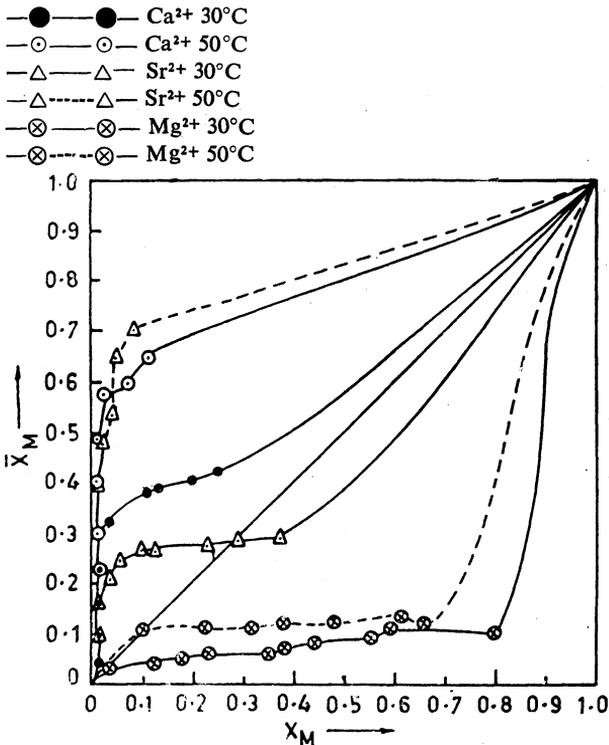| Sl. No.	For Forward Exchanges				For Reverse Exchanges			
	α_H^{Sr}		$\log K_e$		α_{Sr}^H		$\log K_e$	
	30°C	50°C	30°C	50°C	30°C	50°C	30°C	50°C
1.	0.67	28.06	-0.23	1.95	∞	∞	∞	∞
2.	0.80	37.13	-0.19	2.00	0.55	0.08	-0.27	-1.14
3.	1.26	28.02	0.12	1.77	0.66	0.25	-0.20	-0.61
4.	2.70	55.44	0.54	2.03	0.55	0.13	-0.30	-1.27
5.	3.22	76.76	0.60	2.06	0.55	0.21	-0.32	-0.81
6.	5.43	49.96	0.83	1.82	0.36	0.22	-0.56	-0.84
7.	9.32	32.16	1.06	1.58	0.32	0.26	-0.65	-0.78
8.	19.70	19.64	1.36	1.33	0.34	0.18	-0.66	-1.04
9.	10.73	10.69	1.07	1.03	0.24	0.20	-0.84	-1.02
10.	4.17	4.2	0.62	0.60	0.33	0.17	-0.72	-1.17
11.	∞	∞	∞	∞	0.31	0.09	-0.78	-1.34

Fig. 3. Forward exchange isotherms (Ca^{2+}–H, Sr^{2+}–H, Mg^{2+}–H) on antimony (V) phosphate at 30°C and 50°C.

general, a greater preference for the metal ions at both the temperatures,

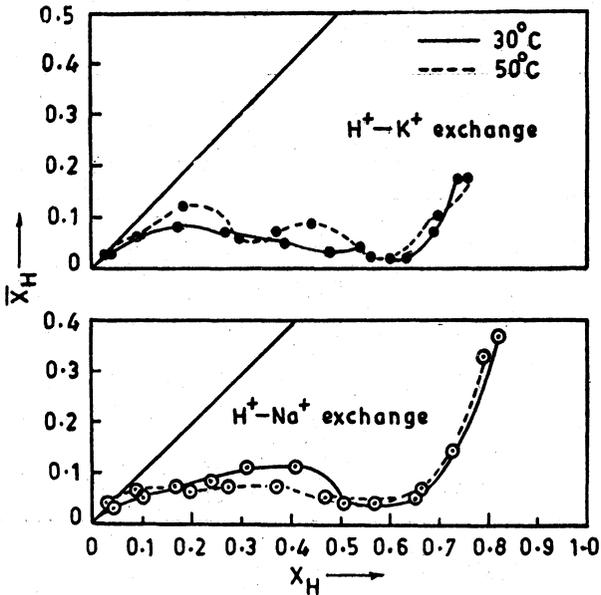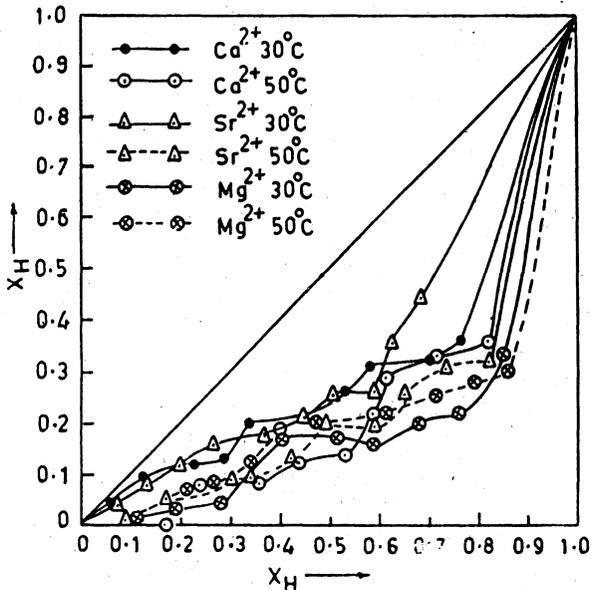Fig. 4. Reverse exchange isotherms (H+–Na+, H+–K+) on antimony (V) phosphate at 30°C and 50°C.

Fig. 5. Reverse exchange isotherms (H+–Mg²+, H+–Ca²+, H+–Sr²+) on antimony (V) phosphate at 30°C and 50°C.

i.e. a difficult removal of the metal ions during the regeneration process. It may be due to the steric hindrances at the exchange stages.

The various thermodynamic parameters at 30° and 50°C are summarized in Table 4. At 30°C, the thermodynamic equilibrium constant (K)

TABLE 4

THERMODYNAMIC VALUES FOR THE FORWARD EXCHANGES
AT 30° AND 50°C ON ANTIMONY (V) PHOSPHATE

Thermo-dynamic → parameters Metal ions ↓	K		$\Delta G°$ (KJ mol^{-1})		$\Delta H°$ (KJ mol^{-1})	$\Delta S°$ (J mol^{-1} deg^{-1})	
	30°C	50°C	30°C	50°C	—	30°C	50°C
Mg^{2+}	0.33	0.34	2.82	2.90	1.57	4.11	4.12
Ca^{2+}	1.04	2.94	−2.10	−2.89	4.31	142.62	142.93
Sr^{2+}	0.63	4.93	1.15	−4.28	85.29	277.66	277.31
Na$^+$	1.57	1.02	−1.13	−0.05	−17.89	−55.32	−55.24
K$^+$	2.01	1.68	−1.76	−1.37	−7.74	−19.75	−19.71
For the Reverse Exchanges							
Mg^{2+}	0.85	1.18	0.40	−0.45	13.53	43.33	43.27
Ca^{2+}	1.62	0.85	−1.22	0.41	−26.48	−83.38	−83.26
Sr^{2+}	1.62	1.20	−1.22	−0.46	−12.52	−37.31	−37.34
Na$^+$	0.29	0.42	3.05	2.23	14.44	37.59	34.64
K$^+$	0.75	0.43	1.09	2.29	−17.64	−61.78	−61.71

is highest for K$^+$ ion in the forward exchange followed by Na$^+$, Ca$^+$, Sr^{2+} and Mg^{2+} indicating the affinities for different metal ions in that order. At 50°C, however, the K values are in the order Sr^{2+} > Ca^{2+} > K$^+$ > Na$^+$ > Mg^{2+}, which is obvious because the adsorption of an ion is inversely proportional to its degree of hydration. Thus the exchanger appears to have its affinity changed from K$^+$ to Sr^{2+} with the increase in the K value for Sr^{2+} at higher temperature. Free energy change is negative for all the forward exchanges except for the Sr^{2+}–H$^+$ at 30°C and for the Mg^{2+}–H$^+$ at both temperatures. These results indicate again that K$^+$, Na$^+$, Ca^{2+} and Sr^{2+} ions are readily exchanged with the H$^+$ ions attached to exchanger surface, Sr^{2+} being the most preferably adsorbed at a higher temperature. The standard enthalpy and entropy changes are both negative and positive for the ion exchanges taking place on the exchanger surface. A positive enthalpy change for Sr^{2+}–H$^+$, Ca^{2+}–H$^+$, Mg^{2+}–H$^+$, H$^+$–Na$^+$ and H$^+$–Mg^{2+} indicate that these exchanges are endothermic while a negative value for the rest exchanges are indicative

of their exothermic nature. Entropy changes are the measure of the disorderness in a system. A positive change in entropy i.e. an increase in its value gives an idea of a ready exchange in that particular direction. In the forward direction $Mg^{2+}-H^+$, $Ca^{2+}-H^+$ and $Sr^{2+}-H^+$ exchanges show a positive entropy change while Na^+-H^+ and K^+-H^+ exchange show a negative change, i.e. a decrease in entropy. In the reverse direction, however, H^+-Mg^{2+} and H^+-Na^+ exchanges are accompanied by a positive entropy change meaning, thereby, that these exchange phenomena easier to achieve as compared to the others ones.

ACKNOWLEDGEMENT

REFERENCES

1. E. M. Larsen and D. R. Vissers, *J. Phys. Chem.*, **64**, 1732 (1960).

2. L. H. Baetsle, *J. Inorg. Nucl. Chem.*, **25**, 271 (1963).

3. G. H. Nancollas and B. V. K. S. R. A. Tilak, *J. Inorg. Nucl. Chem.*, **31**, 3643 (1969).

4. G. Alberti and U. Costantino, *J. Inorg. Nucl. Chem.*, **36**, 653 (1974).

5. J. P. Rawat and D. K. Singh, *Anal. Chim. Acta*, **87**, 157 (1976).

6. J. P. Rawat and K. P. S. Muktawat, *J. Inorg. Nucl. Chem.*, **43**, 2121 (1981).

7. K. G. Varshney, R. P. Singh and S. Rani, *Acta Chim. Acad. Sci. Hung.*, **115**, 403 (1984).

8. ——, *Proc. Ind. Nat. Sci. Acad.*, Part A, **50**, 75 (1984).

9. K. G. Varshney, R. P. Singh and U. Sharma, *Proc. Ind. Nat. Sci. Acad.*, Part A, **51**, 726 (1985).

10. ——, *Coll. Surf.*, **16**, 207 (1985).

11. R. A. Robinson and R. H. Strokes, Electrolyte Solutions, Butterworths, London (1959).

12. J. P. Singhal and R. P. Singh, J. Soil Sci., **27**, 42 (1976).

13. G. L. Gains and H. C. Thomas, J. Chem. Phys., **21**, 714 (1953).

14. S. Glasstone, Text Book of Physical Chemistry, Macmillan and Co. Ltd., London, p. 827 (1960).

15. K. G. Varshney and S. M. Maheshwari, *J. Ecotox. Environ. Safety*, **18**, 1 (1989).