

## Ion Exchange Behaviour of Tin (IV) Molybdophosphate Towards Alkaline Earth Metal Ions

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Samples of tin (IV) molybdophosphate were synthesized by mixing the solutions of tin (IV) chloride and molybdophosphoric acid. A sample which exhibits ion exchange capacity for  $\text{Na}^+$  0.85 Meq/g was selected for the studies. The ion exchange equilibria of  $\text{Mg}^{2+}$ ,  $\text{Ca}^{2+}$ ,  $\text{Sr}^{2+}$  and  $\text{Ba}^{2+}$  with hydrogen form of tin (IV) molybdophosphate have been studied. The values for  $K_H^{\text{II}}$ ,  $\Delta G^\circ$ ,  $\Delta H^\circ$ ,  $\Delta S^\circ$  and  $\Delta S_{\text{ex}}$  have been determined for the equilibria at 30°, 45° and 60°C.

### INTRODUCTION

The synthetic inorganic ion exchangers have been attaining a great importance due to their thermal and chemical stability and better selectivity towards ions over organic resins out of them heteropolyacid salts of polyvalent metals are of current interest. These materials are superior to simple insoluble salts of polyvalent metals as it is possible to vary their compositions and hence to change their selectivity to particular ion. The preferential uptake of the ions depends upon the mole fractions  $\bar{x}_m$  of the exchanging ions in the solid phase and upon the  $\Delta G^\circ$ ,  $\Delta H^\circ$  and  $\Delta S^\circ$  values for the exchange process. All these thermodynamic parameters are composition dependent. In the continuation of our earlier studies on tin (IV) molybdophosphate<sup>1</sup>, we are presenting the ion exchange equilibrium studies on the same materials in this work. The values of  $\Delta G^\circ$ ,  $\Delta H^\circ$  and  $\Delta S^\circ$  have been calculated for  $\text{Mg}^{2+}/\text{H}^+$ ,  $\text{Ca}^{2+}/\text{H}^+$ ,  $\text{Sr}^{2+}/\text{H}^+$  and  $\text{Ba}^{2+}/\text{H}^+$  exchange equilibriums at 30°, 45° and 60°C.

### EXPERIMENTAL

Tin (IV) chloride heptahydrate (J.T. Baker N. Jerry), sodium molybdate dihydrate (Veb Jena Germany) and orthophosphoric acid (BDH, England) were used. All other chemicals were used of A.R. Grade. Spekol spectrophotometer

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(Carl Zeiss Jena, GDR) and thermostate (Toshniwal India) were used for spectrophotometric determinations and thermodynamic equilibrium studies respectively.

*Synthesis of tin (IV) molybdophosphate:* 10 Gms of molybdophosphoric acid (MPA) and 35 gms of tin (IV) chloride were separately dissolved each to prepare 1 litre solution was added to tin (IV) chloride solution in different ratios. A yellow precipitate was obtained, it was refluxed into the mother liquor for 10 hrs, then it was allowed to settle down for 24 hrs., filtered off and washed with distilled water. The product was dried in an air oven and converted into  $H^+$  form in a usual manner. The ion exchange capacity was determined by routine column method. The results are given in Table 1.

TABLE 1  
CONDITIONS OF THE PREPARATION AND THE ION EXCHANGE CAPACITY  
OF TIN (IV) MOLYBDOPHOSPHATE

Sample No.	Reagent <sup>+</sup>	Mixing ratio	Ion exchange capacity for $Na^+$ (meq/g)
1.	Tin (IV) Chloride + Molybdophosphoric acid (MPA)	1 : 1	0.74
2.	— do —	1 : 2	0.85
3.	— do —	1 : 3	0.78
4.	— do —	1 : 4	0.80

\*Refluxing time for all samples was 10 hrs.

Dissolution of all the five samples in 1N  $H_2SO_4$ , 1N HCl, 0.1 N  $HNO_3$  and in 0.1N NaOH solutions were determined spectrophotometrically. The results of sample no. 2 are given in Table 2, because other samples show low chemical stability. Tin (IV) molybdophosphate (sample-2) was converted into  $Mg^{2+}$ ,  $Ca^{2+}$ ,  $Sr^{2+}$  and  $Ba^{2+}$  forms and then water content was determined by heating the respective cationic form of the exchangers to constant weight in an air even at 200°C. The results are given in Table 3.

TABLE 2  
DISSOLUTION (mg/50 ml) OF TIN (IV) MOLYBDOPHOSPHATE  
(SAMPLE-2) IN VARIOUS SOLUTIONS.

Solutions	Sn	Mo	P
1N $H_2SO_4$	0.50	0.90	0.30
0.1N $HNO_3$	0.60	0.10	0.80
1N HCl	3.00	5.00	7.00
0.1N NaOH	dissolved completely		

TABLE 3  
WATER CONTENT IN VARIOUS CATIONIC FORMS  
OF TIN (IV) MOLYBDOPHOSPHATE

Cationic form	Hydrated radii (Å)	Water content (%)
Mg <sup>2+</sup>	7.00	14.00
Ca <sup>2+</sup>	6.30	13.00
Sr <sup>2+</sup>	—	12.00
Ba <sup>2+</sup>	5.90	11.00

Ion exchange equilibrium studies were made at 30°, 45° and 60°C with ± 2°C variations in Toshniwal thermostate.

In forward equilibrium, 200 mg of H<sup>+</sup> form exchanger was equilibrated with 20 ml alkaline earth metal nitrate solution and nitric acid solution in glass stoppered conical flasks.

The ionic strength of this solution mixture was maintain to 0.1 M. The flasks were shaken in thermostate for 2 hrs. The exchanger was filtered off and the concentrations of metal ions and hydrogen ions in the filtrate were determined with standard EDTA and standard NaOH solution titrimetrically. The concentration of metal ions and the hydrogen ions in the solid phase and in solution phase were deduced from the difference between before equilibrium and after equilibrium and after equilibrium concentrations of metal ions in the solution phase. The mole fraction of H<sup>+</sup> ions and M<sup>2+</sup> ions on the solid phase were calculated on the basis of the maximum ion exchange capacity (0–85 meq/g–sample 2). The backward equilibrium 200 mg of M<sup>2+</sup> (Mg<sup>2+</sup>, Ca<sup>2+</sup>, Sr<sup>2+</sup> and Ba<sup>2+</sup>) form was equilibrated with 20 ml of alkaline earth metal nitrate solution and nitric acid solution in glass stoppered conical flasks. Other steps were similar as in forward equilibrium.

## RESULTS AND DISCUSSIONS

Table-1 presents the synthesis of the material, sample no. 2 out of the five samples synthesized has been selected for the detailed studies as it shows higher chemical stability (Table-2) in mineral acids. The water content of the ion exchange material in Mg<sup>2+</sup>, Ca<sup>2+</sup>, Sr<sup>2+</sup> and Ba<sup>2+</sup> forms were determined and the results are shown in Table-3. The water content increases as the hydrated radius of the cation increases. A similar fact was also observed in the ion exchange studies of ferric antimonate<sup>2</sup>.

The ion exchange equilibrium of alkaline earth metal ions with hydrogen ions in tin (IV) molybdophosphate can be represented by the following expression.



Where RH refers to tin (IV) molybdophosphate in H<sup>+</sup> refers to Mg<sup>2+</sup>, Ca<sup>2+</sup>, Sr<sup>2+</sup> or Ba<sup>2+</sup>.

The selectivity coefficient of the above exchange reaction in terms of mole fractions is given by

$$S_{\text{H}}^{\text{M}} = \frac{\bar{X}_{\text{M}} \cdot X_{\text{H}}^2}{X_{\text{M}} \cdot \bar{X}_{\text{H}}^2} \quad (2)$$

Where  $\bar{X}_{\text{M}}$  and  $\bar{X}_{\text{H}}$  refer to mole fractions of metal and hydrogen ions in exchanger phase and  $X_{\text{M}}$  and  $X_{\text{H}}$  to the mole fractions in the solution phase. The ion exchange equilibrium both the forward and backward were studied at 30°, 45° and 60°C.

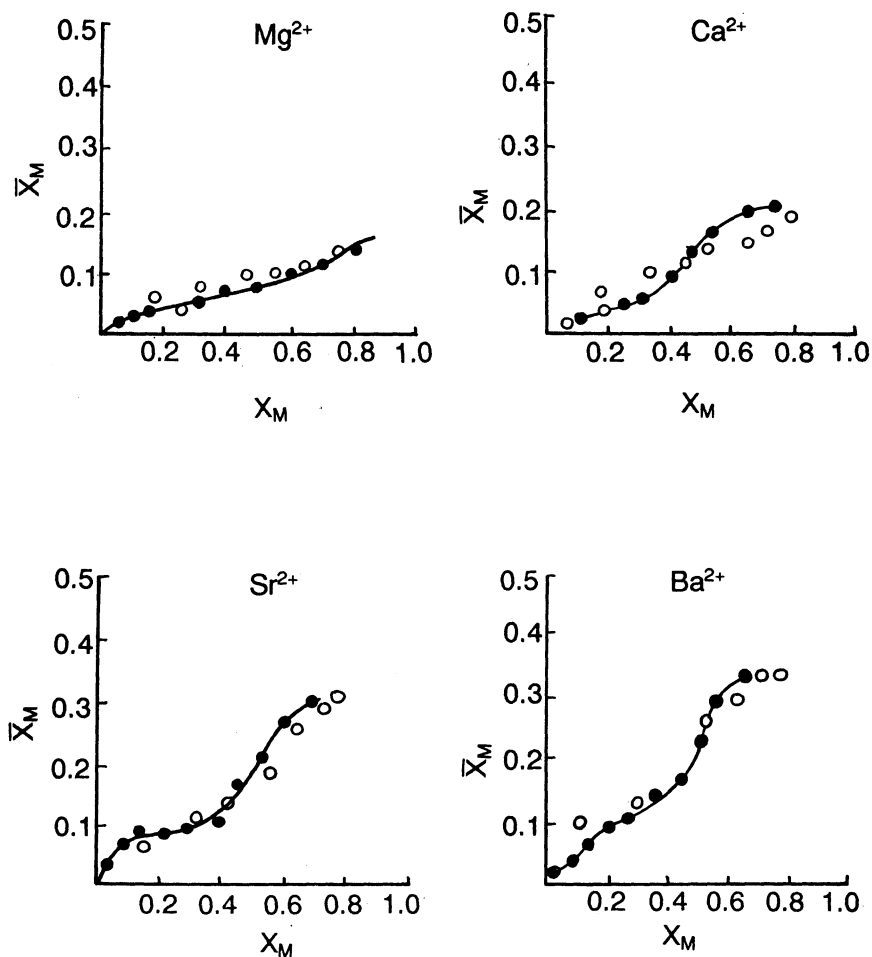


Fig. 1 Ion exchange isotherms of alkaline earth metal ions/ $\text{H}^+$  at 30°C  
O – Forward equilibrium; ● – Backward equilibrium

The exchange isotherms of  $Mg^{2+}/H^+$ ,  $Sr^{2+}/H^+$  and  $Ba^{2+}/H^+$  at  $30^\circ C$  are plotted in Fig.1, No marked hysteresis loops were observed in these isotherms and hence the system may be considered nearly reversible and suitable for thermodynamic studies. The trend in these isotherms reveal that the alkaline earth metal ions are not preferred over hydrogen ions by tin (IV) molybdophosphate exchange material. These isotherms also indicate the preference of alkaline earth metal ions in order of  $Ba^{2+} > Sr^{2+} > Ca^{2+} > Mg^{2+}$ . The selectivity coefficients of the exchanging ions decrease with the increase in  $\bar{X}_M$  as usual. The thermodynamic equilibrium constant for the equilibrium (1) in terms of activity coefficients is given by:

$$K_H^M = \frac{\bar{X}_M \cdot X_H^2}{X_M \cdot X_H} \cdot \frac{\bar{F}_M \cdot F_H^2}{F_M \cdot \bar{F}_H^2} \quad (3)$$

Where  $\bar{F}_M$  and  $\bar{F}_H$  are activity coefficients in the exchanger phase while  $F_M$ ,  $F_H$  are activity coefficients in solution phase.

The solid phase activity coefficients were calculated by Gains and Thomas equation<sup>3</sup>.

$$\ln \bar{F}_M = (1 - \bar{X}_M) \ln S - \int_0^{\bar{X}_M} \ln S \cdot d\bar{X}_M \quad (4)$$

$$\ln \bar{F}_H = -\bar{X}_M + \int_0^{\bar{X}_M} \ln S \cdot \bar{X}_M \quad (5)$$

The plots of selectivity coefficients (logs) vs  $\bar{X}_M$  are presented in Fig. 2 out of these plots  $Mg^{2+}/H^+$  plot shows a fairly good linearship.

The  $\log K_H^M$  vs  $1/T$  plots are shown in Fig. 3. These plots show fairly good linearity over the entire range of temperature studied. This trend reveals that the ion uptake decreases with rise in temperature often other way it indicates that values of  $K_H^M$  increase with increase in temperature.

The free energy change ( $\Delta G^\circ$ ) for the ion exchange equilibrium was calculated using the equation

$$\Delta G^\circ = -\frac{RT \ln K_H^M}{Z_M Z_H} \quad (6)$$

Where R is the gas constant,  $Z_M$  and  $Z_H$  refer to valencies of competing ions and T is the absolute temperature of the exchange equilibrium. The results are shown in Table-4. The values of  $\Delta G^\circ$  varies with the hydrated radius of the exchanging ions i.e. the value of  $\Delta G^\circ$  descreases with increase in hydrated radii of alkaline earth metal ions.  $\Delta H^\circ$  values have been calculated by the following equation(4).

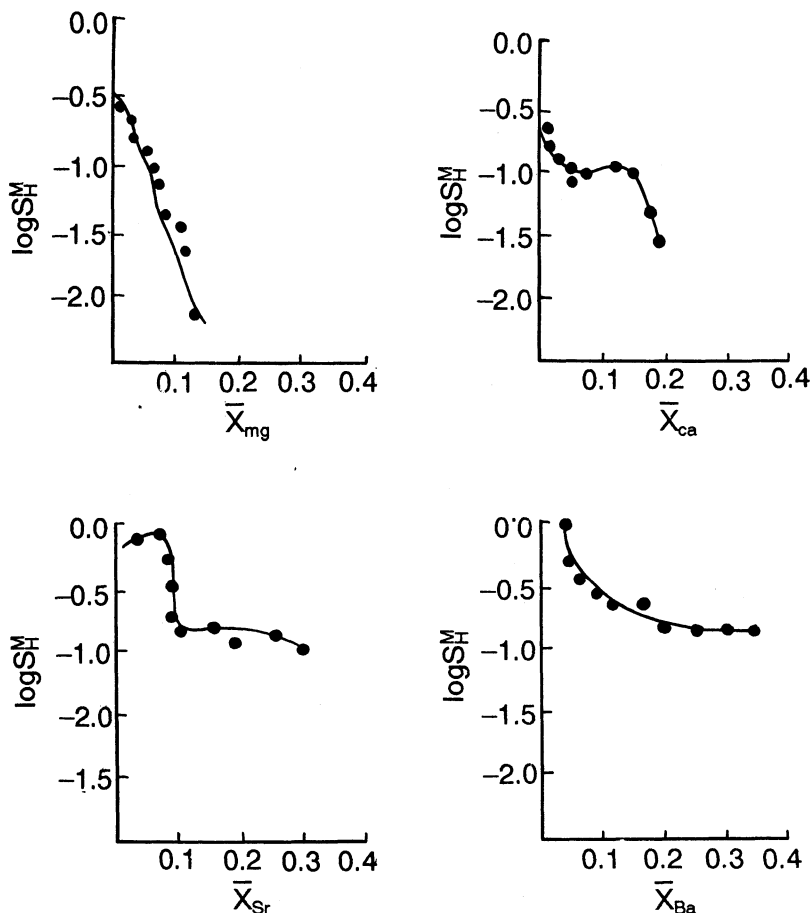


Fig. 2 Plots of  $\log K_H^M$  vs  $\bar{X}_M$

These  $\Delta H^\circ$  values are given in the Table 4. The positive sign of  $\Delta H^\circ$  indicates that the exchange equilibria of alkaline earth metal ions with hydrogen ions seem to be endothermic in nature.

The entropy change ( $\Delta S^\circ$ ) have been calculated by the following equation.

$$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ \quad (7)$$

$\Delta S^\circ$  values show no definite trend.

The entropy difference (5)  $\Delta s_{ex}$  between corresponding ionic forms of the exchanger can be given as

$$\Delta S_{ex} = (S_M^\circ - S_H^\circ) \quad (8)$$

where  $S_M^\circ$ ,  $S_H^\circ$  refer to the aqueous ionic entropies. The values of  $\Delta S_{ex}$  are also presented in Table-4. It becomes quite clear that there is a marked difference

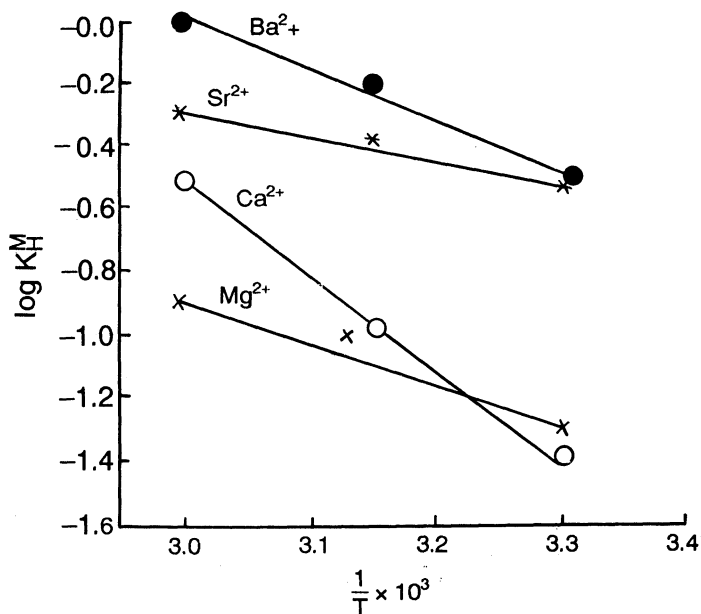


Fig. 3 Plots of  $\log K_H^M$  Vs.  $\frac{1}{T}$

between  $\Delta S_{ex}$  values of  $Mg^{2+}$  and  $Ba^{2+}$  forms. This marked difference in  $\Delta S_{ex}$  values may denote the potentiality for the separation of  $Mg^{2+}$  and  $Ba^{2+}$  ions in aqueous system on the column of tin (IV) molybdophosphate.

TABLE 4  
THERMODYNAMIC DATA FOR THE EXCHANGE OR METAL IONS WITH  
HYDROGEN IONS ON TIN (IV) MOLYBDOPHOSPHATE

ln k	Temp (K)	Mg <sup>2+</sup>	Ca <sup>2+</sup>	Sr <sup>2+</sup>	Ba <sup>2+</sup>
	303	-3.117	-3.273	-1.350	-1.190
	318	-2.046	-2.321	-0.820	-0.470
	333	-2.046	-1.233	-0.830	-0.110
$\Delta G^\circ$ (Cal/mole)	303	939	987	406	358
	318	647	734	259	148
	333	678	408	277	036
$\Delta H^\circ$ (Cal/mole)		3100	4430	795	2465
$\Delta S^\circ$ (Cal/deg/mole)		7	12	11	7
$\Delta S_{ex}$ (Cal/mole)		-8.8	5.8	7.5	8.15

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