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THERMODYNAMICS OF THE Ba^{2+}-H^+ AND Sr^{2+}-H^+ EXCHANGES ON ZIRCONIUM(IV) PHOSPHOSILICATE CATION EXCHANGER

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A thermodynamic study has been made on the exchange of Ba^{2+} and Sr^{2+} ions with the zirconium(IV) phosphosilicate in H^+-form at 30 and 50 °C which gives various thermodynamic parameters for the processes taking place in the material. The excess free energies (ΔG_m^x), enthalpies (ΔH_m^x) and entropies (ΔS_m^x) of mixing have also been evaluated.

Key Words : Thermodynamics; Cation Exchange; Zirconium(IV) Phosphosilicate

INTRODUCTION

INORGANIC ion exchangers are generally used for the metal ion separations. Although a large number of such materials have been synthesized,[1] only few of them have been studied thermodynamically.[2–7] Zirconium (IV) phosphosilicate (ZPS) has shown a semi-crystalline nature, promising ion exchange behaviour and reproducibility.[8] A thermodynamic study on this material should, therefore, be helpful to understand the ion-exchange mechanism underlying in this material.

EXPERIMENTAL

Reagents

Zirconyl chloride and sodium silicate were the B.D.H.(England) and Reidel (DEHAENAG, Seelze, Hannover) products respectively. All other reagents and chemicals were of Analar grade.

Apparatus

A water bath incubator shaker having a temperature variation of $\pm$ 0.5 °C was used for the equilibrium studies.

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Synthesis of Zirconium(IV) Phosphosilicate (ZPS)

It was synthesized by the method described earlier.[7]

Equilibrium Experiments

0.2 g samples of the exchanger in H^+ form were shaken in several stoppered conical flasks at the desired temperatures (30°C and 50°C) for 12hr with the 20ml fractions of metal ion solution having a constant ionic strength (0.03M) by adding appropriate amount of HNO_3 and the supernatant liquids were analysed for the metal and hydrogen ions volumetrically.

Evaluation of Thermodynamic Quantities

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

$$2H^+ZPS + M^{2+} \leftrightarrows M^+ - (ZPS)_2 + 2H^+, \qquad ...(1)$$

where M^{2+} represents the Ba^{2+} and Sr^{2+} ions. The equilibrium between the ionic concentrations in the exchanger and solution phases can be represented as :

$$\bar{C}_H + C_M \leftrightarrows \bar{C}_M + C_H \qquad ...(2)$$

and the equivalent ionic fractions of metal ions in the two phases can be calculated from the expressions :

$$\bar{X}_M = \frac{\bar{C}_M}{\bar{C}},\ X_M = \frac{C_M}{C},\ \bar{X}_H = \frac{\bar{C}_H}{\bar{C}_H},\ X_H = \frac{C_H}{C}. \qquad ...(3)$$

Then, the separation factors can be calculated using the relation

$$\alpha_H^M = \frac{\bar{X}_M}{\bar{X}_H} \cdot \frac{X_H}{X_M}. \qquad ...(4)$$

Since the solutions were taken in the dilute range of concentrations, the selectivity coefficients can be calculated from the expression

$$Kc = \frac{\bar{X}_M}{\bar{X}_H^2} \cdot \frac{X_H^2}{X_M} \qquad ...(5)$$

taking the ratio of activity coefficients as unity.[9] The thermodynamic equilibrium constant K can be obtained[10] from the equation :

$$\ln K = (Z_A - Z_B) + \int_0^1 \ln Kc\, d\bar{X}_M \qquad ...(6)$$

The thermodynamic functions ($\Delta G°$, $\Delta H°$ and $\Delta S°$) can be calculated by utilizing the Van't Hoff reaction isotherm for $\Delta G°$, the Van't Hoff isochore for $\Delta H°$ and the Gibbs-Helmhotz equation for $\Delta S°$.[11]

The activity coefficients of metal and hydrogen ions can be calculated from the expression[12]

$$\ln f_M = (\bar{X}_M - 1) \ln K_C - \int_0^{\bar{X}_M} \ln K_C \, d\bar{X}_M \qquad \ldots(7)$$

and

$$\ln f_H = \bar{X}_M \ln K_C - \int_0^{\bar{X}_M} \ln K_C \, d\bar{X}_M \qquad \ldots(8)$$

and the excess thermodynamic functions from the relations.[13,14]

$$\Delta G_m^x = RT\left[\bar{X}_M \ln f_M + \bar{X}_M \ln f_H\right], \qquad \ldots(9)$$

$$\Delta H_m^x = -RT^2\left[\bar{X}_M\left(\frac{\ln f_M}{T}\right) + \bar{X}_H\left(\frac{\ln f_H}{T}\right)\right] \qquad \ldots(10)$$

and

$$\Delta G_m^x = \Delta H_m^x - T\Delta S_m^x . \qquad \ldots(11)$$

Results and Discussion

The values of equivalent ionic fractions at 30 and 50 °C calculated for Ba^{2+} and Sr^{2+} exchanges in H^+-ZPS applying equation (3) are summarized in Tables I and II and the exchange isotherms are shown in Figs. 1 and 2. As Fig. 1 illustrates the Ba^{2+}-H^+ exchange isotherms are sigmoid and show a selectivity reversal at both the temperatures. It suggests that hydrogen ions are strongly preferred by ZPS upto an equivalent ionic fraction of 0.60 at 30 °C and upto 0.49 at 50 °C. Thereafter, an upward trend is observed for the Ba^{2+} ions. In case of the Sr^{2+}-H^+ exchange (Fig. 2) the isotherms are of Langmuir type. They show a stronger preference for H^+ as compared to Sr^{2+} throughout the range of concentration studied and the affinity is affected by temperature, being higher at 30 °C. It is supported by the separation factors (Table II) also. For the Ba^{2+}-H^+ exchange (Table I), however, some values of separation factor are greater than unity, indicating a selectivity reversal (Fig. 1).

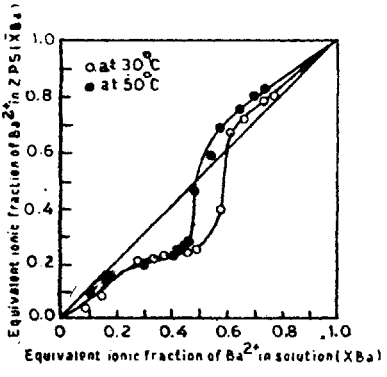

Fig 1 Exchange isotherms of Ba^{2+}-H^+ on *ZPS* at 30 and 50 °C

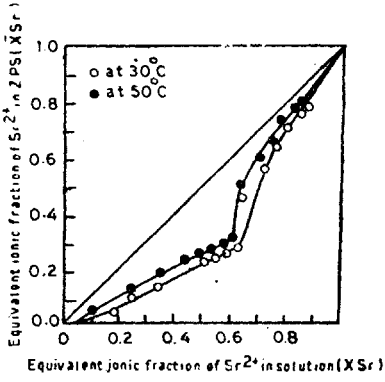

Fig 2 Exchange isotherms of Sr^{2+}-H^+ on *ZPS* at 30 and 50 °C

TABLE I

Values of the equivalent ionic fractions, separation factors and selectivity coefficients at 30° and 50 °C for the Ba^{2+}-H^+ exchange on zirconium(IV) phosphosilicate

Sl. No.	$\bar{X}_{Ba}$	X_{Ba}	$\bar{X}_H$	X_H	α_H^{Ba}	K_c	log K_c
				At 30 °C			
1.	0.04	0.08	0.96	0.92	0.50	0.45	−0.35
2.	0.09	0.14	0.91	0.86	0.60	0.54	−0.27
3.	0.16	0.16	0.84	0.84	0.99	0.96	−0.19
4.	0.16	0.25	0.84	0.75	0.55	0.47	−0.33
5.	0.21	0.27	0.79	0.73	0.52	0.65	−0.19
6.	0.22	0.33	0.79	0.97	0.55	0.45	−0.35
7.	0.23	0.37	0.77	0.63	3.52	0.42	−0.37
8.	0.24	0.43	0.76	0.57	0.42	0.32	−0.50
9.	0.24	0.46	0.76	0.55	0.36	0.28	−0.55
10.	0.25	0.49	0.75	0.51	0.35	0.24	−0.62
11.	0.39	0.53	0.61	0.47	0.58	0.45	−0.35
12.	0.40	0.58	0.30	0.42	0.87	1.31	+0.12
13.	0.67	0.61	0.33	0.39	1.40	1.55	+0.19
14.	0.72	0.63	0.28	0.34	1.34	1.65	+0.22
15.	0.79	0.73	0.21	0.27	1.46	1.96	+0.29
16.	0.80	0.77	0.20	0.23	0.98	1.45	+0.16
				At 50 °C			
1.	0.07	0.02	0.93	0.98	3.38	3.37	+0.53
2.	0.12	0.10	0.88	0.90	1.24	1.21	+0.08
3.	0.15	0.16	0.85	0.84	0.92	0.83	−0.08
4.	0.15	0.28	0.85	0.72	0.47	0.37	−0.43
5.	0.20	0.30	0.80	0.70	0.57	0.48	−0.32
6.	0.22	0.34	0.78	0.66	0.57	0.48	−0.32
7.	0.23	0.41	0.77	0.60	0.43	0.32	−0.49
8.	0.26	0.42	0.74	0.59	0.51	0.39	−0.41
9.	0.26	0.45	0.74	0.55	0.44	0.33	−0.48
10.	0.27	0.46	0.73	0.52	0.21	0.29	−0.54
11.	0.47	0.48	0.53	0.52	0.96	0.94	−0.03
12.	0.59	0.55	0.41	0.45	1.17	0.29	+0.11
13.	0.68	0.57	0.32	0.43	1.58	2.11	+0.32
14.	0.74	0.64	0.26	0.36	1.60	2.22	+0.35
15.	0.80	0.71	0.20	0.29	1.63	2.36	+0.37
16.	0.82	0.74	0.18	0.26	1.56	2.24	+0.35

Values of selectivity coefficients (K_C) obtained with the help of equation (5) are summarized in Tables I and II while the plots of log K_C versus X_M are shown in Figs. 3 and 4. The thermodynamic equilibrium constants were then obtained from the equations 6. The integrals were evaluated from the areas under the curves of Figs. 3 and 4 using the trapezoidal rule,[15] the values being summarized in Table III. In both the systems the K values were higher at 50 °C than at 30 °C indicating a higher affinity of the exchanger for the Ba^{2+} and Sr^{2+} ions at a higher

TABLE II

Values of the equivalent ionic fractions, separation factors aud selectivity coefficients at 30° *and* 50 °C *for the* Sr^{2+}-H^+ *exchange on Zirconium(IV) phosphosilicate*

Sl. No.	$\bar{X}_{Sr}$	X_{Sr}	$\bar{X}_H$	X_H	α_H^{Sr}	K_e	log K_e
			At 30 °C				
1.	0.04	0.17	0.96	0.86	0.21	0.17	−0.77
2.	0.11	0.24	0.79	0.43	0.42	0.37	−0.43
3.	0.15	0.33	0.85	0.76	0.41	0.35	−0.46
4.	0.24	0.33	0.77	0.67	0.62	0.51	−0.29
5.	0.24	0.43	0.76	0.57	0.41	0.29	−0.74
6.	0.24	0.51	0.76	0.49	0.31	0.20	−0.71
7.	0.25	0.54	0.76	0.46	0.80	0.17	−0.78
8.	0.26	0.58	0.74	0.42	0.26	0.15	−0.83
9.	0.27	0.62	0.73	0.38	0.23	0.12	−0.53
10.	0.27	0.63	0.73	0.37	0.22	0.12	−0.96
11.	0.47	0.64	0.73	0.35	0.27	0.30	−0.53
12.	0.57	0.72	0.44	0.28	0.51	0.32	−0.50
13.	0.65	0.76	0.35	0.24	0.57	0.38	−0.43
14.	0.72	0.79	0.28	0.21	0.67	0.48	−0.32
15.	0.77	0.85	0.23	0.15	0.60	0.40	−0.40
16.	0.78	0.87	0.22	0.13	0.53	0.31	−0.50
			At 50 °C				
1.	0.05	0.10	0.91	0.91	0.56	0.55	−0.26
2.	0.12	0.24	0.88	0.76	0.45	0.37	−0.43
3.	0.13	0.25	0.79	0.75	0.51	0.46	−0.34
4.	0.19	0.34	0.46	0.66	0.47	0.39	−0.41
5.	0.24	0.44	0.76	0.56	0.41	0.29	−0.55
6.	0.26	0.49	0.74	0.51	0.38	0.25	−0.50
7.	0.28	0.53	0.72	0.47	0.35	0.22	−0.66
8.	0.29	0.57	0.71	0.43	0.30	1.18	−0.76
9.	0.30	0.59	0.70	0.41	0.29	0.17	−0.78
10.	0.33	0.60	0.67	0.40	0.32	0.18	−0.74
11.	0.51	0.63	0.49	0.37	0.61	0.45	−0.35
12.	0.60	0.70	0.40	0.30	0.64	0.47	−0.33
13.	0.67	0.75	0.33	0.25	0.68	0.50	−0.31
14.	0.74	0.78	0.26	0.23	0.82	0.78	−0.17
15.	0.78	0.84	0.22	0.16	0.68	0.19	−0.31
16.	0.81	0.85	0.20	0.14	0.66	0.46	−0.34

TABLE III

Thermodynamic values for the Ba^{2+}-H^+ *and* Sr^{2+}-H^+ *exchanges on zirconium(IV) phosphosilicate at* 30 °C *and* 50 °C

Thermodynamic parameters	Values in Ba^{2+}-H^+ system		Values in Sr^{2+}-H^+ system	
	30 °C	50 °C	30 °C	50 °C
K	2.12	2.54	1.08	1.41
$\Delta G°$ (KJ mol^{-1})	−1.89	−2.51	−0.19	−0.92
$\Delta H°$ (KJ mol^{-1})	7.40		10.83	
$\Delta S°$ (KJ mol^{-1} degree^{-1})	0.03	0.03	0.04	0.04

TABLE IV

Values of the activity coefficients for the different Ba^{2+}-H^+ *and* Sr^{2+}-H^+ *exchanges on zirconium(IV) phosphosilicate at* 30 °C *and* 50 °C

Sl. No.	Values at 30 °C			Values at 50 °C		
	$\bar{X}_{Ba}$	f_{Ba}	f_H	$\bar{X}_{Ba}$	f_{Ba}	f_H
			Ba^{2+}-H^+			
1.	0.04	1.27	1.01	0.07	2.36	0.94
2.	0.09	1.12	1.02	0.12	1.35	1.00
3.	0.16	1.10	1.05	0.14	1.78	1.03
4.	0.16	1.10	1.05	0.14	1.78	1.03
5.	0.21	0.60	0.96	0.20	0.94	0.53
6.	0.22	1.93	0.92	0.22	2.03	0.91
7.	0.23	0.13	0.91	0.23	2.07	0.90
8.	0.24	2.92	0.82	0.26	2.55	0.84
9.	0.24	2.92	0.82	0.26	2.55	0.84
10.	0.25	2.25	0.70	0.27	2.80	0.79
11.	0.39	0.19	0.96	0.47	1.30	1.30
12.	0.40	2.10	0.98	0.59	1.10	1.49
13.	0.67	1.15	2.03	0.68	0.95	1.93
14.	0.72	1.14	2.05	0.74	0.98	2.00
15.	0.79	1.13	2.11	0.80	0.93	2.02
16.	0.80	1.13	2.11	0.82	0.93	2.03

Sl. No.	Values at 30 °C			Values at 50 °C		
	$\bar{X}_{Sr}$	f_{Sr}	f_H	$\bar{X}_{Sr}$	f_{Sr}	f_H
			Sr^{2+}-H^+			
1.	0.04	5.36	0.93	0.05	3.07	0.91
2.	0.11	3.08	0.98	0.12	2.39	0.91
3.	0.15	2.31	1.03	0.13	1.75	0.96
4.	0.24	3.21	0.86	0.19	1.78	0.96
5.	0.24	3.21	0.86	0.24	1.78	0.96
6.	0.24	3.21	0.86	0.28	3.10	0.80
7.	0.25	4.79	0.81	0.28	3.54	0.76
8.	0.26	5.59	0.77	0.29	4.04	0.72
9.	0.27	6.34	0.78	0.30	3.22	0.79
10.	0.27	6.34	0.78	0.33	4.11	0.72
11.	0.47	3.61	1.06	0.51	2.31	1.08
12.	0.57	3.38	1.09	0.60	2.29	1.09
13.	0.65	3.18	1.20	0.67	2.20	1.10
14.	0.72	2.95	1.37	0.74	2.17	1.14
15.	0.77	3.11	1.18	0.78	2.23	1.07
16.	0.78	3.31	0.69	0.80	2.94	0.65

TABLE V

Values of the excess free energies, enthalpies and entropies of mixing for the Ba^{2+}-H^+ *exchange on zironium(IV) phosphosilicate at* 30 *and* 50 °C

Sl. No.	$\bar{X}_{Ba}$	ΔG_m^E (KJ mol^{-1})	ΔH_m^E (KJ mol^{-1})	ΔS_m^E (KJ mol^{-1} degree^{-1})
		At 30 °C		
1.	0.04	0.04	+0.14	0.00
2.	0.09	0.07	−0.04	0.00
3.	0.16	0.14	+0.35	0.00
4.	0.16	0.14	+0.35	0.00
5.	0.21	0.18	−0.36	0.00
6.	0.22	0.20	+0.09	0.00
7.	0.23	0.25	+0.15	0.00
8.	0.24	0.27	+0.52	0.00
9.	0.24	0.28	+0.55	0.00
10.	0.25	0.31	+1.70	0.00
11.	0.39	0.71	+0.88	0.00
12.	0.40	0.73	+4.94	+0.01
13.	0.67	0.81	+5.98	+0.02
14.	0.72	0.75	+6.98	+0.02
15.	0.79	0.64	+5.95	+0.02
16.	0.80	0.63	+6.35	+0.02
		At 50 °C		
1.	0.07	0.05	−0.63	0.00
2.	0.12	0.10	−0.31	0.00
3.	0.15	0.07	+0.42	0.00
4.	0.15	0.12	+0.40	0.00
5.	0.20	0.19	−0.28	0.00
6.	0.22	0.22	+0.09	0.00
7.	0.23	0.23	−0.41	0.00
8.	0.26	0.31	+0.74	0.00
9.	0.26	0.18	+0.76	0.00
10.	0.27	0.27	+2.03	+0.01
11.	0.47	0.70	+3.83	+0.01
12.	0.59	0.59	+9.24	+0.03
13.	0.68	0.47	+6.39	+0.02
14.	0.74	0.27	+8.05	+0.02
15.	0.80	0.25	+6.80	+0.02
16.	0.82	0.19	+7.33	+0.02

temperature. A comparison of the selectivity coefficients for the Ba^{2+}-H^+ and Sr^{2+}-H^+ exchanges shows that the material is more selective for Ba^{2+} ions.

The standard enthalpy changes, $\Delta H°$, were in accordance with the temperature dependent exchanges and reactions being endothermic for both the systems. The

lower values of Ba^{2+}-H^+ exchanges than the Sr^{2+}-H^+ exchanges confirm the above conclusion. A gain in standard entropy changes ($\Delta S°$) for both exchanges reveals their endothermic behaviour.

The deviation of activity coefficients from unity (Tables IV & V) indicates a heterogeneous distribution of ions at the ZPS surface. Also, the values are high, a characteristic shown earlier[16,9] by solid phases in case of ions with unlike charges interacting on non-ideal surfaces.

TABLE VI

Values of the excess free energies, enthalpies and entropies of mixing for the Sr^{2+}-H^+ *exchange on zirconium(IV) phosphosilicate at* 30 *and* 50 °C

Sl. No.	X_{Sr}	G^E_m (KJ mol^{-1})	H^E_m (KJ mol^{-1})	S^E_m (KJ mol^{-1} degree^{-1})
		At 30 °C		
1.	0.04	0.01	1.81	0.01
2.	0.11	0.25	3.39	0.01
3.	0.15	0.38	3.91	0.01
4.	0.24	0.40	2.19	0.01
5.	0.24	0.41	2.28	0.01
6.	0.24	0.41	0.50	0.01
7.	0.25	0.57	4.90	0.01
8.	0.26	0.66	5.26	0.02
9.	0.27	0.82	6.64	0.02
10.	0.27	0.82	6.95	0.02
11.	0.47	1.60	7.68	0 02
12.	0.57	1.82	8.32	0.02
13.	0.65	2.05	7.83	0.02
14.	0.72	2.17	10.30	0.02
15.	0.77	2.30	10.71	0.03
16.	0.78	2.33	11.18	0.03
		At 50 °C		
1.	0.05	0.02	2.37	0.00
2.	0.12	0.07	3.97	0.01
3.	0.13	0.23	3.98	0.01
4.	0.19	0.29	1.23	0.00
5.	0.24	0.28	2.73	0.00
6.	0.26	0.35	2.79	0.00
7.	0.28	0.43	5.92	0.02
8.	0.29	0.44	6.23	0.02
9.	0.30	0.64	8.34	0.02
10.	0.33	0.63	8.67	0.02
11.	0.51	1.38	9.66	0.03
12.	0.60	1.43	10.02	0.02
13.	0.67	1.51	9.34	0.03
14.	0.74	1.63	11.81	0.03
15.	0.78	1.72	12.32	0.03
16.	0.80	1.78	12.55	0.03

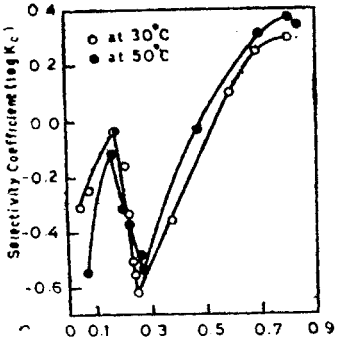

FIG 3 Plots of log K_e *Vs.* $\bar{X}M$ on *ZPS* for Ba^{2+}-H^+ at 30 and 50 °C

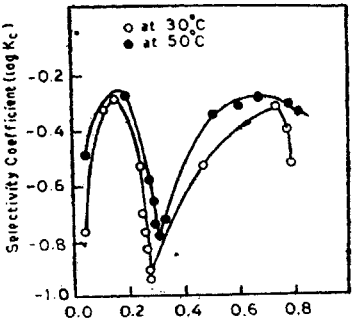

FIG 4 Plots of log K_e *Vs.* $\bar{X}M$ on *ZPS* for Sr^{2+}-H^+ at 30 and 50 °C

To further examine the deviation of these heterogeneous systems from an ideal situation, the excess thermodynamic functions were calculated using the equations 9, 10 & 11. Table VI summarises the values. The excess free energy values are positive and increase with the concentration of Ba^{2+} and Sr^{2+} ions. The values of excess enthalpy and entropy changes are in accordance with the observations of Vansant and Utterhoeven,[13] Gast and Klobe,[14] Howery and Thomas[12] on clays.

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