SYNTHESIS, CHARACTERIZATION AND THERMODYNAMICS OF EXCHANGE USING ZIRCONIUM TITANIUM PHOSPHATE CATION EXCHANGER

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Received December 29, 2006
Accepted July 1, 2007

A mixed material of the class of tetravalent bimetallic acid (TBMA) salt – zirconium titanium phosphate (ZTP) – has been synthesized by the sol-gel technique. ZTP has been characterized by elemental analysis, thermal analysis (TGA, DTA), FTIR, X-ray diffraction and SEM. Ion exchange capacity (IEC) of the material has been determined and the effect of calcination (373–773 K) on IEC studied and chemical stability of the material in various media (acids, bases and organic solvents) assessed. Further, the equilibrium exchange of H in ZTP for Mg^{2+}, Ca^{2+}, Sr^{2+} and Ba^{2+} ions has been studied at 303, 313, 323 and 333 K at constant ionic strength. On the basis of the exchange isotherms, various thermodynamic parameters such as equilibrium constant (K), standard gibbs energy change (ΔG^o), entropy change (ΔS^o) and enthalpy change (ΔH^o) have been calculated. The parameters were correlated with the ion exchange characteristics of the material.

Keywords: Thermodynamics of ion exchange; Ion exchange equilibria; Zirconium titanium phosphate; Cation exchanger; Tetravalent metal acid salt; Tetravalent bimetallic acid salt; Inorganic ion exchanger; Ion exchange isotherm; Thermodynamic parameters.

Although well known[1,2] and investigated in the last 50 years, acid salts of tetravalent metals (TMA) are emerging as promising materials owing to their robust properties. TMA salts[3] are cation exchangers, obtainable in both amorphous and crystalline forms, with the general formula $M(IV)(HXO_4)_2 \cdot nH_2O$, where M(IV) = Zr, Ti, Sn, Ce, Th, etc. and X = P, W, As, Mo, Sb, etc. These materials possess structural hydroxy groups, the H of which being the exchangeable sites. A number of cations can be exchanged with H^+ due to which the material possesses cation exchange properties.

There is currently high interest in mixed engineering materials leading to the formation of new solid-state structures and materials with new complex properties. Mixed materials are novel multifunctional materials, which offer a wide range of interesting properties. New mixed materials of the TMA

Collect. Czech. Chem. Commun. 2007, Vol. 72, No. 9, pp. 1306–1318

doi:10.1135/cccc20071306

salts class, i.e. compounds containing two different cations and an anion or two different anions and a cation, show improved ion exchange properties and selectivity for particular metal ions in comparison with their single-salt counterparts. A literature survey shows that mixed materials containing two anions and a cation have been widely investigated[4–8]. However, not much work has been done on mixed materials containing two cations and an anion.

Zirconium phosphate has shown a number of advantages as an ideal host lattice[9–17] for the development of new ion exchange materials. Zirconium phosphate[1] and titanium phosphate[3] of the TMA salts class are now well-known inorganic ion exchange materials. Although these compounds are not very different as exchangers, slight differences do exist, owing to difference in their ion size parameters. It was assumed that if Ti^{4+} is incorporated in the matrix of zirconium phosphate or vice versa, the ion exchange properties of mixed zirconium titanium phosphate (ZTP) could change considerably compared with the single salt counterparts.

Clearfield and Yazawa[18,19] have earlier reported the synthesis of crystalline ZTP with varying zirconium to titanium ratios. Though structures of crystalline materials are well known and favor a large ion exchange capacity (IEC), useful for ion exchange, they have not found substantial use as they are produced in powder form, which prevent their use in column operations. Amorphous materials are obtained in granular form which is very suitable for column operations[20–24]. ZTP being synthesized by sol-gel routes, materials with varying water content, composition, ion exchange capacity and crystallinity can be obtained by varying parameters such as stoichiometry and concentration of the reagents used, temperature at which they are mixed, rate of addition, mode of mixing, pH, etc. Ion exchange materials with higher selectivities are continuously being investigated[25].

Kinetics of exchange enables us to understand the utilization of an ion exchange material in separation technology. Thermodynamic studies provide information relating to the mechanism and feasibility of ion exchange processes occurring on the surface, as well as the ability to predict correlations of experimental results in the absence of detailed knowledge of the structure of the system. Thermodynamics of exchange in ZTP is of considerable interest because of their possible use as cation exchangers at high temperatures.

In the present endeavor, mixed material of the class of tetravalent bimetallic acid (TBMA) salt – zirconium titanium phosphate (ZTP) – has been synthesized by a modified sol-gel technique. The material has been characterized by elemental analysis, thermal analysis (TGA, DTA), FTIR, X-ray diffraction and scanning electron micrograoh (SEM). IEC of the material has been determined and the effect of calcination (373–773 K) on IEC was studied. Chemical stability of the material in various media (acids, bases and organic solvents) has been assessed. Kinetics of ion exchange of alkaline earth metals using ZTP has been reported by us earlier[26]. Herein, we report the equilibrium exchange of Mg^{2+}, Ca^{2+}, Sr^{2+} and Ba^{2+} ions with H contained in ZTP at 303, 313, 323 and 333 K at a constant ionic strength. On the basis of the exchange isotherms, various thermodynamic parameters such as equilibrium constant (K), standard gibbs energy change (ΔG^o), entropy change (ΔS^o) and enthalpy change (ΔH^o) have been calculated. Correlations of these parameters have been made with the ion exchange characteristics of the material.

EXPERIMENTAL

All materials used were of AR grade. Double-distilled water was used for all the studies.

Synthesis of ZTP: A mixture of 0.1 M $TiCl_4$ and 0.1 M $ZrOCl_2 \cdot 8H_2O$ in 10% w/v H_2SO_4 (100 ml) was prepared, to which 0.2 M $NaH_2PO_4 \cdot 2H_2O$ (200 ml) was added dropwise (flow rate, 1 ml min^{-1}) with continuous stirring at room temperature. After complete precipitation, the obtained gel was stirred for another 5 h. The precipitates was kept in contact with mother liquor overnight, filtered, washed with conductivity water to remove adhering ions (chloride and sulfate) and dried at room temperature. The material was then disintegrated to the desired particle size (30–60 mesh (ASTM)) by grinding and sieving. This material (5 g) was treated with 1 M HNO_3 (50 ml) with occasional shaking for 30 min. The sample was then separated from acid by decantation and treated with conductivity water to remove adhering acid. This process (acid treatment) was repeated at least five times. After final washing, the material was dried at room temperature.

Ion exchange capacity (IEC): IEC values for Na^+ as well as for Mg^{2+}, Ca^{2+}, Sr^{2+} and Ba^{2+} were determined by the column method[27]. For Na^+ exchange capacity determination, the column was prepared in a burette, provided with glass wool at the bottom. It was filled half way with distilled water, preventing air traps. The ion exchanger (0.5 g) was accurately weighed and transferred through a dry funnel. The water inside the column was kept at a level of about 1 cm above the material. A 250-ml solution of sodium acetate was added into the column and the elution was carried out at a flow rate of 0.5 ml min^{-1}. The effluent was collected in a 500 ml conical flask and then titrated against 0.1 M NaOH solution. The capacity of the exchanger in milliequivalent per gram is given by av/w where a is the molarity of the NaOH solution, v is the volume of NaOH required for titration and w is the weight of the exchanger. Mg^{2+}, Ca^{2+}, Sr^{2+} and Ba^{2+} exchange capacities were determined by taking respective metal acetate solution and following the same procedure.

Calcination studies: The effect of heating on IEC was studied by heating several 1-g portions of the material at 373,473,573,673 and 773 K for 2 h in a muffle furnace and determining the Na^+ exchange capacity by the column method[27] at room temperature.

Chemical stability: The chemical stability of the material in various media – acids (HCl, H_2SO_4, HNO_3), bases (NaOH and KOH) and organic solvents (ethanol, benzene and acetone) – was studied by taking 500 mg of a sample in 50 ml of the particular medium and standing for 24 h. The change in color, nature and weight was observed.

Instrumentation: ZTP has been analyzed for zirconium, titanium and phosphorus by induced coupled plasma atomic emission spectrophotometer (ICP AES) using Labtam, Model 8440 Plasmalab. Thermal analysis was performed on a Shimadzu DT-30 thermal analyzer at a heating rate of 10 K per minute in nitrogen atmosphere. FTIR spectra were obtained using KBr wafers on a Perkin–Elmer Paragon 1000 Spectrophotometer. X-ray diffractogram (2θ = 5–90°) was obtained on an X-ray diffractometer Brucker AXS D8 using CuKα radiation with a nickel filter. SEM of the sample was scanned on Jeol JSM-5610-SLV scanning electron microscope. For thermodynamic studies, a shaker having a temperature variation of ±0.5 K was used.

Equilibrium experiments: The equilibrium experiments were performed by shaking 200 mg (30–60 mesh (ASTM)) of the exchanger in H^+ form at the desired temperature (303, 313, 323 and 333 K) in an electric, temperature-controlled shaker for 6 h with 20 ml of a solution containing 0.06 м HCl and the appropriate metal ion of varying volume ratios (1, 3, 5, ..., 19 ml of 0.02 м metal ion solution and 19, 17, 15, ..., 1 ml of 0.06 м hydrogen ion solution, respectively) were prepared having constant ionic strength (0.06 м). In aliquots of the supernatants, the respective metal ion content were estimated by EDTA titration. During reverse exchange, similar experiments were performed with the exchanger in the respective metal ion forms at constant ionic strength (0.06 м).

RESULTS AND DISCUSSION

Characterization

The synthesized ZTP obtained as white hard granules. Elemental analysis by ICP AES shows the ratio of Zr:Ti:P to be 1:1:2.

X-ray diffractogram of ZTP does not exhibit any sharp peak indicating ZTP to be an amorphous material (Fig. 1). The FTIR spectra of ZTP exhibit a broad band in the region ~3400 cm^{-1}, which is attributed to asymmetric and symmetric OH stretching in OH groups and water. A sharp medium band at ~1620 cm^{-1} is attributed to the H–O–H bending. The bonds indicate the presence of structural OH protons in the material. This fact is more evident from the IEC values that have been evaluated. A band at ~1032 cm^{-1} is attributed to P=O stretching. The Na^+ IEC of ZTP at room temperature is 3.36 mequiv g^{-1}. The IEC values on calcination at 373, 473, 573, 673, 773 K were 3.25, 3.04, 2.67, 2.28 and 1.86 mequiv g^{-1}, respectively. The IEC values decrease on heating due to condensation of structural OH groups at higher temperatures. This fact is also evident from the FTIR spectra of the heated samples. In Fig. 2, it is observed that the intensity of the peaks at ~3400 and 1620 cm^{-1}, representing the OH group, diminishes as the heating temperature increases. TGA of ZTP shows a sharp change in the temperature range 353–453 K, corresponding to the loss of external water, after which a gradual weight loss is observed up to 793 K (Fig. 3). This may be due to the condensation of structural OH groups. The observations are further supported by the fact that IEC values decrease on calcination, as discussed above. SEMs of the materials zirconium phosphate, titanium phosphate and zirconium titanium phosphate are presented in Figs 4a–4c, respectively, which indicate the ZTP is distinguished from their single salt counterpart zirconium phosphate and titanium phosphate. Variations in surface morphology as well as irregular particle size indicate amorphous nature of the material.

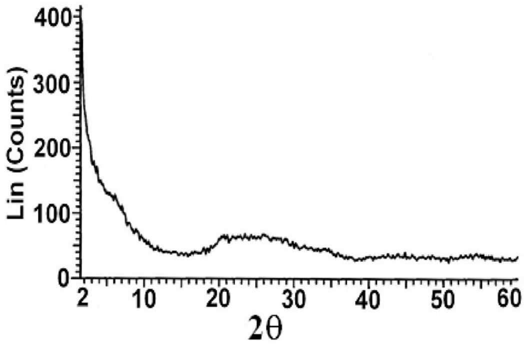

FIG. 1
XRD of zirconium titanium phosphate

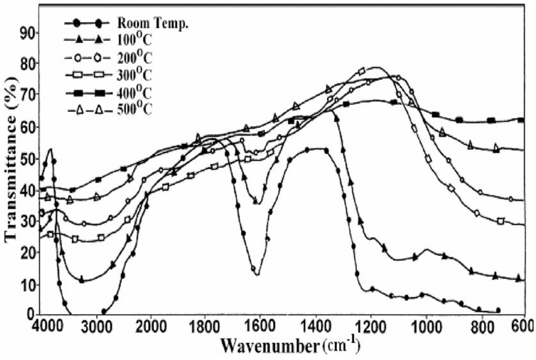

FIG. 2
FTIR of zirconium titanium phosphate at different temperatures: ● room temperature, ▲ 100, ○ 200, □ 300, ■ 400 and △ 500 °C

ZTP exhibits good chemical stability in acid media, (maximum concentration limits being 9 M H_2SO_4, 16 M HNO_3 and 11.3 M HCl) and in organic solvents (ethanol, benzene and acetone), but a lower stability in alkaline media (maximum concentration limits being 5 M NaOH and 5 M KOH). The values of exchange capacity for Mg^{2+}, Ca^{2+}, Sr^{2+} and Ba^{2+} are 1.18, 2.46, 2.50 and 2.56 mequiv g^{-1}, respectively. These values have been used for computing thermodynamic parameters.

Thermodynamic Study

As it is clear from Fig. 5, the exchange equilibrium on zirconium titanium phosphate appears to have attained within 4 h and hence all the equilibrium studies were performed after shaking for 6 h.

The ion exchange process occurring on the surface of ZTP can be represented by the equation

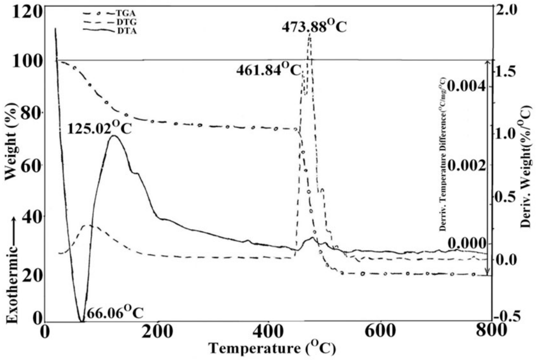

FIG. 3
Thermograms of zirconium titanium phosphate; TGA (– · – ·), DTG (- - - -) and DTA (——)

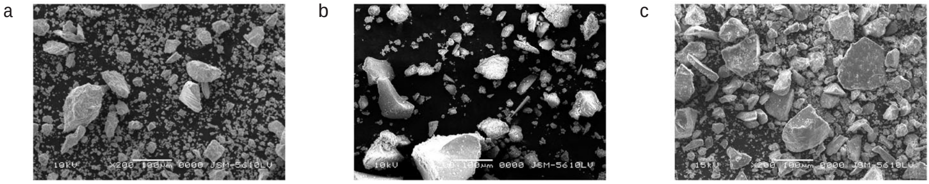

FIG. 4
SEM of zirconium phosphate (a), titanium phosphate (b) and zirconium titanium phosphate (c)

$$2\ (H^+–ZTP) + M^{2+} \rightleftharpoons M^{2+}(ZTP)_2 + 2\ H^+ \tag{1}$$

where M^{2+} is Mg^{2+}, Ca^{2+}, Sr^{2+} or Ba^{2+}.

This equation can also be written in a generalized form as

$$\overline{C}_H + C_M = \overline{C}_M + C_H \tag{2}$$

where the barred and unbarred quantities represent the concentrations in the exchanger and solution phases, respectively. The equivalent ionic fractions of the counter-ions in the ZTP and solution phases ($\overline{X}_M$, $\overline{X}_H$, X_M and X_H) were calculated from the expressions

$$\overline{X}_M = \overline{C}_M/\overline{C}; \quad X_M = C_M/C; \quad \overline{X}_H = \overline{C}_H/\overline{C} \quad \text{and} \quad X_H = C_H/C \tag{3}$$

where $\overline{C}$ and C are the total electrolyte concentrations in the solid ($\overline{C} = \overline{C}_M + \overline{C}_H$) and solution phases ($C = C_M + C_H$).

The ion exchange isotherm for $Mg^{2+}–H^+$, $Ca^{2+}–H^+$, $Sr^{2+}–H^+$ and $Ba^{2+}–H^+$ exchanges at 303, 313, 323 and 333 K show that the exchanges are reversible in all cases. This could be explained by the fact that the forward and reverse isotherms exhibit similar trends. The forward and reverse exchange isotherms for $Mg^{2+}–H^+$, $Ca^{2+}–H^+$, $Sr^{2+}–H^+$ and $Ba^{2+}–H^+$ exchanges are presented in Figs 6a–6d and Figs 7a–7d, respectively. The exchange isotherms[28] show that ZTP prefer metal ions to H^+.

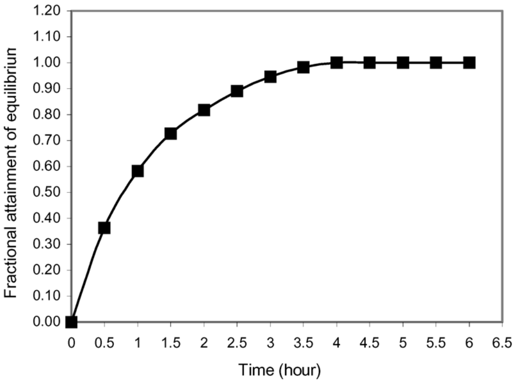

FIG. 5
A plot of the fractional attainment of equilibrium for $Mg^{2+}–H^+$ exchange on ZTP vs time

For equilibrium (*1*), the selectivity coefficients (K_c) were calculated from the expression

$$K_c = \frac{\overline{X}_M (X_H)^2}{(\overline{X}_H)^2 X_M} . \tag{4}$$

The corrected selectivity coefficient (K_c') is defined by

$$K_c' = \frac{\overline{X}_M (X_H)^2}{(\overline{X}_H)^2 X_M} \frac{(\gamma_H)^2}{\gamma_M} \tag{5}$$

where $\overline{X}_M$ and $\overline{X}_H$ are equivalent ionic fractions of metal ions and hydrogen ions in the ion exchanger phase, X_M and X_H are equivalent ionic fractions

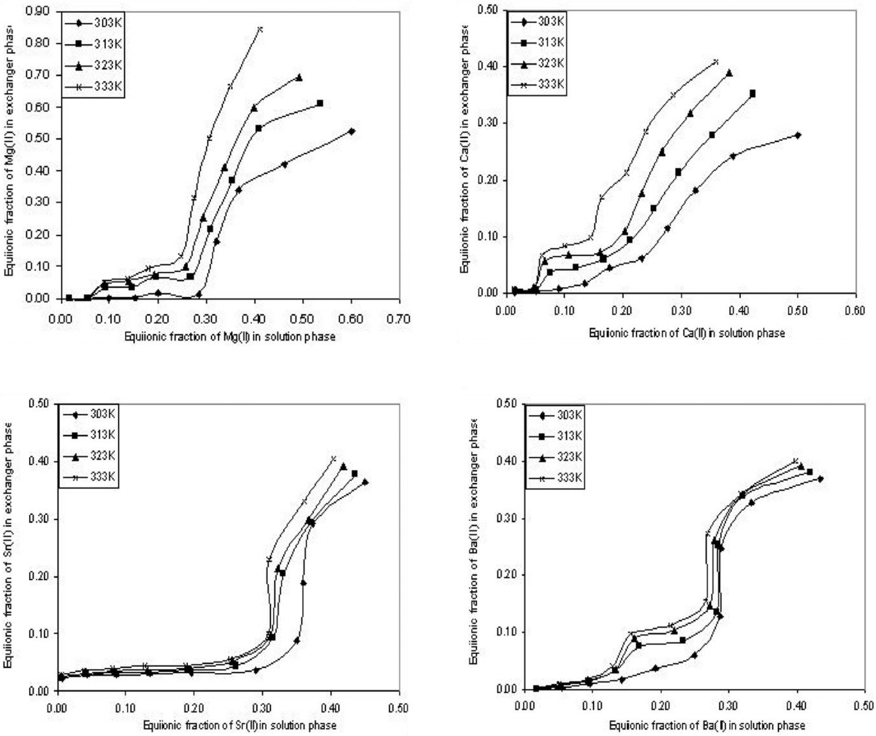

FIG. 6
Exchange isotherms for the Mg^{2+}–H^+ (a), Ca^{2+}–H^+ (b), Sr^{2+}–H^+ (c) and Ba^{2+}–H^+ (d) exchange on ZTP; ◆ 303, ■ 313, ▲ 323 and × 333 K

of metal ions and hydrogen ions in solution phase, respectively, γ_M and γ_H are the activity coefficients of metal ion and hydrogen ion, respectively, in the solution phase and n is the valence of the metal ion. The solution phase activity coefficients for hydrogen and metal ions were calculated using the Debye–Hückel limiting law

$$\log\gamma_i = -A\, Z_i^2 \sqrt{\mu_i} \tag{6}$$

where γ_i is the activity coefficient, A is a constant, the values of which were taken from the table of Mannov[29], Z_i is charge of the ions and μ_i is the ionic strength. The plots of ln K_c' vs $\overline{X}_M$ are drawn. The thermodynamic equilibrium constant K was calculated at different temperatures from plots of ln K_c' vs equivalent ionic fractions of metal ions in the exchanger phase, $\overline{X}_M$, following the expression given by Gaines and Thomas[30]

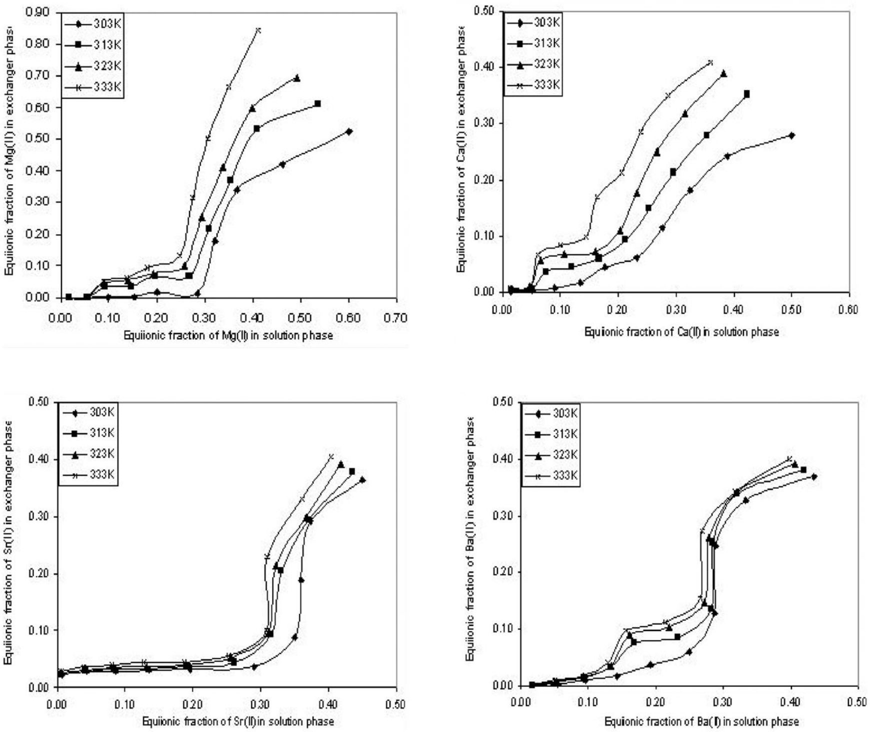

FIG. 7

Exchange isotherms for the H^+–Mg^{2+} (a), H^+–Ca^{2+} (b), H^+–Sr^{2+} (c) and H^+–Ba^{2+} (d) exchange on ZTP; ◆ 303, ■ 313, ▲ 323 and × 333 K

$$\ln K = (Z_{\mathrm{M}} - Z_{\mathrm{H}}) + \int_0^1 \ln K_{\mathrm{c}}' \; \mathrm{d}\overline{X}_{\mathrm{M}} \tag{7}$$

where Z_{M} and Z_{H} are charges on the competing metal and hydrogen ions. The integrals were evaluated from the areas under the curve of ln K_{c}' vs $\overline{X}_{\mathrm{M}}$ using the trapezoidal rule[31] or computer (curxpt) software and the K values are summarized in Table I.

The standard gibbs energy, ΔG^{o}, was calculated from the thermodynamic equilibrium constant K, using the general equation

$$\Delta G^{\mathrm{o}} = \frac{-RT \ln K}{Z_{\mathrm{M}} \; Z_{\mathrm{H}}} \, . \tag{8}$$

The standard enthalpy change, ΔH^{o}, was calculated form the van't Hoff isochor

$$\Delta H^{\mathrm{o}} = [\ln K_2 - \ln K_1] \frac{T_1 T_2}{T_2 - T_1} R \, . \tag{9}$$

The standard entropy change, ΔS^{o}, has been calculated using the expression

$$\Delta S^{\mathrm{o}} = \frac{\Delta H^{\mathrm{o}} - \Delta G^{\mathrm{o}}}{T} \, . \tag{10}$$

Thermodynamic parameters for M^{2+}–H^+ exchanges on ZTP at various temperatures are presented in Table I. The values of K increase with increasing temperature, indicating that the metal ions have higher affinity to the exchanger at higher temperature and also that the mechanism is ion exchange. When solid ion exchanger is in contact with electrolyte solution, mainly two reactions may take place, either ion exchange or sorption. As physical forces are responsible for the sorption, the value of equilibrium constant, K, may decrease with increasing temperature. Ion exchange being a chemical reaction, some energy is required for crossing the barrier (energy of activation). In such cases therefore as the temperature increases, the ion exchange will increase. Thus as K increases with increase in temperature, this indicates that the mechanism is ion exchange.

The gibbs energy change, ΔG^{o}, over the whole temperature range is negative, indicating that the exchange of H^+ for M^{2+} is spontaneous. At higher temperature, more negative values of ΔG^o indicate higher preference to metal ions.

A positive enthalpy change indicates that the exchange reaction is endothermic. The value of ΔH^o appears to be a function of the hydrated ionic radii of the exchanging metal ions. Probably partial dehydration occurs and some energy must be supplied to the cation as it leaves the hydration sphere to undergo ion exchange. The extent of hydration of an ion in aqueous solution depends on the size and charge of the ion. Mg^{2+} with the smallest ionic radii is heavily hydrated, while Ba^{2+} with the highest ionic

TABLE I
Thermodynamic parameters for M^{2+}–H^+ exchanges on ZTP at various temperatures

Exchange	Temperature K	K	ΔG^0 kJ mol^{-1}	$\Delta H^{0\,a}$ kJ mol^{-1}	ΔS^0 J mol^{-1} K^{-1}
Mg^{2+}–H^+	303	2.99	–1.38	49.30	167.26
	313	5.85	–2.30		164.86
	323	9.53	–3.03		162.01
	333	17.42	–3.96		159.93
Ca^{2+}–H^+	303	2.07	–0.92	36.31	122.87
	313	3.33	–1.56		121.01
	323	5.43	–2.27		119.46
	333	7.63	–2.81		117.49
Sr^{2+}–H^+	303	3.00	–1.38	13.67	49.67
	313	3.36	–1.57		48.69
	323	4.04	–1.87		48.11
	333	4.86	–2.19		47.62
Ba^{2+}–H^+	303	6.33	–2.32	3.78	20.13
	313	6.61	–2.46		19.92
	323	6.56	–2.53		19.51
	333	7.21	–2.74		19.56

[a] Average values calculated from the van't Hoff isochore equation.

radii is least hydrated. The hydrated ionic radii of these metal ions thus follow the order[32] $Mg^{2+} > Ca^{2+} > Sr^{2+} > Ba^{2+}$. Maximum dehydration therefore occurs in the case of Mg^{2+} resulting in higher positive values of the enthalpy change. The positive values of entropy change, ΔS^o, is also attributed to changes in hydration sphere of the exchanging cation, which indicates the disorder produced in the forward reaction, i.e. M^{2+}–H^+ exchange.

CONCLUSIONS

Zirconium titanium phosphate, a mixed material of the tetravalent bimetallic metal acid salt class, exhibits good ion exchange capacity, thermal stability and chemical stability, which are characteristics of a good ion exchange material. Ion exchange equilibria of alkaline earth metal ions with hydrogen form of ZTP shows that the exchange of H^+ for M^{2+} is spontaneous and that the alkaline earth metal ions have a high affinity to the exchanger; the mechanism of the process is an ion exchange. The study thus reveals the promising use of ZTP as a cation exchanger.

The authors thank the Head of Sophisticated Advanced Instrument Facility, Indian Institute of Technology, Bombay, for ICP AES analysis.

SYMBOLS AND ABBREVIATIONS

ASTM	American Standards Testing Method
DTA	differential thermal analysis
ICP AES	induced coupled plasma atomic emission spectrophotometry
IEC	ion exchange capacity, mequiv g^{-1}
TBMA	tetravalent bimetallic acid salt
TGA	thermogravimetric analysis
TMA	tetravalent metal acid salt
ZTP	zirconium titanium phosphate
C	equivalent concentration of in-going cation in the liquid that remains in the solution after attaining equilibrium
$\overline{C}$	equivalent concentration of in-going cation exchanged in the exchanger
X	equivalent fraction of in-going cation exchanged in the solution phase
$\overline{X}$	equivalent fraction of in-going cation exchanged in the exchanger phase

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