Synthesis and thermal stability of some inorganic ion exchangers based on silicon and tin

S. D. Sharma · K. G. Varshney · S. C. Mojumdar

Abstract A number of silicon-based inorganic ion exchangers were synthesized under different conditions of preparation. The original and regenerated ion exchange capacities (IECs) were determined. Thermal stability of these materials was investigated in the temperature range of 40–800 °C. The gain/loss of IEC was studied as a function of temperature. These exchangers show a higher IEC and its retention to a considerable extent at elevated temperatures when compared to that of corresponding ion exchangers which do not contain silica. The thermogravimetric curve shows greater percent mass loss in H^+ form of the exchanger than in K^+ form. Dehydration studies seem to throw some light on the state of water molecules present in various samples. The empirical formula and the tentative structure for stannic arseno silicate have also been proposed.

Keywords Inorganic ion exchangers · Characterisation · TG · Thermal stability · Heat treatment

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Introduction

Inorganic ion exchangers have been of great interest for the last six decades, zirconium(IV) phosphate being the most extensively studied material [1, 2]. Next to this are the tin(IV)-based materials, due to their high ion exchange capacity (IEC) and chemical stability on one hand and the thermal stability on the other. Addition of silicon in their structure was found to be promising as the thermal stability was observed to be enhanced further. Double salts containing two polyacidic groups are of added advantage in their ion exchange behaviour. They can, now, release H^+ ions in different steps due to the difference in the stability constants.

Varshney et al. [3] have observed an increase in the IEC of zirconium(IV) arseno phosphate cation exchanger when heated up to 200 °C. They have also prepared zirconium arseno phosphate in a crystalline phase and studied its thermal behaviour [4]. The compound has been found to have reversible phase transformation at around 250 °C which permits its use as a catalyst for certain reactions when employed at this temperature. Recently, they reported synthesis, characterisation and analytical applications of some new hybrid fibrous ion exchangers of Th(IV) [5–8], Ce(IV) [5, 9–11], Zr(IV) [12] and Sn(IV) [12, 13] and also studied the thermal behaviour of Ce(IV) phosphate [5, 10] and Th(IV) phosphate [5, 8] hybrid fibrous ion exchangers.

In our laboratory, a number of silicon-based inorganic ion exchangers have been synthesized and their ion exchange properties studied [14, 15]. The analytical utilities of stannic selenite silicate [16] and stannic phosphate silicate [17] have also been established using them as an adsorbent in TLC of metal ions in DMSO–HNO_3 and buffered EDTA solutions. However, no effort has been made to examine the thermal behaviour of these materials.

Table 1 Conditions of preparation, original and regenerated IEC and chemical composition of various ion exchangers

Sample	Molarity	Mixing ratios (V/V) Sn:Si:A	Precipitation pH	Drying temperature/°C	Colour of the beads	IEC for K^+/meq g^{-1}		Sn:Si:X ratio
						Original	Regenerated	
Stannic arseno silicate								
SnAsSi-1	0.1	1:1:1	0.0	40	Dull white	1.23	1.23	3.9:1:1.8
SnAsSi-6	0.1	2:1:1	2.0	40	White	1.24	1.06	2:2:1:1.8
SnAsSi-11	0.1	1:1:2	2.0	40	White	1.60	1.14	1.6:1:1.0
SnAsSi-12	0.1	3:1:2	2.0	40	Shining white	1.38	1.38	4.2:1:2.05
Stannic tungsto silicate (SnWSi)	0.25	3:1:2	2.0	40	White	0.82	0.82	1.8:1:1.1
Stannic molybdo silicate (SnMoSi)	0.25	3:1:2	2.0	40	Greenish yellow	0.80	0.80	1.8:1:1.2
Stannic phospho silicate (SnPSi)	0.25	1:1:1	2.0	40	White	1.50	1.50	1:1:1
Stannic seleno silicate (SnSeSi)	0.1	1:1:1	3.0	40	Shining pinkish white	0.52	0.52	2.6:1:1.1
Stannic antimony silicate (SnSbSi)	0.1	1:1:2	3.0	40	Yellowish green	0.88	0.88	1.2:1:1.4

X = As, W, Mo, P, Se, Sb

Thermal analyses are very useful techniques for materials' characterisation. Therefore, many authors have applied these methods for various materials' characterisation [5, 18–37]. The aim of the present study is to synthesize and observe the thermal behaviour of some silicon-based inorganic ion exchangers so that their future utility may be visualized.

Experimental

An electrical muffle furnace was used for heat treatment. Thermogravimetric (TG) analysis was performed on an FCI (Sindri) thermo balance.

Stannic chloride pentahydrate (PPH, Poland), sodium selenite, sodium arsenate heptahydrate (Riedel), sodium tungstate, sodium molybdate, sodium phosphate and potassium antimonate (BDH) were used. All other regents and chemicals were of AnalaR grade.

Synthesis

Aqueous solution of $SiO_2 \cdot xH_2O$, prepared in a minimum quantity of NaOH, was added with constant stirring to an aqueous solution of $SnCl_4 \cdot 5H_2O$ followed by the addition of aqueous solution of

(a) $Na_2HAsO_4 \cdot 7H_2O$ (for stannic arseno silicate)
(b) $Na_2WO_4 \cdot 2H_2O$ (for stannic tungsto silicate)
(c) $Na_2MoO_4 \cdot 2H_2O$ (for stannic molybdo silicate)
(d) $Na_3PO_4 \cdot 12H_2O$ (for stannic phospho silicate)
(e) Na_2SeO_3 (for stannic seleno silicate)
(f) $KSb(OH)_6$ (for stannic antimony silicate)

A number of samples (10–16) for each ion exchanger were obtained by varying the molarity and mixing ratios of the three solutions, adjusting the precipitation pH by adding NH_4OH or HCl, refluxing, varying the precipitation temperature and the drying temperature. The results were reported in our previous work [14, 15]. In all cases, a gelatinous precipitate was obtained which was allowed to settle down for 24 h. It was then filtered, washed with demineralized water (DMW), dried and cracked in DMW to obtain granules which were converted into H^+ form by putting in 2 M HNO_3 for several hours, replacing the liquid intermittently. After washing with DMW, till the pH of the effluent became 6–7, the granules were dried at 40 °C. The samples were converted into the K^+ form by passing 50 mL of 1 M KNO_3 over 1 g of ion exchanger (H^+ form) in a column. The conditions of preparation, original and regenerated IECs of few samples, chosen for thermal studies owing to their greater IEC are given in Table 1.

Ion exchange capacity (IEC)

The K^+ IEC of various samples was determined by the column method and the results are given in Table 1.

Chemical composition

Composition studies were performed for nine samples owing to their greater IEC as compared to other samples. For all the ion exchangers, insoluble silica was filtered, washed, dried at 100 °C for 2 h after dissolving them in conc. H_2SO_4 or conc. HCl, thus retaining only a small water content (0.16 mol H_2O/SiO_2) [38] and weighed as

such. Other constituents of the different materials were determined by different analytical methods. The results are given in Table 1. The inorganic ion exchangers of known composition were chosen for thermal studies.

Heat treatment

The samples in H^+ form (2 g in each case) were heated at different temperatures up to 800 °C in the muffle furnace for 2 h and the IEC was determined. Results are shown in Figs. 1, 2 and Table 2.

TG analysis

Samples in H^+ form and K^+ form were subjected to TG analysis over the temperature range 40–800 °C. The rate of heating was 10 °C/min. Results are shown in Figs. 3, 4, 5, 6 and 7. TG at a heating rate of 6 °C/min for H^+ form of all the samples gave identical results with those at a heating rate of 10 °C/min.

Results and discussions

The IEC of the materials was determined after heating at different temperatures. Stannic arseno silicate (SnAsSi-12) showed a 30 % increase in its initial IEC at 300 °C. This increase was reduced to 20 % when the material was

heated up to 700 °C (Fig. 1). It is difficult to explain this behaviour satisfactorily, but it appears that sharp increase in IEC up to 300 °C may be due to the removal of a large number of external water molecules from the material. On further heating, the gain in IEC reduces probably because of the loss of exchangeable hydroxyl groups during condensation. In order to check this interesting behaviour, other samples of arseno silicate (SnAsSi-1, 6 and 11) were also subjected to similar heat treatment. It was observed that for all the four samples, there is an increase in the IEC up to 500 °C. At 700 °C, SnAsSi-1 and 11 lost about 20 % of their IEC, whereas SnAsSi-6 and 12 retained the gain though to a lesser extent (Fig. 1). It may be because all the four samples contain different amount of free water as well as water containing replaceable hydrogen ions. The varying amount of water seems to be responsible for the change in the ion exchange properties and the stability of the exchanger.

Thermal studies were carried out on other ion exchange materials also. Stannic tungsto silicate shows a gradual loss in its IEC on heating which is about 60 % at 800 °C. For stannic molybdo silicate, IEC remains unchanged up to 600 °C. Beyond it, there is a gradual loss up to 800 °C. At temperatures higher than 600 °C, volatilization of molybdenum trioxide occurs, and hence the loss in IEC above 600 °C. The IEC of stannic phospho silicate does not show any change up to 100 °C, but at 200 °C there is a 60 % loss which is increased to 65 % at 400 °C. On further heating, there is no more loss. Stannic seleno silicate shows a 30 %
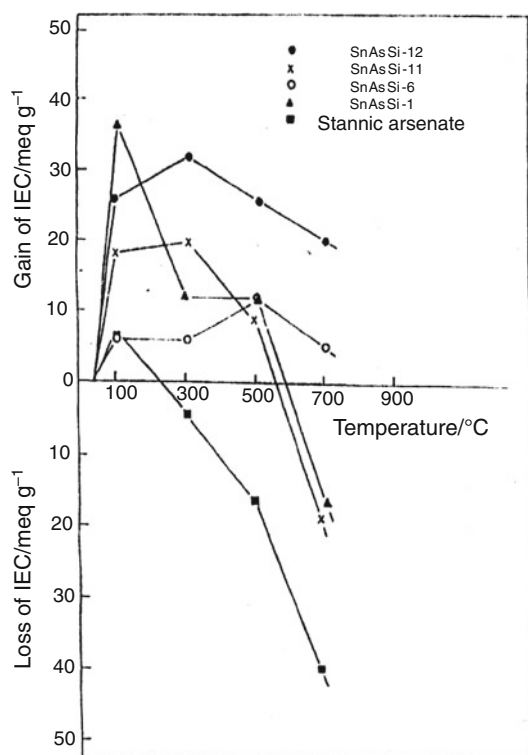

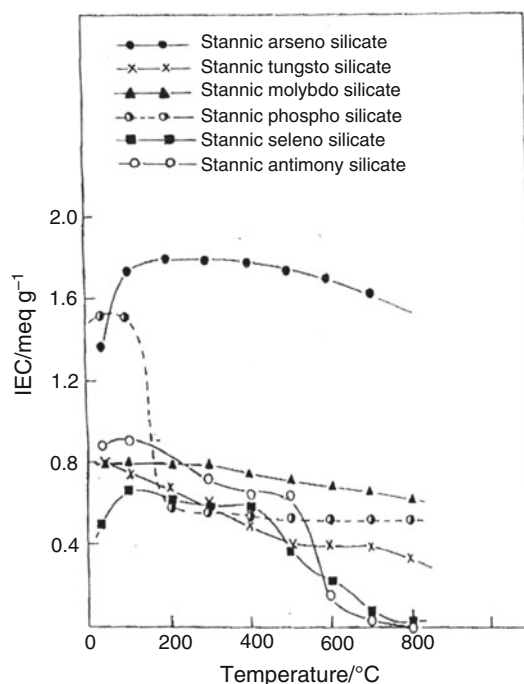Fig. 1 Gain/loss of IEC of stannic arseno silicate samples

Fig. 2 IEC of silicon based inorganic ion exchanges as a function of temperature

Table 2 Change in colour and IEC of various ion exchangers on heating

°C	Stannic arseno silicate (SnAsSi-12) Colour	IEC/ meq g^{-1}	Stannic tungsto silicate Colour	IEC/ meq g^{-1}	Stannic molybdo silicate Colour	IEC/ meq g^{-1}	Stannic phospho silicate Colour	IEC/ meq g^{-1}	Stannic seleno silicate Colour	IEC/ meq g^{-1}	Stannic antimony silicate Colour	IEC/ meq g^{-1}
40	Shining white	1.38	White	0.82	Greenish yellow	0.80	White	1.50	Shining pinkish white	0.52	Yellowish white	0.88
100	White	1.70	White	0.75	Yellow	0.80	White	1.50	Pinkish white	0.68	Light yellow	0.90
200	Dull white	1.75	White	0.70	Yellow	0.80	White	0.60	Dull white	0.64	Light yellow	0.80
300	Light brown	1.72	Dull white	0.60	Yellow	0.78	White	0.60	Dull white	0.60	Light yellow	0.70
400	Brown	1.70	V. light brown	0.50	Grey	0.75	White	0.50	Grey	0.60	Light yellow	0.65
500	Brown	1.68	V. light brown	0.41	Grey	0.70	White	0.50	Black	0.40	Yellowish orange	0.65
600	Dark brown	1.67	V. light brown	0.41	Grey	0.68	White	0.50	Black	0.22	Yellowish orange	0.20
700	Brown black	1.66	V. light brown	0.41	Grey	0.64	White	0.50	Black	0.08	Orange	0.02
800	Brown black	1.65	V. light brown	0.35	Grey	0.63	White	0.50	Charcoal	0.02	Orange	0.00

increase in its IEC at 100 °C which is reduced to 15 % at 300 °C. Above 500 °C, the material begins to lose its IEC which becomes nearly zero at 800 °C. Stannic antimony silicate shows 4 % gain in its IEC at 100 °C. From 200 °C onwards, there is a gradual decrease and the IEC is completely lost at 800 °C. All the ion exchangers, except stannic phospho silicate, undergo a change in their physical appearance when heated at higher temperatures (Table 2).

The silicon-based materials show a higher IEC, and its retention to a considerable extent at elevated temperatures when compared to the corresponding ion exchangers which do not contain silica [39–43]. This is obviously due to the presence of silica which appears to increase the porosity of these materials resulting in more exchange sites.

It appears that these ion exchange materials are a combination of hydrated oxides of tin and silicon with arsenic, tungsten, molybdenum, phosphorus, selenium and antimony in a gel form structure. These hydrated oxides form a network structure with different size of cavities or surface area responsible for the selectivity of the exchanger towards the inorganic ions. The size of cavities or surface area seems to be dependent of the degree of hydration of these oxides.

X-ray studies for some materials reveal that the formation of oxides is facilitated as the drying temperature increases [44]. This behaviour of silicon-based exchange

materials resemble that of hydrous oxides [45] of zirconium, titanium, thorium and a number of inorganic ion exchangers based on tin synthesized by Qureshi et al. [40–42]. The process of oxide formation in each exchanger occurs at different temperatures.

The TG curves for all the ion exchangers (Figs. 3, 4, 5, 6, 7) show a greater percent mass loss in H$^+$ form of the exchanger as compared to K$^+$ form. The removal of water molecules by condensation is not possible in K$^+$ form, and therefore the mass loss is only due to the removal of external water molecules. Hence, it can be said that water incorporated within the various ion exchangers is in two different forms:

(1) In the form of OH groups hydrogen of which can be exchanged by any other cation.
(2) In the form of free water molecules which do not play any role in ion exchange but are responsible for the cavity size.

This view is supported by the infra red spectra of these materials which show peaks at 3,300 and 1,600 cm^{-1} confirming thereby the presence of OH groups and water molecules.

To understand the thermal stability of stannic arsenate silicate, it is important to know the TG behaviour of the oxides of arsenic. For arsenous oxide (As$_4$O$_6$), the TG
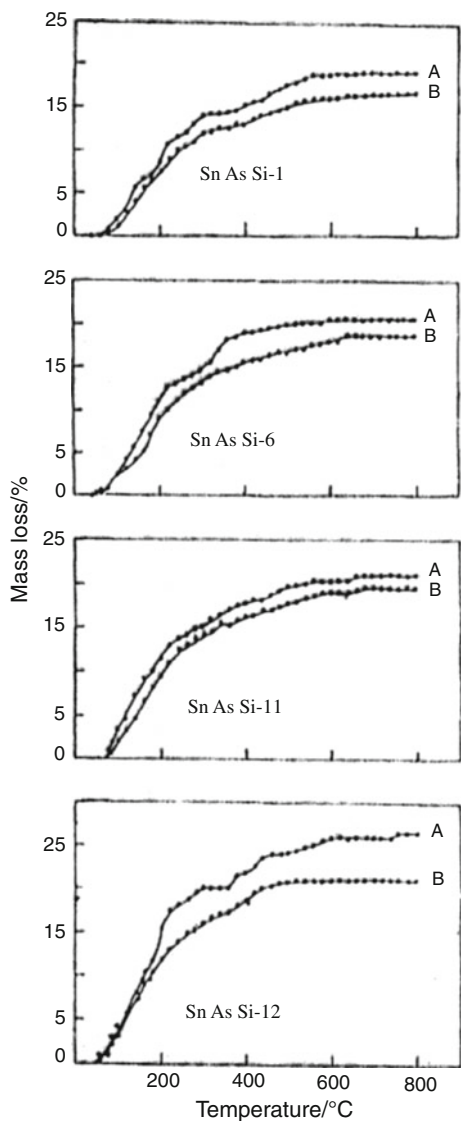
Fig. 3 TG *curves* of stannic arseno silicate samples. (*a*) Exchanger in H$^+$ forms. (*b*) Exchanger in K$^+$ forms

Fig. 4 TG *curves* of stannic tungsto silicate. (*a*) Exchanger in H$^+$ forms. (*b*) Exchanger in K$^+$ forms
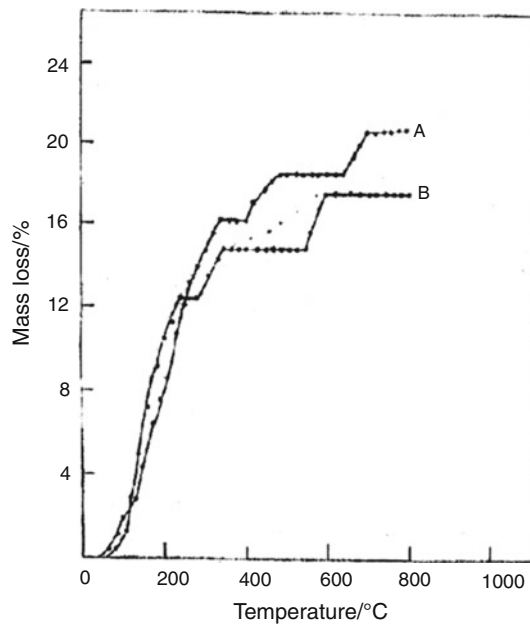
Fig. 5 TG *curves* of stannic molybdo silicate. (*a*) Exchanger in H$^+$ forms. (*b*) Exchanger in K$^+$ forms

curve remains horizontal up to 200 °C. Thereafter, the sublimation begins abruptly and continues as far as 350 °C. There is very marked inflexion between 350 and 450 °C. However, arsenic oxide (As$_2$O$_5$) exhibits a different behaviour. Although Backstrom gives 435–450 °C as the limiting temperatures for the existence of As$_2$O$_5$ and though Auger on the contrary reports 400 °C as the upper limit, the thermolysis curve of material composition of which approximated As$_2$O$_5$·3/2H$_2$O showed that the anhydrous oxide (As$_2$O$_5$) starts to appear at 193 °C and decomposition into arsenous oxide sets in at 246 °C. Guerin et al. do not agree with this finding and believed that the arsenic oxide, which they themselves prepared by oxidising arsenous oxide with HNO$_3$, does not decompose below 400 °C either in air or in vacuums. Thus, it is almost
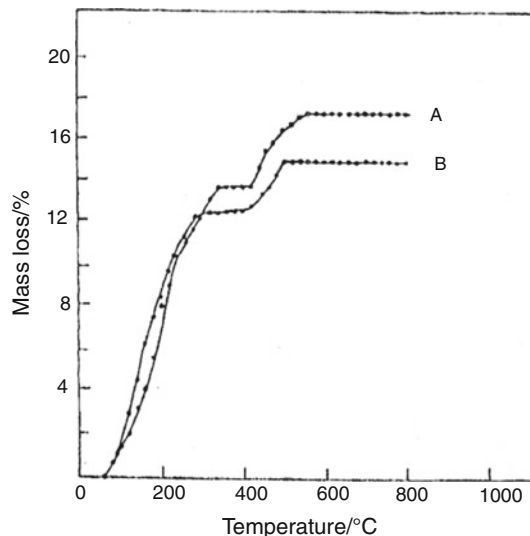
certain that the process of formation of arsenic oxide is completed up to 400 °C and at temperatures higher than 450 °C volatilization of arsenic oxide occurs, which is responsible for the complete loss of arsenic. With the help of percent mass loss up to 450 °C in the H$^+$ and in the K$^+$ form, the following calculations are made.

Stannic arseno silicate: sample SnAsSi-12 (Fig. 3)

(SnO$_2$)$_{4.2}$·SiO$_2$·(HAsO$_3$)$_{2.05}$ (mol. mass = 947.02)

(composition data given in Table 1).

Now, the H_2O molecules hydrogen of which is exchangeable = total percent mass loss in H^+ form up to 400 °C − Total percent mass loss in K^+ form up to 400 °C = 3.5 % (as from Fig. 3).
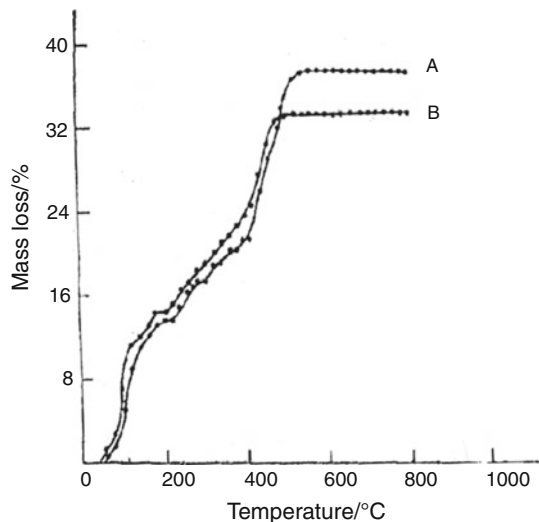

Fig. 6 TG *curves* of stannic seleno silicate. (*a*) Exchanger in H^+ forms. (*b*) Exchanger in K^+ forms
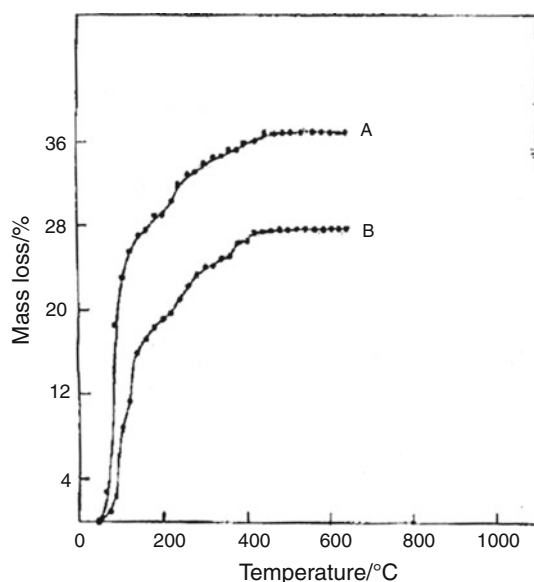

Fig. 7 TG *curves* of stannic antimony silicate. (*a*) Exchanger in H^+ forms. (*b*) Exchanger in K^+ forms

From Alberti's equation

$$\% \text{ Mass loss in exchanger is } = \frac{1,800n}{947.02 + 18n} = 3.5$$

where n = number of external H_2O molecules as from Fig. 3.

Therefore $n = 1.91$.

Now, the proposed formula will be

$(SnO_2)_{4.2} \cdot SiO_2 \cdot (HAsO_3)_{2.05} \cdot (H_2O)_{1.91}$, mol. mass = 981.40

The H_2O molecules whose hydrogen is un-exchangeable = total % mass loss in K^+ form up to 400 °C = 18 %. Therefore, using Alberti's equation

$$\frac{1,800n}{981.40 + 18n} = 18\% \quad n = 11.97$$

Thus, the empirical formula for SnAsSi-12 will be

$(SnO_2)_{4.2} \cdot SiO_2 \cdot (HAsO_3)_{2.05} \cdot (H_2O)_{1.91} \cdot 11.97H_2O$ (mol mass = 1,197).
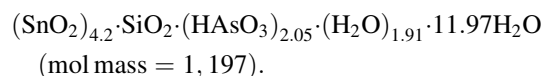
Therefore, the IEC per dry g of exchanger

$$= \frac{1.91 \times 2 \times 10^3}{1,197} = 3.19 \text{ meq g}^{-1}$$

In this way, calculations have also been made for the remaining three SnAsSi samples. The results are recorded in Table 3.

The saturation IEC determined experimentally (as given in Tables 1 and 2) is lower than the theoretical IEC (Table 3) because of the amorphous nature of the exchanger samples as in that case replacement of all hydrogen ions by other cations is not possible.

These calculations show that the four different samples of SnAsSi contain different amounts of free water as well as water containing replaceable hydrogen ions. The varying amounts of water seem to be responsible for the change in the ion exchange properties and the stability of the exchanger. The pH titration curves for all the samples suggest a monofunctional behaviour. On the basis of these observations and reported species [25] of tin, silicon and arsenic, the following tentative structure for stannic arseno silicate (sample SnAsSi-12) may be postulated. Similar structures may be drawn for the other Sn(IV)-based exchangers.

Table 3 TG analysis results

Sample	Composition	Mol. mass	Water molecules in the form of OH group	Water molecules in the form of H_2O	IEC/meq g^{-1}
SnAsSi-12	$(SnO_2)_{4.2} \cdot SiO_2 \cdot (HAsO_3)_{2.05}$	947.02	1.91	11.97	3.19
SnAsSi-1	$(SnO_2)_{3.9} \cdot SiO_2 \cdot (HAsO_3)_{1.8}$	870.83	0.99	7.25	1.94
SnAsSi-6	$(SnO_2)_{2.2} \cdot SiO_2 \cdot (HAsO_3)_{1.8}$	614.66	1.24	6.74	3.27
SnAsSi-11	$(SnO_2)_{1.6} \cdot SiO_2 \cdot (HAsO_3)_{1}$	425.11	0.38	4.74	1.47

Conclusions

The effect of addition of silica during the synthesis of tin-based inorganic ion exchangers is quite promising as it increases their IEC which is retained to a considerable extent at elevated temperatures. The water incorporated within the ion exchanger is in the form of OH groups and as free water molecules. On heating, there is greater percent mass loss in H^+ form than in K^+ form of the exchanger. On the basis of percent mass loss up to 450 °C in H^+ and K^+ form of stannic arseno silicate and using Alberti's equation, an empirical formula for the exchanger is given. The tentative structure for stannic arseno silicate is postulated.

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