Novel Stannosilicates. Part 2.[1] Cation-exchange Studies

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The ion-exchange properties of a novel sodium stannosilicate $Na_{13.5}Sn_{10}Si_{15}O_{36}(OH)_5\cdot13.5H_2O$ have been studied for the replacement of Na^+ by Li^+, K^+, Tl^+, Ag^+, NH_4^+, Mg^{2+}, Ca^{2+}, Sr^{2+}, Ba^{2+} and Zn^{2+}. Thermodynamic parameters have been calculated from isotherm data, and lead to a general conclusion that the exchanges were of zeolite character and that the stannosilicate behaves as a microporous solid with heteroenergetic exchange sites.

Recent years have seen an upsurge of interest in the study of inorganic materials with ion-exchange properties. Most of this work has centred on zeolites in conjunction with their use as detergent 'builders' (ref. 2) and for the treatment of aqueous nuclear wastes.[3] These materials also are convenient model substrates for the extension of ion-exchange theory.[4] Their advantages lie in their highly selective cation-exchange properties, purity and reproducible stoichiometry. In addition their microporous nature promotes their well known uses as catalysts and sorbents[2] both of which applications require detailed knowledge of zeolite cation-exchange properties.

This paper describes the ion-exchange nature of a new stannosilicate, synthesised to contain $[SnO_6]^{8-}$ and $[SiO_4]^{4-}$ polyhedra, which has properties indicative of a microporous framework structure. The synthesis and characterization of this material has been described in Part 1 of this series.[1]

Experimental

Synthesis and Characterization.—The stannosilicate was synthesised in its sodium form from autoclaved aged gels produced from sodium stannate and sodium silicate aqueous solutions.[1] The synthesis products were characterized by chemical and neutron activation analysis and their characteristic X-ray powder pattern.[1] In addition differential scanning calorimetry (DSC) and thermogravimetry were carried out on the cation-exchanged forms using a Dupont 910 and 990 thermal analyser. The material used for the ion-exchange study can be expressed *via* the formula: $Na_{13.5}Sn_{10}Si_{15}O_{36}(OH)_5\cdot13.5H_2O$.

Ion Exchange.—(*i*) *Equilibrium measurements.* To construct ion-exchange isotherms aliquots (0.05 g) of the sodium stannosilicate were equilibrated in Polythene bottles with isonormal salt solutions (20 cm^3) of 0.05 total normality. The bottles were rotated about their horizontal axes in a thermostatically controlled air oven at three different temperatures (297, 313 and 333 K). Periods of 3 (1:1 cation exchange) and 7 d (1:2) were allowed for the attainment of exchange equilibria. Previous kinetic experiments carried out using the same total normalities and liquid/solid ratio showed that equilibria were attained well within the time period. After equilibration the liquid phases were removed and allowed to stand for 1 d to allow any small solid particles to sediment prior to analysis. The exchanges of sodium for Li^+, K^+, Ag^+, Tl^+, NH_4^+, Mg^{2+}, Ca^{2+}, Sr^{2+}, Ba^{2+} and Zn^{2+} were followed.

Analyses for Tl^+ and Ag^+ were carried out radiometrically whilst those for Mg^{2+}, Ca^{2+}, Sr^{2+}, Ba^{2+} and Zn^{2+} were by ethylenediaminetetraacetate titrimetry. Both K^+ and Li^+ were measured by flame photometry and estimations of NH_4^+ concentrations were carried out using an automatic Kjeldahl instrument (Tecator 1030). Prior to analysis liquid portions were centrifuged for 1 h. Solid-phase analysis was carried out by methods outlined in Part 1 of this series.[1]

The reversibilities of exchange were checked using the method of Fletcher and Townsend[5] which avoided washing, drying and transfer of liquid and solid phases. Samples of the solid phase at maximum exchange for the ingoing ion were retained for X-ray powder diffraction (XRD) and water-content measurements.

(*ii*) *Elucidation of isotherms.* Before interpretation the exchange isotherms were 'smoothed' using a 'best-fitting' polynomial. This procedure was extended to provide a predicted maximum equivalent fraction of the ingoing cation in the stannosilicate phase [M_z(max.)]. This coincided ($\pm$ 10% at worst) with the M_z(max.) value indicated by experimental points, and was used to normalize isotherm data.

More detailed analyses followed the usual methods, as outlined by Fletcher and Townsend.[5] Computer programs were used to calculate activity coefficients, thermodynamic constants K_a, and values for the standard free energy of exchange per equivalent of exchange, ΔG°.[6,7]

Results and Discussion

The kinetic plots (Fig. 1) showed that, at 298 K, the extent of replacement of sodium was a function of the nature of the ingoing cation. Only Ag^+ attained 100% exchange based upon the capacity calculated from the sodium content of the stannosilicate. These limits to exchange were confirmed when the isotherms were constructed (Fig. 2) but access to further ion-exchange sites was possible at higher exchange temperatures. (Note M_z is the equivalent fraction of the ingoing cation in the solid phase, M_s is its equivalent fraction in solution.)

The XRD results showed that change in cation content had no obvious effect on the maximum '*d*' spacing observed. The only changes noted were those of intensity. An exception to this was when Ag^+ was the exchanging ion and XRD indicated that the process caused a large loss of crystallinity. Table 1 summarizes the interpretation of the isotherms and Table 2 contains a summary of the extent of exchange with details of water content and ion sizes.

Ion-exchange Isotherms.—(*i*) Na^+ for Li^+, Tl^+, $\frac{1}{2}$ Zn^{2+}, $\frac{1}{2}$ Ca^{2+}, *or* $\frac{1}{2}$ Sr^{2+} (Ag^+). All the above isotherms showed a selectivity for the ingoing ion. When the latter was Li^+, Tl^+, Zn^{2+}, Ca^{2+} or Sr^{2+} the exchange was reversible (at 298 K). Reversibility checks for the Na^+ for Ag^+ exchange confirmed that the original structure had been irreversibly destroyed. Contact between the silver form of the sodium stannosilicate with Ag/Na salt solutions over 2 weeks did not restore crystallinity. In some cases (Sr^{2+}, Li^+) there were indications of slight hysteresis but the variations from the forward isotherm were close to analytical error. Despite the broad similarities noted in these ion pairs the processes being observed obviously differed.

When Tl^+ was the ingoing ion the process was temperature independent in the range (298–333 K) studied but only two of the 13.5 Na^+ ions initially present were replaced. The Na^+ for $\frac{1}{2}$ Ca^{2+} replacement also was temperature insensitive but close to four Na^+ were removed. The Na^+ for Li^+ exchange again did not vary with temperature but now about five Na^+ were involved.

When Zn^{2+} and Sr^{2+} were ingoing an increase in temperature altered the isotherm observed. In the case of Zn^{2+} this increase created a more selective replacement of Na^+ but made a relatively small impact on the number of Na^+ ions participating in the exchange. At 298 and 313 K about eight sodiums exchanged and this rose to nine at 333 K. The Na^+ for $\frac{1}{2}Sr^{2+}$ exchange increased from about 1.5 Na^+ at 298 K, through 2.2 at 313 K to a maximum close to 4 at 333 K.

(*iii*) Na^+ for K^+, NH_4^+, $\frac{1}{2}Mg^{2+}$, *or* $\frac{1}{2}Ba^{2+}$. The Na^+ for NH_4^+ exchange (at 298 K) showed a marked hysteresis and the first point on the reverse isotherm was clearly in error, probably analytical in origin. No further attempts to devolve thermodynamic quantities were made for this ion pair. The Na^+ for K^+ exchange was one of low selectivity but, whereas the

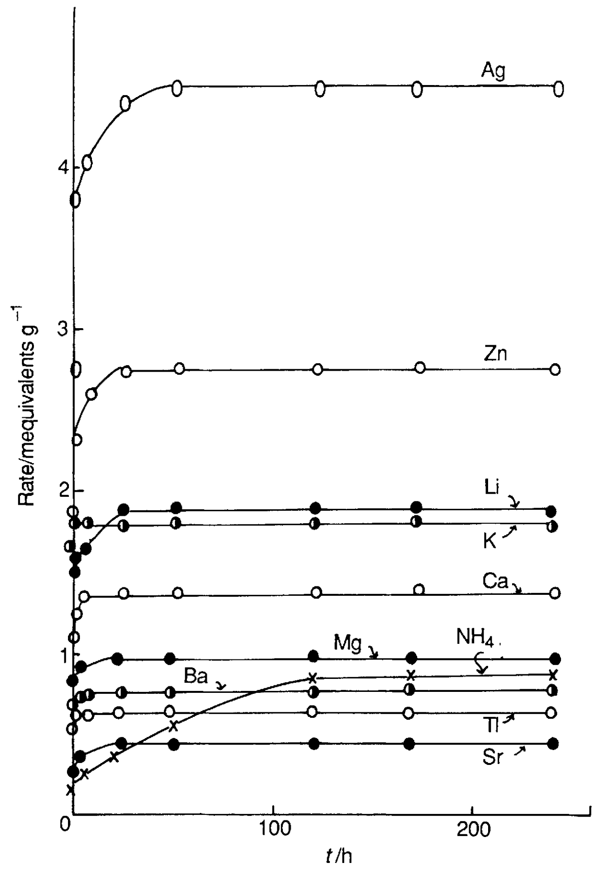

Fig. 1 Rates of exchange of Na^+ in the stannosilicate by various cations at 298 K

Table 1 Values of K_a, ΔG° and the polynomial fit selected for Kielland plot interpretation for ion exchanges in the sodium stannosilicate at various temperatures

Ingoing ion	T/K	Order	K_a	ΔG°/kJ mol^{-1}
K^+	298	3	0.89	3.30
	333	2	2.93	−2.66
Li^+	298	2	5.96	−4.44
Tl^+	298	2	3.85	−3.33
Mg^{2+}	298	2	1.89	−0.79
	333	2	11.5	−3.01
Ca^{2+}	298	2	9.33	−2.76
Sr^{2+}	298	2	1.17	−0.20
	313	2	0.63	0.56
	333	2	0.32	1.42
Ba^{2+}	298	3	0.14	2.46
	313	3	0.26	1.66
	333	2	0.67	1.30
Zn^{2+}	298	2	15.8	−3.41
	333	2	22.8	−3.86

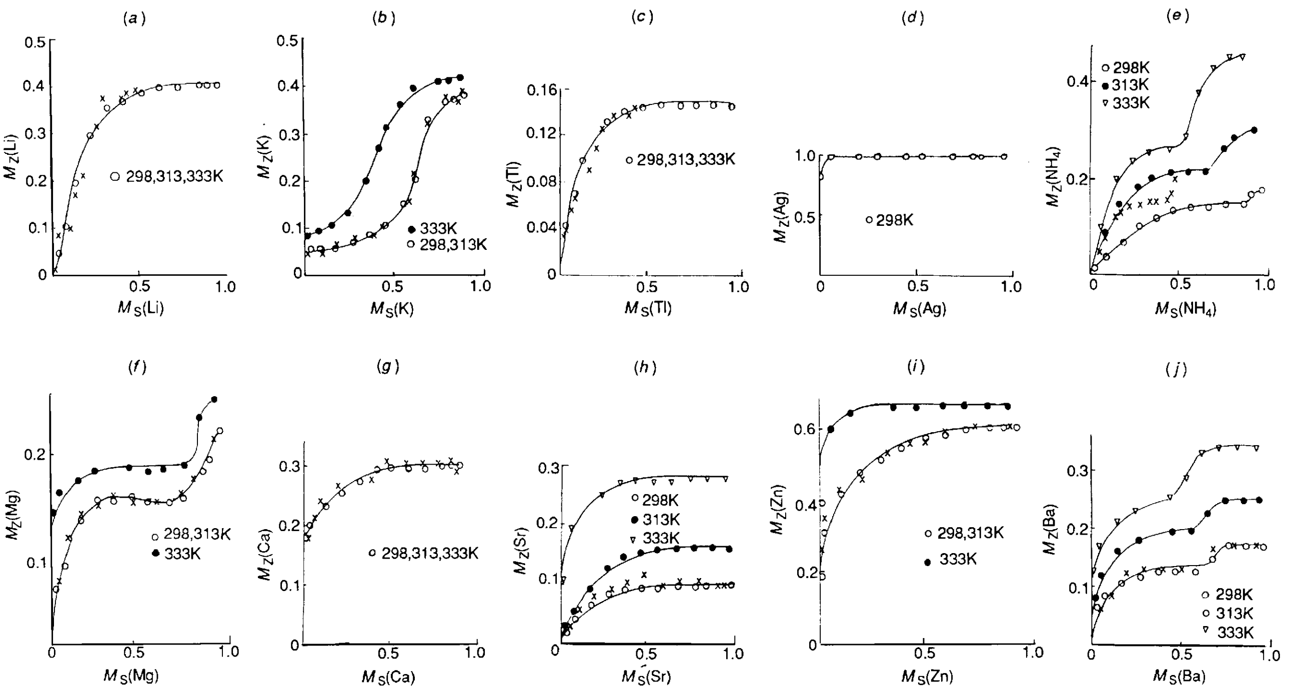

Fig. 2 Ion-exchange isotherms for replacement of Na^+ in the stannosilicate by (*a*) Li^+, (*b*) K^+, (*c*) Tl^+, (*d*) Ag^+, (*e*) NH_4^+, (*f*) $\frac{1}{2}Mg^{2+}$, (*g*) $\frac{1}{2}Ca^{2+}$, (*h*) $\frac{1}{2}Sr^{2+}$, (*i*) $\frac{1}{2}Zn^{2+}$ and (*j*) $\frac{1}{2}Ba^{2+}$. In each case reverse isotherm at 298 K is indicated by X

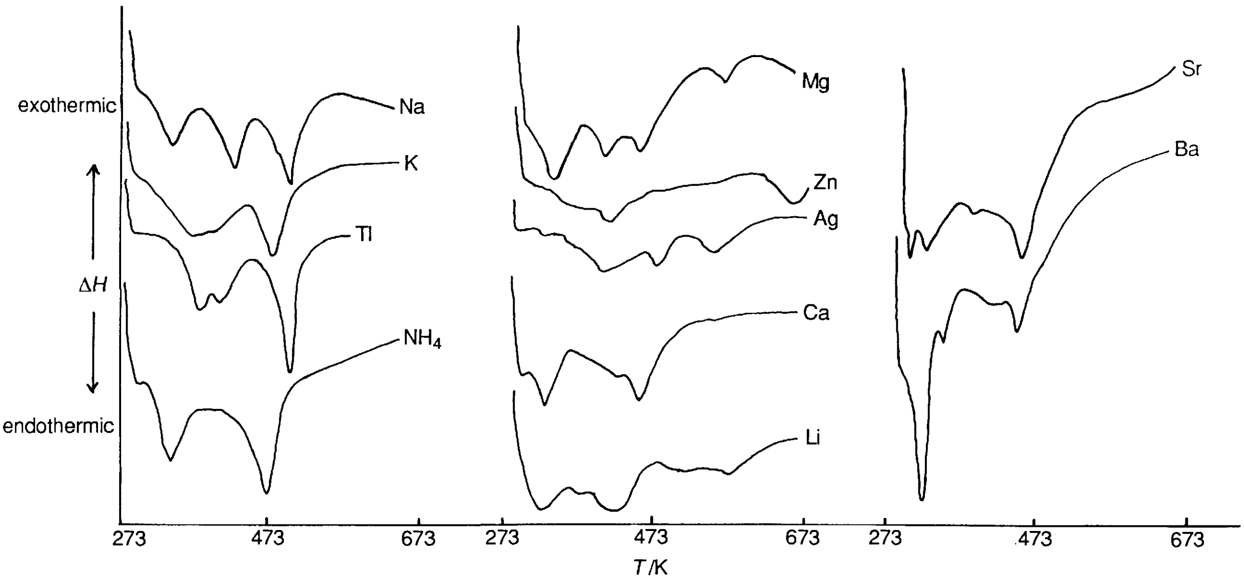

Fig. 3 DSC profiles for cation-exchanged forms of the stannosilicate

Table 2 Comparison of the number of Na^+ exchanged from the sodium stannosilicate with the size of the ion and hydrated ion (at 298 K)

Cation	No. of Na^+ replaced	Ionic radius[8] /Å	Hydrated ionic radius[9]/Å	Water content (%)
Zn^{2+}	8.2	0.74	4.30	8.4
Li^+	5.4	0.60	3.82	8.4
K^+	5.1	1.33	3.31	6.6
Ca^{2+}	4.1	0.99	4.20	8.0
Mg^{2+}	3.0	0.65	4.40	8.8
NH_4^+	2.4	1.48	3.31	10.6*
Ba^{2+}	2.3	1.35	4.10	7.4
Tl^+	2.0	1.40	3.30	6.4
Sr^{2+}	1.4	1.13	4.12	9.0
(Ag^+	13.5	1.26	3.41	3.7)
(Na^+	—			6.6)

* Likely to include NH_3 loss.

processes at 298 and 313 K were nearly identical, that at 333 K showed some tendency to increase selectivity for the ingoing ion. The shape of the isotherms indicated a non-selective replacement of two Na^+ followed by a more favoured replacement to a maximum of six Na^+.

When NH_4^+ or Ba^{2+} was the ingoing ion 'S'-shaped isotherms were observed at each of the temperatures studied; Ba^{2+} can replace a maximum of about five Na^+ whilst NH_4^+ achieved removal of just over six Na^+.

(*iii*) *Thermodynamic data.* (*a*) *Free-energy values.* Observed ΔG° values are listed in Table 1 and suggested a selectivity series at 298 K of $Li^+ > Zn^{2+} > Tl^+ > Ca^{2+} > Mg^{2+} > Sr^{2+} > K^+ > Ba^{2+}$. This follows a pattern of decrease in selectivity with unhydrated cation (see Table 2) apart from Tl^+ (an ion of high polarizability) and Mg^{2+} (an ion likely to retain water of hydration). Series constructed at the higher temperatures were very similar except for a marked increase in preference for Mg^{2+} indicative of loss of its hydration shell at these temperatures. The continued lack of preference for Li^+ at high temperatures suggested that it did not shed waters at these temperatures. The magnitudes of the ΔG° values were broadly similar to those observed for zeolite ion exchange.

Clearly to attempt close correlation would be unjustified but for certain exchanges similarities can be noted, *viz.* Na^+ for $\frac{1}{2}Ca^{2+}$ in zeolite A ($\Delta G^{\circ} = -2.68$ kJ mol^{-1}),[10] Na^+ for K^+ in zeolites X and Y ($\Delta G^{\circ} = -0.05$ and -0.09 respectively)[11] and Na^+ for $\frac{1}{2}Sr^{2+}$ in X and Y ($\Delta G^{\circ} = -0.17$ and -0.03 kJ mol^{-1} respectively).[12] In some cases where ΔG° values for zeolite exchanges were different from those in the stannosilicate there was a clear indication that in the zeolite processes a strong influence of ion hydration was involved (unlike the three cases cited above). Examples of this were the unfavourable exchange of Mg^{2+} into zeolite A[10] (ΔG° + 3.26 kJ mol^{-1}) and that of Li^+ into X and Y ($\Delta G^{\circ} = +0.32$ and $+0.68$ kJ mol^{-1} respectively).[11] Other values of ΔG° available for comparison inevitably included cases where the behaviour noted in zeolites was unlike that in the stannosilicate and where deviations could not be explained in terms of ion-hydration effects. Examples of ΔG° values in this category were Na^+/Tl^+ in Y[11] (-0.36 kJ mol^{-1}), $Na^+/\frac{1}{2}Zn^{2+}$ in A (-0.21 kJ mol^{-1})[12] and Na^+/Ba^{2+} in X and Y (-0.21 and -0.09 kJ mol^{-1} respectively).[11]

(*b*) *Effect of temperature.* For two ion exchanges (Na^+ for $\frac{1}{2}Sr^{2+}$ or $\frac{1}{2}Ba^{2+}$) the thermodynamic analysis was extended to calculation of ΔH° and ΔS° values. Both processes gave a measured ΔH° of 0.37 kJ mol^{-1} which was of the same order as those in zeolites X and Y.[11] The ΔS° values were quite different. For the strontium process an increase in temperature made the entropy change more negative (1.92 J K^{-1} mol^{-1} at 298 K to -3.14 J K^{-1} mol^{-1} at 333 K). On the other hand the entropy change when Ba^{2+} was the ongoing cation became less negative with the same temperature increases (-7.00 J K^{-1} mol^{-1} at 298 K to -2.78 J K^{-1} mol^{-1} at 333 K). Entropy changes for these exchanges in zeolites have not been measured. In conclusion it should be noted that the parameters referred to in this section in zeolites X and Y were measured by calorimetry.

(*iv*) *DSC profiles* (see Fig. 3). Broadly all the profiles reflect the three endothermic events associated with three heteroenergetic cation sites in the parent stannosilicate.[1] When replacement of sodium was low (Tl^+, NH_4^+, Mg^{2+}, Sr^{2+}, Ba^{2+}) this heterogeneity generally was retained but with some changes at low temperatures consistent with ingoing cations entering sites of easy access. Caveats to this generalization were the appearance of events at high temperatures (about 570 K) in the traces for Mg^{2+}, Ca^{2+}, Zn^{2+} and Li^+ and it might be that these are linked to the OH^- groups in the stannosilicate. Furthermore in some cases the definition in the two low-temperature endotherms, clear for the stannosilicate, is reduced. This is seen in the NH_4^+, K^+ and Tl^+ forms and may reflect the similarities in ionic radii of these ions.

Conclusion

The ion exchanges observed were facile and of zeolite character. Not all cations studied replaced Na^+ from the stannosilicate

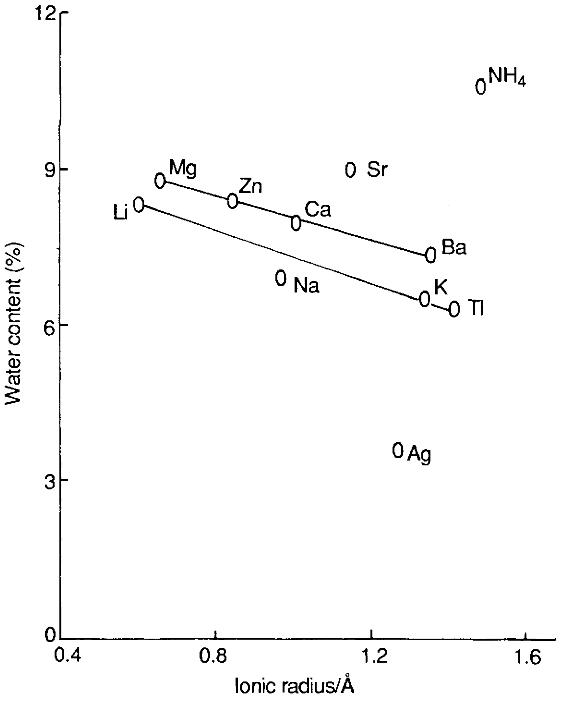

Fig. 4 Variation of water content in the stannosilicate with ingoing cation

and both kinetic and equilibrium results indicated that five cations were difficult to replace. Perhaps these were associated in some way to the $5[SnO_5(OH)]^{5-}$ octahedra proposed for the stannosilicate structure.[1]

Those cations which were replaced could be loosely categorized into two or three which were always replaced, four to six which were replaced by smaller ions at lower temperature and some larger ions at the higher temperatures studied, and six to eight only replaced by Zn^{2+}. This was indicative of site heterogeneity within the stannosilicate structure, also suggested by the 'S'-shaped nature of some isotherms.[13] The complex nature of the DSC curves observed for the cation-exchanged forms of the stannosilicate also indicated at least three cation/water environments (see above).

When water contents were plotted against the size of the cation present in the stannosilicate a reasonable straight line plot (Fig. 4) was obtained for both monovalent ions (except Ag^+ and NH_4^+) and the divalent ions (except Sr^{2+}). This confirmed the earlier observation that no unit-cell expansion, or contraction, was noted in the XRD patterns when the cation content was changed, so it seemed that the stannosilicate does not possess a layer structure.

In summary all the indications from this study were that the novel sodium stannosilicate had a framework structure as suggested by Part 1 of this series.[1]

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