The Equilibrium of Strontium Ion Exchange on Sodium Titanate, $Na_4Ti_9O_{20}{\cdot}xH_2O$

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The equilibrium of the ion exchange of strontium on sodium titanate, $Na_4Ti_9O_{20}{\cdot}xH_2O$, has been studied. The ion exchange isotherm and selectivity coefficient showed high selectivity for strontium over sodium. The distribution coefficient was determined as a function of pH, and of the sodium and strontium concentrations. Special attention was paid to the three-component system H^+–Na^+–Sr^{2+}, which exists in acidic to slightly alkaline solutions.

Among the great number of sodium titanates studied, most have belonged to the series $Na_2Ti_nO_{2n+1}$. Cation exchange by members of this series with $n = 2$, 3, or 4 has been extensively investigated by Izawa *et al.*[1–3] and Sasaki *et al.*[4–8] Recently, Clearfield and Lehto[9] reported on $Na_4Ti_9O_{20}{\cdot}xH_2O$, which is a member of the less common series $Na_4Ti_nO_{2n+2}$. They noted that this sodium titanate is a low-temperature compound, previously known only in amorphous form.[10–12] The titanate $Na_4Ti_9O_{20}{\cdot}xH_2O$ behaves as a layered ion exchanger, the exchangeable sodium ions being located between layers of TiO_6 octahedra chains. It is a difunctional exchanger with an ion exchange capacity of 4.74 mequiv. g^{-1}.

Three exchange processes are involved in strontium exchange by $Na_4Ti_9O_{20}{\cdot}xH_2O$. In acidic solutions the exchanger is mainly in the hydrogen form ($H_4Ti_9O_{20}{\cdot}xH_2O$) and exchange of Sr^{2+} for H^+ is the primary process. The proportion of exchange of Sr^{2+} for Na^+ increases with pH. In alkaline solutions exchange of the hydrolysed species of strontium, $[Sr(OH)]^+$, for sodium also takes place. No sharp transitions from one exchange process to another occur; rather, the processes overlap in certain pH ranges.

Lehto and Clearfield[13] have reported the general features of strontium exchange on $Na_4Ti_9O_{20}{\cdot}xH_2O$, including characterisation of the exchanged forms. This paper considers the equilibrium of the strontium exchange, with particular attention paid to the three-component system H^+–Na^+–Sr^{2+}, which forms in acidic to slightly alkaline solutions.

Experimental

Sodium titanate was prepared hydrothermally from titanium isopropoxide at 250 °C. The composition of $Na_4Ti_9O_{20}{\cdot}xH_2O$ was determined from neutron activation analysis (Ti:Na = 2.25), thermal analysis (at 700 °C decomposition to $Na_2Ti_3O_7$ and $Na_2Ti_6O_{13}$), and ion exchange capacity (4.90 mequiv. g^{-1} observed, 4.74 mequiv. g^{-1} calculated).[9] The compound $Na_4Ti_9O_{20}$ is, according to *X*-ray diffraction studies, a layered compound, the interlayer distance being 6.9 (anhydrous form), 8.6 (semi-hydrated), or 10.0 Å (fully hydrated).[9] The water content of the exchanger was 15%.

Ion exchange experiments were carried out using the following batch technique: a 0.2 g sample of exchanger was shaken with 20 cm^3 of solution for 3 d. The solid phase was separated from the solution by centrifugation using a *g* value of 28 000. The concentration of strontium in the solution was determined by measuring the ^{85}Sr tracer activity with a NaI crystal and a single channel analyser. The pH was measured both before and after equilibration.

The distribution coefficient (K_D) was calculated as follows, where C_0 and C are the strontium concentrations in the solution before and after equilibration, respectively, and b.f. (batch factor) is the ratio of solution volume to weight of exchanger.

$$K_D = \left(\frac{C_0}{C} - 1\right) \times \text{b.f.}$$

In these experiments the b.f. was 100 cm^3 g^{-1}. The calculations were based on the dry weight of the exchanger.

In determining the isotherm for the exchange of Sr^{2+} for Na^+, which presents the equilibrium concentration of strontium in the exchanger as a function of that in the solution, varying batch factors, of 10—1 000 cm^3 g^{-1} (1 g + 10—1 000 cm^3), were used. The initial concentration of $Sr(NO_3)_2$ solution was 0.01 mol dm^{-3}. In determining K_D as a function of pH, the pH was adjusted by adding 5—120 µl of concentrated HCl to the shaking vials.

Results and Discussion

Equilibrium Reactions in Strontium Ion Exchange by Sodium Titanate.—According to Clearfield and Lehto[9,13] the following three processes are involved in strontium exchange by $Na_4Ti_9O_{20}{\cdot}xH_2O$. The lower the pH, the greater is the proportion of the exchanger in the hydrogen form and the higher the proportion of reaction (1). The proportion of reaction (2) increases with pH.

$$H_4Ti_9O_{20} + 2\,Sr^{2+} \rightleftharpoons Sr_2Ti_9O_{20} + 4H^+ \qquad (1)$$

$$Na_4Ti_9O_{20} + 2\,Sr^{2+} \rightleftharpoons Sr_2Ti_9O_{20} + 4Na^+ \qquad (2)$$

$$Na_4Ti_9O_{20} + 2\,[Sr(OH)]^+ \rightleftharpoons Na_2(SrOH)_2Ti_9O_{20} + 2\,Na^+ \qquad (3)$$

At pH > 10 exchange of the hydrolysed species of strontium takes place, as well, and at pH about 13 (in nitrogen atmosphere) exchange is entirely due to this species.

When considering ion exchange by sodium titanate, the hydrolysis of the exchanger also must be taken into account [equation (4)].[9]

$$Na_4Ti_9O_{20} + 4\,H_2O \rightleftharpoons H_4Ti_9O_{20} + 4\,Na^+ + 4\,OH^- \qquad (4)$$

Determination of Thermodynamic Equilibrium Constant.—The ion exchange equilibrium can be graphically expressed as an isotherm, which presents the equivalent ionic fraction of the exchanging ion in the solution as a function of that in the exchanger. The thermodynamic equilibrium constant for the ion exchange reaction can then be calculated from the isotherm. For example, for the Sr^{2+}–$2Na^+$ exchange [equation (2)] the corrected selectivity coefficient, which takes into account the activity coefficients of the ions in the solution, is expressed as shown in equation (5), where $\bar{X}_{Sr}$ and $\bar{X}_{Na}$ are the equivalent ionic fractions of strontium and sodium ions in the exchanger,

$$K^{Sr'}_{Na} = \frac{\bar{X}_{Sr} \cdot m^2_{Na}}{m_{Sr} \cdot \bar{X}^2_{Na}} \cdot \frac{f^2_{Na}}{f_{Sr}} \qquad (5)$$

respectively, m_{Sr} and m_{Na} are the molalities of the respective ions in the solution, and f_{Sr} and f_{Na} are the activity coefficients of the ions in the solution. The ratio $f^2_{Na}:f_{Sr}$ for the individual ions is equal to $f^4_{NaNO_3}:f^3_{Sr(NO_3)_2}$, where f_{NaNO_3} and $f_{Sr(NO_3)_2}$ are the mean molal activity coefficients of $NaNO_3$ and $Sr(NO_3)_2$, respectively. Values of $f_{Sr(NO_3)_2}$ and f_{NaNO_3} for the mixed 0.01 mol dm^{-3} $NaNO_3$–$Sr(NO_3)_2$ solution were calculated by the method of Glueckauf.[14] When the corrected selectivity coefficient is presented as a function of degree of exchange, *i.e.*, the equivalent ionic fraction of strontium in the exchanger [$K' = f(\bar{X}_{Sr})$], the selectivity for strontium can be seen at any level of loading.

The thermodynamic equilibrium constant, K^{Sr}_{Na}, which also takes into account the activity coefficients of the ions in the exchanger phase, is expressed as given in equation (6), where $\bar{f}_{Na}$

$$K^{Sr}_{Na} = \frac{\bar{X}_{Sr} \cdot m^2_{Na}}{m_{Sr} \cdot \bar{X}^2_{Na}} \cdot \frac{\bar{f}_{Sr} \cdot f^2_{Na}}{f_{Sr} \cdot \bar{f}^2_{Na}} = K^{Sr'}_{Na} \frac{\bar{f}_{Sr}}{\bar{f}^2_{Na}} \qquad (6)$$

and $\bar{f}_{Sr}$ are the activity coefficients of the ions in the exchanger.

The activity coefficients of the ions in the exchanger phase cannot be determined directly. Instead, the thermodynamic equilibrium constant can be determined by integrating the curve $K' = f(\bar{X}_{Sr})$ from $\bar{X}_{Sr} = 0$ to $\bar{X}_{Sr} = 1$ [equation (7)],[15] where Z_{Sr} and Z_{Na} are the valences of the ions.

$$\log K^{Sr}_{Na} = (Z_{Na} - Z_{Sr}) + \int_0^1 \log K^{Sr'}_{Na} \, d\bar{X}_{Sr} \qquad (7)$$

Ion Exchange Isotherm and Thermodynamic Equilibrium Constant for Sr^{2+}–$2Na^+$ *Exchange.*—The ion exchange isotherm for the Na^+ to Sr^{2+} exchange shows high selectivity for strontium over sodium (Figure 1). At low equivalent ionic fractions in the solution all the strontium is absorbed; practically no strontium was found in the solution up to about 0.5 equivalent ionic fraction of strontium in the exchanger. This indicates that any errors in the measurement of solution radioactivity, due to the possibility of colloidal exchanger in the solution, were insignificant. In these experiments the equilibrium pH of the solution was 7—10. Therefore, practically only Sr^{2+}–$2Na^+$ exchange [equation (2)] took place.

The shape of the log K' *vs.* $\bar{X}_{Sr}$ curve is assumed to reflect three processes. The first one, up to 0.15 degree of exchange, is probably exchange on the surface of the crystals. Thereafter, the corrected selectivity coefficient first increases up to about 0.5 degree of exchange and then goes down at higher levels of loading. This behaviour probably reflects the presence of two different kinds of exchange sites. According to the titration curves $Na_4Ti_9O_{20} \cdot xH_2O$ is indeed a difunctional exchanger, half of the exchange sites having different acidity from the other half.[9]

Calculating the thermodynamic equilibrium constant for Sr^{2+}–2 Na^+ exchange from Figure 1(*b*) gives a value of 5.9. From this value the equilibrium of the exchange reaction can be predicted for any concentration.

Distribution Coefficient of Strontium as a Function of Strontium Concentration.—Figure 2 presents the distribution coefficient of strontium on sodium titanate as a function of strontium ion concentration in the solution. Two different ranges are clearly visible. First, up to a strontium concentration of 10^{-2} mol dm^{-3} K_D is high, about 10^5 cm^3 g^{-1}. At these concentrations the pH of the solution in equilibrium is high, 11.2, which is due to hydrolysis of the exchanger [see equation (4)]. Moreover, the K_D value is seen to increase slightly in this concentration range. This is due to the increasing amount of Na^+ ions in the solution as they exchange with Sr^{2+}, which then causes a shift to the left in equation (4), and a decrease in the proportion of the hydrogen form. The sodium titanate discussed here prefers hydrogen ions to sodium ions, and therefore absorption of strontium on the sodium form is more favourable. In the second range, at strontium concentrations higher than 10^{-2} mol dm^{-3}, K_D decreases rapidly after saturation of the exchange capacity. The equilibrium pH is only slightly higher than the initial pH indicating only very minor hydrolysis of the strontium form.

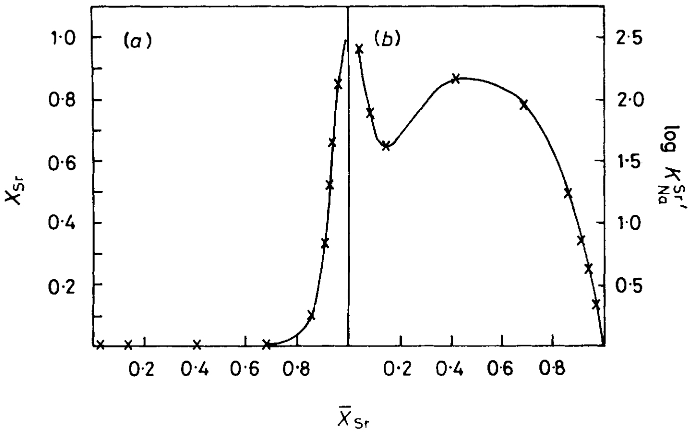

Figure 1. (*a*) Ion exchange isotherm and (*b*) corrected selectivity coefficient $K^{Sr'}_{Na}$ for Na^+ to Sr^{2+} exchange on $Na_4Ti_9O_{20} \cdot xH_2O$. $\bar{X}_{Sr}$: equivalent ionic fractions of strontium in the exchanger and in the solution, respectively. Initial Sr^{2+} concentration is 0.01 mol dm^{-3}, pH$_{equil}$ = 7—10

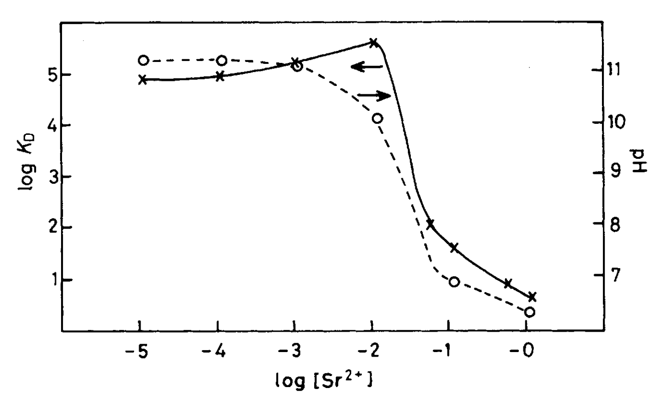

Figure 2. Distribution coefficient (K_D) (X) of strontium on $Na_4Ti_9O_{20} \cdot xH_2O$ and the corresponding equilibrium pH (O) as a function of strontium ion ($SrCl_2$) concentration. Exchanger weight 0.2 g, solution volume 20 cm^3, pH initially 5—6

Distribution Coefficient of Strontium as a Function of pH.—The distribution coefficient of strontium on $Na_4Ti_9O_{20} \cdot xH_2O$ is shown as a function of pH in Figure 3. The value of K_D is very high, 10^5 cm^3 g^{-1}, in alkaline solutions. At pH <7 K_D for the 10^{-3} mol dm^{-3} solution was lower by a factor of 3—5 compared with 10^{-5} and 10^{-7} mol dm^{-3} solutions, which gave identical curves. At first glance, this would seem to conflict with Figure 2, which shows that K_D is higher in a 10^{-3} mol dm^{-3} solution than in a 10^{-5} mol dm^{-3} solution, and the drop in K_D does not begin

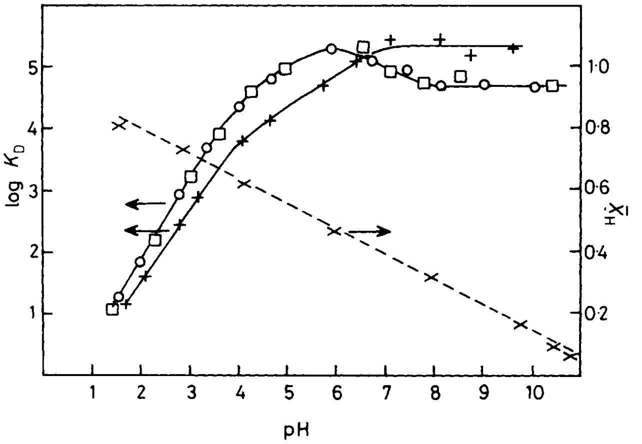

Figure 3. Distribution coefficient (K_D) of strontium on $Na_4Ti_9O_{20}\cdot xH_2O$ and equivalent fraction of hydrogen ions in the exchanger ($\bar{X}_H$) (X), as a function of pH. Sr^{2+} concentrations are: (+) = 10^{-3}, (○) = 10^{-5}, (□) = 10^{-7} mol dm^{-3}; solution volume 20 cm^3; exchanger weight 0.2 g; pH adjusted with HCl

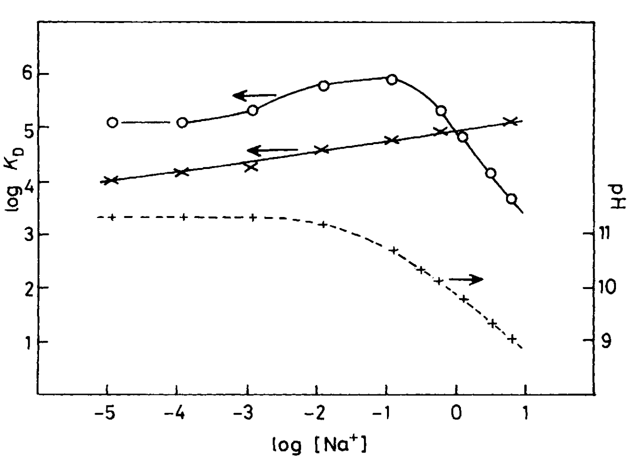

Figure 4. Distribution coefficient (K_D) of strontium on $Na_4Ti_9O_{20}\cdot xH_2O$ and corresponding equilibrium pH (+) as a function of sodium ion (NaCl) concentration. Sr^{2+} concentration: (○) = 10^{-3} mol dm^{-3}, (X) = ^{85}Sr tracer; exchanger weight 0.2 g; solution volume 20 cm^3; pH initially 5—6

until the concentration is 10^{-2} mol dm^{-3}. However, in Figure 2 the pH was alkaline in this concentration range, and the exchanger was almost entirely in the sodium form. In Figure 3 the exchanger was essentially in the hydrogen form at pH < 7. Exchange of strontium on the hydrogen form is less favourable and the drop in K_D probably begins at lower strontium concentration. This may be the reason for the lower level of strontium exchange from 10^{-3} mol dm^{-3} solution in the acidic region.

The situation is reversed in the alkaline region: K_D for a 10^{-3} mol dm^{-3} solution is higher, in good agreement with Figure 2. Higher concentrations of strontium ions bring a higher concentration of sodium ions into the solution. This, on the other hand, results in a higher proportion of the sodium form of the exchanger, which is more selective for strontium. The equivalent fraction of hydrogen ions in the exchanger ($\bar{X}_H$) shows a linear relation with pH (Figure 3), which can be expressed by equation (8). The concentration of strontium in the

$$\bar{X}_H = -0.08 \text{ pH} + 0.93 \qquad (8)$$

solution was so low that only a small fraction of the exchange capacity was filled with strontium ions. Hence the exchanger was almost entirely in its hydrogen and sodium forms and equation (8) was valid.

Distribution Coefficient of Strontium as a Function of Sodium Concentration.—The dependence of the distribution coefficient on sodium ion concentration is rather unexpected (Figure 4). As a whole the situation is favourable: K_D remains high even at very high sodium ion concentrations. However, there are some peculiarities. Up to a sodium concentration of 0.1 mol dm^{-3} K_D increases slightly, for the same reason as discussed in connection with Figures 2 and 3 [a shift to the left in equation (4)]. Above the sodium concentration of 0.1 mol dm^{-3} K_D continues to increase when strontium is present in a trace concentration. This indicates a very favourable equilibrium. In the case of a higher strontium concentration (10^{-3} mol dm^{-3}) K_D decreases linearly, with a slope of -1.65, in the sodium concentration range 0.5—5.0 mol dm^{-3}. This value diverges slightly from the expected value of -2, characteristic of the exchange of a divalent ion for a univalent ion.[16] At high pH values the contribution of $[Sr(OH)]^+$ exchange decreases the slope, because of the univalency of this species.

The pH in Figure 4 remains constant at 11.2, up to a sodium ion concentration of 10^{-2} mol dm^{-3}. At higher concentrations it decreases because of an essential shift to the left in equation (4). In the concentration range of 0.1—5.0 mol dm^{-3} the decrease is approximately linear according to the relation (9).

$$\text{pH} = -0.96 \log[Na^+] + 9.67 \qquad (9)$$

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