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The sorption of anionic species on hydrous tin dioxide

D.A. White *, R. Rãutiu

Department of Chemical Engineering, Imperial College, London SW7 2BY, UK

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Abstract

This paper describes the anion exchange properties of hydrous tin dioxide and of a composite silica–tin dioxide. The anions studied were fluoride, iodide, iodate and antimonate. Some isotherm data have been obtained and have been correlated with the Langmuir isotherm in which the coefficient in the denominator is negative. Generally speaking the uptake of anions drops as the pH of the contacting solution rises. The balance of evidence would seem to indicate that the process is classical ion exchange. The extent of the pH range over which this occurs is surprising and contradicts classical notions of hydrous oxide ion exchange theory. © 1997 Elsevier Science S.A.

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1. Introduction

At neutral and high pH levels hydrous metal dioxides are regarded as cation exchangers with virtually no capacity for anions, as shown by Amphlett [1] and Clearfield [2]. Hydrous tin dioxide, with the approximate formula $SnO_2 \cdot xH_2O$, is a good cation exchanger under these conditions. Hydrous oxides contain around 10% water of hydration and are amorphous. This water can be removed gradually by heating, and at 300 °C the oxide loses its ion exchange properties. As well as being a sorbing material for alkali and alkali earth metals, it can also take up base metal cations such as Cu^{2+} [3]. However, Mancilla [4] showed that hydrous tin(IV) oxide and, to a lesser extent hydrous uranium(IV) oxide, were effective sorbent materials for anionic iodine species in mildly alkaline solution. He showed that the other hydrous oxides, those of titanium, manganese and zirconium, showed virtually no sorption for these anionic species at higher pH values. Hydrous tin dioxide is the most amphoteric of these dioxides. It is also stable as insoluble hydrous oxide over the pH domain between 2 and 12. Previous studies on hydrous tin dioxide and silica–tin oxide [5] have shown that these materials are very good cation exchangers. This paper is concerned with the study of anion sorption onto hydrous tin dioxide and a composite silica–tin oxide ion exchanger.

Though not extensively studied, the anion exchange properties of hydrous tin dioxide have been known for some time. As early as 1970, Donaldson and Fuller [6] reported anion separations for quite a range of anionic species such as oxalate and permanganate. Italian workers [7] have shown that tin dioxide will sorb arsenic, selenium and antimony containing anions. Sen and Ghatuary [8,9] described chemical separations of a number of anions using tin dioxide; thus the hexacyanoferrate(II) and the hexacyanoferrate(III) ions could be separated from each other using sulphuric acid of different strengths. Egyptian workers [10] have recently worked out the sorption isotherms of the nitrate, chloride, bromide and thiocyanate ions on hydrous tin dioxides. This suggests that anion exchange on hydrous tin dioxides may be complex and involve two or more active sites on the exchanger.

The use of complex hydrous dioxide exchangers has been more widely reported. Thus Shibata et al. [11] and Tanabe et al. [12] reported that binary metal oxides formed from tetravalent metal cations have a marked higher acidity than do component simple oxides. There have been some studies of the properties of binary and simple hydrous metal oxides. Composite exchangers of titanium and silica, manganese and silica and titanium and zirconium dioxides were synthesized and both their ion-exchange properties and thermal stability investigated [13–18]. There is ample scope for further investigation into the anion exchange properties of tin dioxide and its composites. In this study, in particular the sorption isotherms as a whole were investigated for a number of anionic species as a function of the solution pH, as this is such an important variable in inorganic ion exchange.

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* Corresponding author.

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2. Experimental details

Two types of ion exchanger were synthesized; a simple hydrous tin(IV) oxide and a composite hydrous silica–hydrous tin(IV) oxide exchanger. Tin(IV) chloride pentahydrate and sodium silicate solution were supplied by BDH Chemicals. Hydrous tin(IV) oxide and composite tin(IV) oxide were prepared by neutralizing a tin(IV) chloride solution with ammonia in a batch-reactor. For the composite exchanger a 30% sodium silicate solution was also added with the ammonia. The slurries were aged in the liquor for 48 h. After this they were washed on a vacuum filter with double distilled water until no chloride was detected in the supernatant. This was done by adding silver chloride solution to the supernatant; an absence of a visible precipitate was the end point for the washing process. The precipitates were either vacuum dried at 80 °C or dried in air at 110 °C, then ground and sieved. Ammonia was driven off and this converted the ion exchanger into the hydrogen form on the cationic sites with the hydroxyl ion occurring on the anionic sites. The fraction below 100 μm was used and the ion exchangers stored in a desiccator over a saturated solution of ammonium chloride which gives a constant humidity of 75%.

A sample of 1 g of each exchanger was calcined at 800 °C and the total water content was calculated from the weight loss. A part of the calcined oxide was then dissolved in 1 M HNO_3 and analysed for tin content. The residue was filtered, washed and weighed as silica for the composite ion exchanger. The total water content of the ion exchangers was 8%–10%. The composition of the dried composite exchanger was 64% SnO_2 and 36% SiO_2. The ion exchange capacity was measured with a strontium 0.1 M solution. The hydrous tin oxide has an ion exchange capacity of 1.49 meq g^{-1} whilst the composite's figure was 2.75 meq g^{-1}. The latter would thus be the more efficient cation exchanger. Both ion exchange capacities were calculated for the conditioned ion exchanger (fixed water content).

Porosimetric studies were done on a Micromeritics ASAP 2000 surface analyser. The BET sorption area, micropore sorption area and average pore size were measured in a nitrogen–xenon atmosphere. The zeta potential, electrophoretic properties and particle size of the synthesized ion exchangers were measured with a Malvern Zetasizer 3 equipment. The conditioned ion exchangers were suspended in a 0.01 M potassium nitrate solution and measured against a neutral potassium nitrate electrolyte. The slurry concentration was 0.5 g l^{-1}.

Samples of conditioned exchanger were mixed with the contacting solutions of anions and shaken for 72 h on a thermostatic shaker bath at 25 °C. Contacting solutions were prepared from pure potassium salts of iodide, fluoride, iodate and antimonate in double distilled water. The samples were then centrifuged and supernatant taken for analysis. The experimental layout is presented in Table 1. All the anions tested in this set of experiments are non-hydrolysable anions for the pH domain between 2 and 10. In Table 1 the initial concentrations of the contacting solution for each ion, the volume of each solution taken *V*, the mass of exchanger *m* and the pH levels for the contacting solutions are given.

The concentrations of the anionic species at the end of the contact tests were determined by atomic absorption spectrophotometry (AAS) and the details of the conditions used are given in Table 2. The ions were precipitated out of solution as a very insoluble salt by excess of a cation that could be determined by AAS. In these cases the solutions were placed in a centrifuge so that precipitate and supernatant could be separated. Reverse AAS proved to be a very reliable, reproducible and sensitive method.

Table 1
Experimental layout for anion exchange

Ion	Initial concentration (meq ml^{-1})	pH	*V* (ml)	*m* (g)
F^-	0.1, 0.05, 0.01, 0.005	2, 4, 6, 8, 10, 12	40	0.5
I^-	0.1, 0.05, 0.01, 0.005	2, 4, 6, 8, 10	40	0.5
IO_3^-	0.1, 0.05, 0.01, 0.005	2, 4, 6, 8, 10, 12	10	0.2
$Sb(OH)_6^-$	0.01, 0.005, 0.002	2, 4, 6, 8, 10	10	0.2

Table 2
Absorption spectrometry conditions

Species analysed	Species determined	Wavelength λ (nm)	Sensitivity (ppm)	Observations
Sn^{4+}	Sn	286.3	3.2	N_2O–C_2H_2 flame
SiO_3^{2-}/SiO_2	Si	251.6	2.1	N_2O–C_2H_2 flame
I^-	Pd	247.6	0.25	N_2O–C_2H_2 flame
$Sb(OH)_6^-$	Sb	217.6	0.55	
IO_3^-	Ag	328.1	0.06	Air–C_2H_2 flame
F^-	Pb	283.3	0.45	

Table 3
Surface analysis data

Ion exchanger	Average particle size (μm)	BET surface area ($m^2 g^{-1}$)	Micropore surface area ($m^2 g^{-1}$)	Average pore size (nm)
HSnO [a]	43	196	57	2.1
HSnSiO [b]	84	394	111	4.9

[a] Hydrous tin(IV) oxide.
[b] Composite tin–silica hydrous oxide.

3. Results

The average particle sizes of the ion exchangers were determined to be 43 μm for the hydrous oxide and 84 μm for the composite silica–tin oxide with the Malvern Zetasizer. Porosimetry determinations are showed in Table 3. The composite oxide is more porous, but the size of the pores for both exchangers shows that multilayer sorption of anions is possible in their structure.

To illustrate the possible ion exchange properties of the exchangers, their zeta potential measurements are shown in Fig. 1. The hydrous tin dioxide measurements show the classical behaviour of an amphoteric ion exchanger and the point of zero charge (pzc) occurs at a pH of 4.0 [19]. Classical theory [1] would therefore predict that this exchanger would act as a cation exchanger above this pH value and as an anionic exchanger below this value. The silica–tin composite shows that it is a much more acidic exchanger with a pzc at a lower pH value of 2.3. In fact, the zeta potential measurements show that this substance has no significant region where it is clearly an anionic ion exchanger as it has a large zeta potential at low pH values. From these results it would be predicted that hydrous tin dioxide would be the better substance for the removal of anionic species from solution.

A comprehensive series of data was made to determine the equilibrium isotherms of the fluoride ion on hydrous tin dioxide at pH equal to 2, 4, 6, 8 and 10. This anion was chosen since it is stable and unhydrolysed over most pH and redox ranges and also because it can be easily determined by indirect AAS methods. These results involved the calculation of the quantity of fluoride on the exchanger (y mmol g^{-1}) as a function of the equilibrium concentration of this ion in the contacting solution (x molar). The interesting point about these results is that they can be correlated by a 'Langmuir'-like isotherm where $y = Ax/(1-Bx)$ and A and B are constants. If the above expression is rearranged it will be seen that a plot of x/y as a function of x will give a straight line plot with a negative slope of $-B/A$. This is shown in Fig. 2. Similar data were predicted by Misak [20] and the relevant expression is his Eq. (7) with a negative slope for selectivity coefficients less than unity.

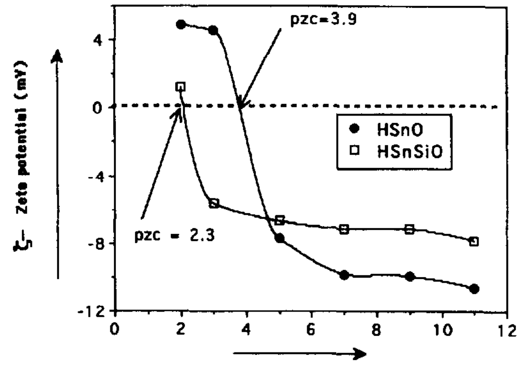

Fig. 1. Zeta potential data.

Converting these data back to a normal x–y isotherm is done in Fig. 3, which shows that the lower the pH of the contacting solution the higher the value of y for a given x. These data can be compared with isotherm results for the caesium cation which were correlated with the normal 'Langmuir' isotherm in which $y = Ax/(1-Bx)$. The caesium data are given in Fig. 4 and these show the normal shape of the data where the slope of the x–y curve decreases with x. In this

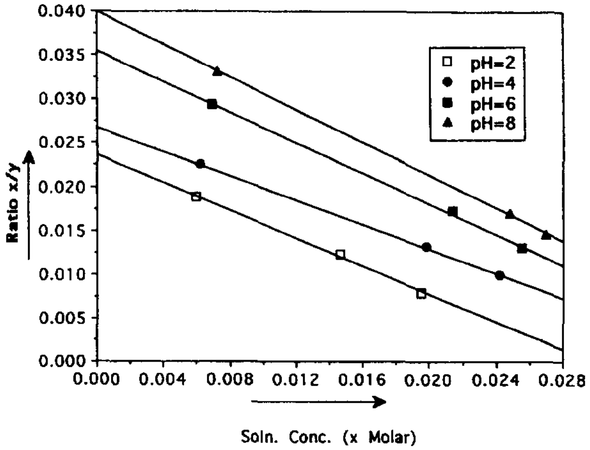

Fig. 2. Langmuir plot for fluoride.

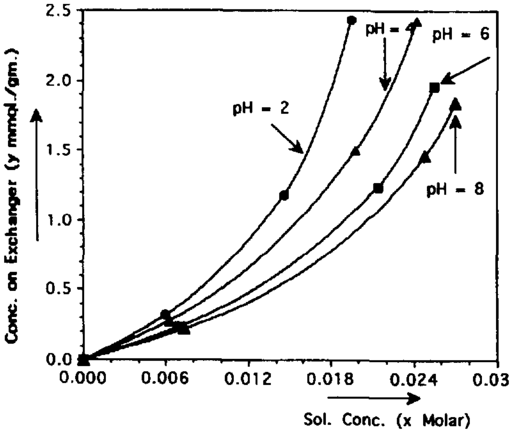

Fig. 3. Fluoride isotherms.

case where the normal Langmuir isotherm occurs, a capacity equal to A/B can be defined for the ion being exchanged. It should also be noted that the capacity for Cs^+ increases with pH which is converse to the behaviour of the fluoride ion. In the data for the fluoride anion the slope of the isotherm increases with the value of x and a capacity for the case of the reverse isotherm cannot be defined.

The other non-hydrolysable anion studied in this particular series of experiments was the iodate ion (IO_3^-). Mancilla [4] had shown that this particular ion was very readily sorbed onto hydrous tin dioxide. Values of the uptake Q for fluoride, iodide, iodate and antimonate ions studied in this part of the investigation are given in Fig. 5 as a function of the pH of the contacting solution. These tests give a qualitative estimate of the affinity of the ion for the hydrous dioxide exchanger. In these tests the initial solution was 0.01 M in the anion of interest. In the case of the fluoride and iodide ions, the results are very similar with the fluoride ion having the larger value of Q. In these two cases the value of Q is around 0.3 mmol g^{-1} at pH 2, falling to 0.05 at pH 12. The fact that Q falls to a low value in alkaline media suggests that the sorption could be reversible and a true ion exchange process. However, the value of Q for iodate falls from a much higher value of 0.5 at the lower pH to only 0.35 in alkaline solution. This suggests that the sorption process for this particular ionic species is not reversible, a point which is considered later.

Although it is not possible to define a true capacity for data correlated by the 'Langmuir'-like isotherm, the traditional K_d value, equal to A in this case, can be worked out from the correlation and the data for the fluoride and iodide ions are given in Fig. 6. This shows that K_d decreases with an increase in pH. However, the most important point to notice is that the ability of the hydrous oxides to sorb significantly non-hydrolysable ions at a high pH is indeed remarkable. For fluoride, K_d is around 40 at the pzc and just under 30 at a pH of 10, a contradiction of the classical theory.

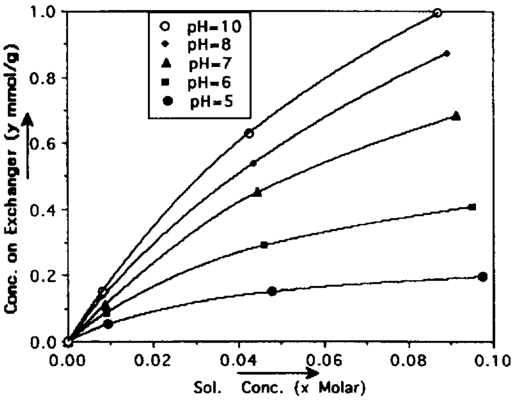

Fig. 4. Caesium isotherms.

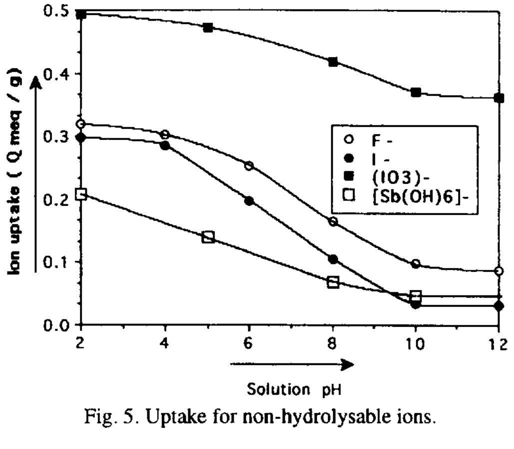

Fig. 5. Uptake for non-hydrolysable ions.

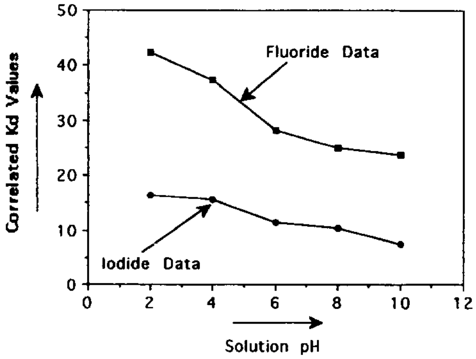

Fig. 6. K_d data for F^- and I^- ions.

4. Conclusions

Classical ion exchange theory predicts that for the equilibrium of two monovalent ions the fraction of sites on the exchanger occupied by the counter ion η is related to the ionic fraction of that ion in solution ξ by the expression

$$\eta=\frac{\alpha\xi}{1+(\alpha-1)\xi} \tag{1}$$

α is the selectivity of the exchange, which can take any positive value. Now, in terms of actual concentrations, the ion concentration in solution is given by $x=E\xi$ and the concentration on the ion exchanger is $y=C\eta$. Here E is the ionic strength of the contacting solution and C is the total exchange capacity of the exchanger. Substituting these values into Eq. (1) gives the following expression:

$$y=\frac{(\alpha C/E)x}{1+\{(\alpha-1)/E\}x} \tag{2}$$

If this last equation is compared with the classical Langmuir isotherm, in which $y=Ax/(1+Bx)$ then

$$A=\frac{\alpha C}{E}\quad B=\frac{(\alpha-1)}{E} \tag{3}$$

Therefore the Langmuir isotherm will describe the exchange process for monovalent exchange if α is less than unity. The value of B can be large if E is small. In the present case the counter ion is hydroxyl which occurs in very dilute amounts in neutral solution. With cation sites available, even though α is small, significant ion exchange would occur.

Under these circumstances the evidence would seem to prove that anion sorption on hydrous tin dioxide is an ion exchange process. Certainly this would be more certain if the exchange is shown to be reversible in stronger caustic solutions. Mancilla [4] has shown that iodine ions could be eluted with a 1 M NaOH solution. Though the majority of the anionic species examined in this paper are of particular interest to the nuclear industry as fission products occurring in nuclear reprocessing streams, they do have wider application in pollution control [21]. The anionic properties of hydrous tin dioxide make it worthy of future study and the confirmation that MnO_2 and TiO_2 have no anionic exchange properties is also suggested by this work.

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