STUDIES ON INORGANIC ANION EXCHANGERS

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Abstract—The commercially available inorganic anion exchangers Polyan, Polyan HT, Oxtain and Oxti have been studied by the construction of exchange isotherms for the ions SO_4^{2-}, NO_3^-, Cl^-, Br^- and I^-. They were characterized by X-ray powder diffraction and thermal analyses when appropriate. Conclusions are as to selectivities and reversibilities, and comments made on the thermal and chemical stabilities of the exchangers.

INTRODUCTION

The earliest experiments on ion-exchange involved inorganic exchangers of clay mineral or zeolitic types. These were cation exchangers and the first useful anion exchangers were the well known resins.

In recent years there has been increased interest in inorganic exchangers because of their temperature and radiation stability and potential selectivity. This has been reflected in the volume of work done on natural and synthetic zeolite minerals, which includes the only recent major advances in the theory of cation exchange [1, 2].

This interest has not been matched in anion exchangers and the literature on the theory and application of inorganic ion exchangers is slight and confined, in the main, to "hydrated oxides" presumed to exchange OH^- groups under appropriate pH conditions.

This paper attempts to characterize commercially available inorganic anion exchange materials by X-ray powder and thermal analyses, and to construct ion-exchange isotherms to compare their effectiveness.

EXPERIMENTAL

Materials and analyses. The exchangers examined were as supplied by Applied Research SPRL, Brussels, Belgium as 0.1–0.5 mm granules. They were described as: Polyan (polyantimonic acid), Polyan HT (poly-antimonic acid dried at high temperature), Oxtain (hydrated tin oxide) and Oxti (hydrated titanium oxide).

Other chemicals used were AnalaR grade or the purest available GPR. Some radiochemical measurements were made using $^{35}Na_2SO_4$ obtained from The Radiochemical Centre, Amersham. Activity was measured by a Kontron SL30 Liquid Scintillation Spectrometer. Samples were prepared for counting as a colloid composed of 4 ml Triton 100X, 4 ml PPO in toluene ($4 gl^{-1}$), and 2 ml of aqueous sulphate solution in the range 0.01→0.09M.

The halogen ions were determined by Mohrs method using a $K_2Cr_2O_7/KCrO_4$ indicator for Cl^- and Br^-, and di-iododi-methylfluorescien for I^-. Titration was by 0.025M silver nitrate of samples diluted five-fold by phosphate buffer (pH 6.8) prior to titration. Nitrate analysis was by specific ion electrode (Orion).

Preparation of exchangers in anion form. Each exchanger was washed well with deionized water to remove fine particles. 20g of exchanger then was soaked, with occasional stirring, in 1l of the appropriate 0.1M acid for 3 days. They were then filtered, washed and dried at less than 80°C for 1 day. In the preparation of sulphate forms the isotope solution was added to the 0.1M sulphuric acid.

Ion-exchange experiments. Capacities were measured by immersing 1g of exchanger in a 30 ml mixture of 0.09N NaCl +

0.01N acid solution for one week. Ion-exchange isotherms were constructed from 1g lots of exchanger allowed to equilibrate, with stirring, in 20 ml of isonormal solution composed of the ions and counter ions in varying concentrations. Forward and reverse isotherm points were plotted from solution phase analysis by the methods quoted. All equilibrations were at 20°C.

Other experiments. Thermal analyses (dta and tg) were made using a Dupont 900 Thermal analyser with a tg attachment. Guinier X-ray powder photographs were taken using Cu K_α radiation.

RESULTS

The isotherms measured are shown in Figs. 1 and 2. Capacities are given in Table 1. All exchangers and their exchanged forms were amorphous except Oxtain for which "d" spacings were determined (Table 2). Water contents are listed in Table 3 and the dta curves are shown as Figs. 3 and 4.

DISCUSSION

Polyan and Polyan HT. A negligible anion exchange capacity was measured for both these materials. This conflicted with results of Viallate *et al.* [3] who reported an uptake of 3 ± 0.5 mg F^- per g from an ammonium and hydrochloric acid solution (11M) with pH 7.5. This was for a polyantimonic acid (i.e. not Polyan). They did not check reversibility and so their process may well not have been an exchange. Hydrated antimonic acid has been used extensively as a cation exchanger particularly for Na removal prior to neutron activation analysis [4].

Thermal analysis data showed an expected lower water content for the "HT" polyan and the dta profiles suggested that some of the water loss from Polyan below 300°C was that of a non-reversible dehydroxylation. This may have created porosity into which water could be trapped and appear as tightly bound water lost at higher temperatures from Polyan HT than in Polyan.

Oxtain. None of the processes observed were truly reversible, NO_3^- was able to replace only 50% of Cl^- and Br^-, and 65% I^-. The NO_3^-—SO_4^{2-} isotherm displayed a large hysteresis.

The anion selectivity sequence for Oxtain,

$$SO_4^{2-} \gg Cl^- > I^- > Br^- > NO_3^-$$
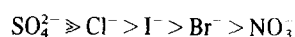
was similar to the sequence suggested by Donaldson and Fuller,[5]

i.e. $$SO_4^{2-} > Cl^- > Br^- > I^- > NO_3^-.$$
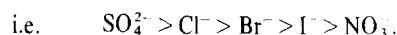
It was noted in this work that the I^- form of Oxtain
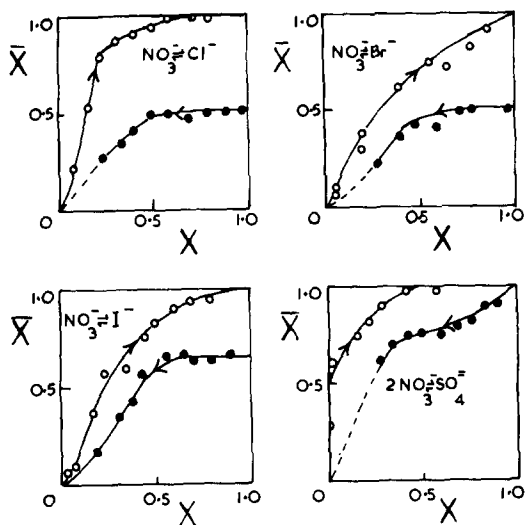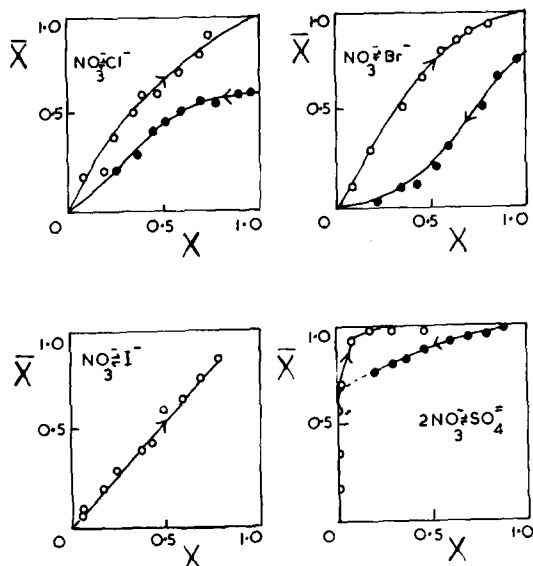
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Fig. 1. Anion isotherms for Oxtain at 20°C ($\bar{X}$ refers to solid phase). O $NO_3^- \to X^-$ (X^- ingoing ion = Cl^-, Br^-, I^-, $\frac{1}{2}SO_4^{2-}$). ● $X^- \to NO_3^-$ (reverse process).

Fig. 3. Differential thermal analysis of Polyan, Polyan HT. and various forms of Oxtain.

Fig. 2. Anion isotherms for Oxti at 20°C ($\bar{X}$ refers to solid phase). O $NO_3^- \to X^-$ (X^- ingoing ion = Cl^-, Br^-, I^-, $\frac{1}{2}SO_4^{2-}$). ● $X^- \to NO_3^-$ (reverse process).
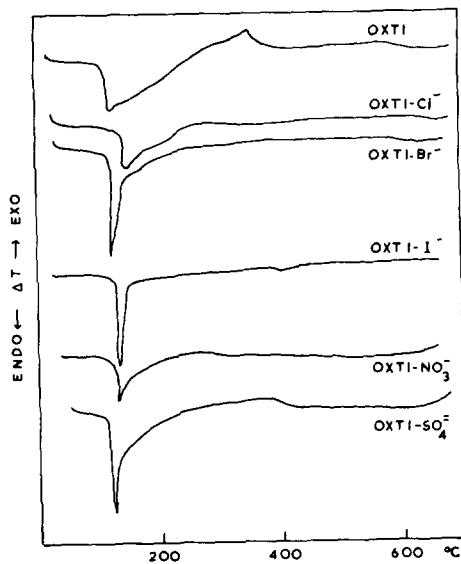
Fig. 4. Differential thermal analyses of Oxti and its anion exchanged forms.

was a deep brown colour in contrast to the other anionic forms which were all white. Probably iodine compound formation had taken place, hence the difference in sequence noted.

All the isotherms indicated "exchange" occurring in two sites and tg results showed two regions of water loss. This was not evident from dta where only one water loss feature was observed. The X-ray results indicated a loss of structure for the anion forms and this may well have accounted for the variations in capacity.

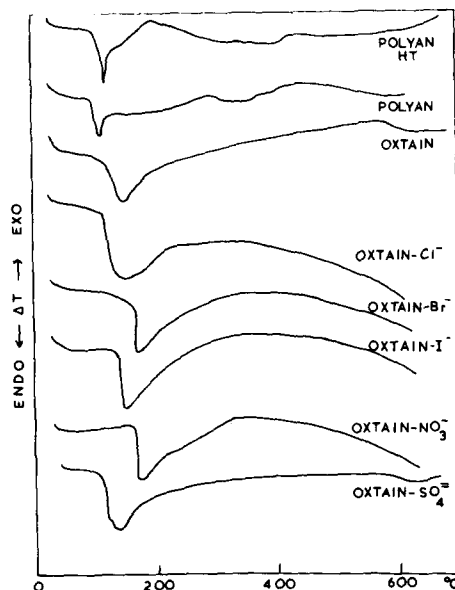*Oxti.* Again the exchange processes were not truly reversible. For the $Cl^- \to NO_3^-$ process 60% Cl^- was

recovered compared to 80% of Br^- in the $Br^- \to NO_3^-$ process. Nitrate was unable to replace I^-. The water content of the I^- form was high but its dta profile was similar to the other anion forms of Oxti. However, again the I^- form was coloured (orange) whereas the other forms were not.

The selectivity sequence was

$$SO_4^{2-} \gg Br^- > Cl^- > I^- > NO_3^-.$$
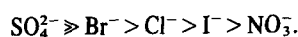
No comparable information was found in the literature.

It was noted that Oxi showed two features in its dta.