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Inorganic Ion-exchange Materials Based on Insoluble Antimony(V) Compounds

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Studies of inorganic ion exchangers based on insoluble compounds of antimony(V) are reviewed [polymeric antimonic acid and its numerous derivatives containing one or two multivalent elements (P, Zr, Nb, Ti, Te, etc.)]. Different approaches to the discussion of their composition, structure, and ion-exchange properties are analysed. Examples of the preparation and of the characteristics of different types of exchanger are given, and their possible practical applications are outlined.
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I. INTRODUCTION

The scientific and technological need for selective ion-exchange materials with a high stability towards heat and radiation was responsible for the interest shown in the 1950's in inorganic ion exchangers and for the extensive studies which began at that time of the ion-exchange properties of various sparingly soluble inorganic compounds. Among the most important of the modern inorganic ion exchangers are the insoluble oxygen compounds of quinquevalent antimony: polymeric antimonic acid and its derivatives, including (in addition to antimony) one or two multivalent elements such as P, Zr, Nb, Ti, Te, etc.

Many papers have been published on the synthesis, properties, and applications of these cation exchangers, because of their unusually high selectivity (which allows many important practical problems to be solved by ion exchange methods). Previously published reviews of inorganic ion exchangers[1-5], including Sb(V) compounds, do not mention the advances made in the last few years. Furthermore, none of the foreign reviews deals adequately with the work done in the Soviet Union.

The aim of this review was to fill this gap by generalising the results of research on ion exchangers based on Sb(V) compounds, both published and still in progress in the ion exchange laboratory of the physical chemistry department of Leningrad State University. Thus we aim to bring to the reader's attention not only problems which have been solved but also controversial questions on the synthesis of these materials and on different approaches to studies of their composition, structure, and ion-exchange properties. When discussing the characteristics of different types of ion exchanger we shall specially emphasise their advantages, their shortcomings, and their possible practical applications.

II. POLYMERIC ANTIMONIC ACIDS

The study of the ion-exchange properties of polymeric antimonic acids (hydrated Sb(V) oxides, Sb(V) hydroxide, hydrated antimony pentoxide, hydrates of antimony pentoxide) began almost simultaneously in several countries. The earliest widely available publications appeared in 1965–1969. These include the work of Lefebvre[6], Lefebvre and Gaymard[7], Abe and Ito[8,9], Baetsle and Huys[10], and Girardi and Sabbioni[11]. In the Soviet Union the ion-exchange properties and the structure of antimonic acids began to be studied in 1965, and the first publications appeared in 1967–1969.[12,13]

This work made clear the high exchange capacity of antimonic acid (up to 5 mg-equiv g^{-1} or 20 mg-equiv cm^{-3}), its ability to undergo ion exchange in acid solutions, and its selectivity towards Sr^{2+}, Ba^{2+}, Cd^{2+}, Pb^{2+}, Ag^{+}, Na^{+}, and K^{+} ions. However, even at that early stage different points of view on the origin of the ion-exchange properties of these materials and on the composition and structure of polymeric antimonic acid began to emerge: in particular, it was shown that the selectivity is very sensitive to the method of preparation.

The fundamental aspects of the preparation of sparingly soluble ("precipitated") antimonic acids and antimonates were first examined during the previous century. Since then there have been many changes in our understanding of the nature of these compounds. It is now generally accepted[14-21] that monomeric antimonic(V) acid—the starting material for the preparation of the insoluble forms—is a strong monobasic complex acid (hexahydroxoantimonic acid $H[Sb(OH)_6]$), which can exist in solution for a short time but is converted by condensation (in 2 or 3 days) into a precipitate of polymeric antimonic acid[18,19-22]. The salts of $H[Sb(OH)_6]$ (the hexahydroxoantimonates) also show a tendency towards polymerisation[23-25].

The state of antimony(V) in solution and the mechanism of the ageing processes of antimonic acid and antimonate solutions have been studied in detail[26-35]. Some substances were found to be a "stabilising" effect on solutions of antimonic acid (H_2O_2, oxo-compounds[19,36,37], and arsenious acid[38]), whereas other substances (such as KCl[19,36]) accelerate the precipitation.

It is therefore essential in the synthesis of insoluble antimonic acids (and especially in the preparation of mixed sorbents) to fix a large number of parameters in order adequately to characterise the initial solution: its concentration and pH, method of preparation, conditions and time of storage, presence of other substances, etc.

1. Preparation of Amorphous Antimonic Acid

Amorphous antimonic acid (AAA) can be prepared by the following methods:

a) by adding solutions of mineral acids (HCl, HNO_3) to solutions of the so-called "acid potassium or sodium pyroantimonates"†[10,13,23,39,40–43];

b) by hydrolysing $SbCl_5$ with water, chlorine water, or a dilute solution of NH_4OH;[13,23,42–44,47];

c) by treating $SbCl_3$ with oxidising agents such as HNO_3 or $HNO_3 + HCl$,[44,48–50] or H_2O_2,[24,45,51] and diluting the solution with a large volume of water;

d) by dissolving metallic antimony in *aqua regia* and evaporating the solution with repeated additions of nitric acid[43,52,53];

e) by dissolution of Sb_2O_3 in *aqua regia*[54] followed by hydrolysis;

f) by dissolving freshly precipitated antimonic acid and removing the solvent by freezing[44];

g) by a recently developed ion exchange method[55]. A solution of $K[Sb(OH)_6]$ is passed through the hydrogen form of a strongly acid cation exchanger in order to give a solution of $H[Sb(OH)_6]$,[18,19] which is then frozen or slowly evaporated, and the residue is dried over P_2O_5[13,42] or $CaCl_2$.[57,58]

Production of the amorphous acid is assisted by a low hydrolysis temperature, short time of contact between the precipitate and the mother liquor (4 h,[43] or 1 day[42]), and a low drying temperature[44,56]. These same factors favour the production of an amorphous product with a high solubility[44].

Washing AAA precipitates with water causes dispersion of the solid, increasing as the electrolyte is removed by the wash liquid. In order to minimise the loss of antimonic acid and to obtain a more stable product Abe and Ito[43,59] recommend washing the precipitate with cold water and separating it from the wash liquid by centrifuging. Colin and Lefebvre[56] froze the solution of antimonic acid prepared by ion exchange and treated the residue with alcohol at −4 °C. The granular material thus obtained was rapidly filtered and dried at 25 °C. Loss of antimony during washing of the AAA can be reduced still further[13] by introducing an additional drying stage (after partial removal of the chloride ions).

The composition of the AAA can vary over a wide range. Immediately after precipitation the value of n in the empirical formula $Sb_2O_5.nH_2O$ (which defines the composition of the samples) can be as high as 29–30,[43,47] but the water is rapidly lost. Relatively stable AAA samples, amorphous to X-rays, may contain between 3 and 8 molecules of water per molecule of Sb_2O_5 (reported values include $n = 5–8$,[13,42] $n = 4–5$,[43] and $n = 3$[57,58]).

Amorphous antimonic acid is not a stable product. It is spontaneously converted into crystalline antimonic acid on storage. When dry samples are kept at room temperature the first indications of crystallinity are observed after 3 months, and crystallisation is complete after 1.5–2 years[13,42].

† The term "pyroantimonate", which reflects the early, erroneous belief that antimony (like phosphorus) can form meta-, ortho-, and pyroantimonic acids and salts, is still used in textbooks as well as in research publications. Doubts concerning the validity of this analogy were expressed even in the last century (see, for example, Ref.44). More recent work has shown that the "pyroantimonates" are really hexahydroxoantimonates of the type of $M(I)[Sb(OH)_6]$,[15,16,20,21] or their partial condensation products[45,46].

2. Preparation of Crystalline Antimonic Acid

Crystalline antimonic acid (CAA) can be prepared by the methods used in the preparation of AAA. Crystallisation of the antimonic acid can be induced either in the mother liquor (by allowing very long ageing times, by increasing the temperature of the mother liquor, or by increasing the concentration of mineral acid[32,43,54,59,60,61]), or it can be induced by heat treatment of the precipitate (separated from the solution).

For example, Abe and Ito[43,59] prepared samples showing a high degree of crystallinity by hydrolysing $SbCl_5$ in a large volume of water and allowing the precipitate to stand in the mother liquor at 30 °C for 20 days. The time could be shortened to 4 h by raising the temperature to 60 °C and increasing the concentration of mineral acid present during the hydrolysis.

The preparation conditions of CAA by thermal dehydration of the amorphous acid and the optimum drying conditions for the crystalline acid are more complex. The usually recommended procedure[13,42,62] involves drying the amorphous phase for 2–3 days at 110–180 °C, i.e. in the temperature range corresponding to reversible sorption of water according to thermal analysis data[13,42,59,61]. The CAA samples obtained in this way are white powders or free-flowing granules of composition $Sb_2O_5.nH_2O$ (where $n = 3–4$), showing no tendency to peptisation; under the electron microscope they appear as cubic crystals ~0.1 μm in size[13]. At lower temperatures the crystallisation is slower, and at higher temperatures structural changes are possible (reduction of Sb(V) to Sb(III)), leading to changes in the ion-exchange properties of the material.

We should note that in many laboratories the CAA samples (including the hydrated antimony pentoxide marketed by the Italian Carlo Erba firm) are prepared by heat treating the amorphous material at 270 °C.[11,54,61] These samples have good mechanical properties[54], but they appear to have undergone some thermal changes (yellow colour[54,61], lower intensity of the odd-index X-ray reflections[13,61,69], weight losses at 900–1000 °C smaller than those of samples which have not been heat treated[54,61]).

In addition to AAA and CAA, we can prepare glassy antimonic acid by dissolving freshly precipitated antimonic acid in hot water and rapidly evaporating and cooling the solution[43,57–59].

The choice of crystallisation conditions and temperature for the preparation of CAA is determined mainly by the views of individual workers on the composition, structure, and mode of operation of the ion-exchange groups and on the processes which accompany thermal decomposition. We shall therefore discuss some of the most important results obtained in physicochemical studies of antimonic acid.

3. Results of Physicochemical Studies of the Structure of Antimonic Acids

Physicochemical studies of the oxygen compounds of Sb(V) can be arbitrarily divided into two periods. The first was concerned mainly with the composition of Sb(V) oxides, and it included some early applications of X-ray diffraction methods. The second period has been concerned with the ion exchange and catalytic properties of the Sb(V) oxides. It has coincided with the extensive introduction of new methods of analysis (differential thermal analysis, high-temperature X-ray diffraction, i.r. spectroscopy, etc.).

Work done during the first period could not establish whether the hydrates formed by Sb_2O_5 have a fixed or an indeterminate composition. The reported dehydration and thermal decomposition products included the hydrates $Sb_2O_5.nH_2O$ with $n = 3$, 2, and 1 (by analogy with the phosphoric acids), and also $n = 6$, 5, $4\frac{1}{2}$, 4 (see Ref.47), or $n = 6$, 4, 3, 2, 1.5,[63] or anhydrous Sb_2O_5, Sb_3O_6OH, Sb_6O_{13}, Sb_2O_4, and Sb_2O_3.

The initial oxide $Sb_2O_5.nH_2O$ and the products obtained by baking it at 800 °C (with formation of Sb_2O_4) have similar crystal structures (pyrochlore type, *Fd3m* space group[64-67]). X-ray data for the hydrates ($n = 3$, 1) and for the heat treatment products are given in the ASTM tables, although the existence of definite hydrates and of some of the heat treatment products is still being debated.

Thus, Sb_3O_6OH[64] was not detected by some workers[43,68], and was categorically excluded by others[69]. In place of Sb_6O_{13},[70] the compound $Sb_2O_{4.35}$ (of almost identical composition) has been suggested[69]. Doubts on the existence of anhydrous Sb_2O_5 have been expressed[64,71].

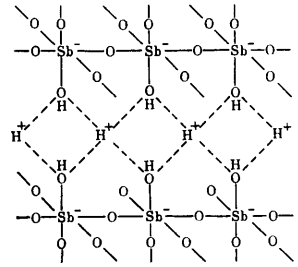
Natta and Baccareda[66,67], when reporting their X-ray diffraction results for $Sb_2O_5.3H_2O$, $Sb_2O_5.H_2O$, Sb_2O_5, and Sb_2O_4, pointed out that the compound which they had denoted Sb_2O_5 contained not less than one mole of water per mole of Sb_2O_5. However, this reservation was ignored by later workers and the original results[66,67] are still referred to anhydrous Sb_2O_5 [43,57,58,68,71].

A more recent comparison of the diffraction patterns and microwave resonance spectra of commercial samples of "anhydrous" Sb_2O_5[69] has shown that all these materials either contain water or show evidence of thermal decomposition (since all the samples dried at high temperatures contain Sb(III), including the Sb_2O_5 discussed in Ref.72). Only in the initial CAA of composition $Sb_2O_5.4H_2O$ (which had not been dried at high temperature) was the whole of the antimony in the Sb(V) form. Heating the CAA to 700 °C does not alter the crystal lattice type (pyrochlore, *Fd3m* space group), but the relative intensity of the reflections with odd indices is decreased by the treatment, suggesting structural rearrangements involving the cations. A decrease in the intensity of the odd reflections has been observed even in CAA held at 150 °C for 2 h.[69] It is thought that materials of reproducible composition cannot be produced by heat treatment up to 700 °C, and the breaks observed on the TG curves are ascribed to changes in the rate of dehydration and decomposition processes.

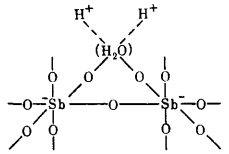
Other workers, however, interpret[73-76] the breaks in the TG curves (and the corresponding extrema on the DTG curves) as evidence for the formation at these temperatures of stable pyrochlore phases of composition $H_xSb(III)_tSb(V)_{16}.O_{56}$ (the composition of the elementary cell). Transitions between the phases are accompanied by the loss of O_2 and H_2O, and by reduction of some of the Sb(V) to Sb(III), the Sb(III) being transferred from a B position to an A position of the $A_2B_2X_7$ pyrochlore structure. The latter effect accounts for the decreased intensity of the odd reflections in the diffraction patterns. The number of pyrochlore phases stable up to 820–840 °C corresponds to the number t of Sb(III) cations which can be accommodated in the first coordination sphere of the $Sb(V)O_{6/2}$ octahedra without infringing the electrical neutrality of the pyrochlore structure as a whole. These views on the thermal decomposition processes deserve to be taken seriously and to be developed further.

Even the first studies of the ion-exchange properties of CAA led to rejection of the formula $Sb_2O_5.nH_2O$ and showed the need to establish a correlation between the exchange capacity of the ions and the structure of the CAA. Thus, in 1965 Lefebvre[6] examined the ion-exchange properties of crystalline CAA (in particular, the equivalent exchange of H^+ and Ag^+), and they compared the composition of the Ag^+ form ($AgSbO_3.0.5H_2O$) with that of the original CAA ($Sb_2O_5.4H_2O$) by using the formula $HSbO_3.yH_2O$ for the CAA. In 1972 Jolivet and Lefebvre[77] arrived at the formula $H(H_2O)SbO_3.0.5H_2O$, which reflects the non-equivalence of the water molecules, by studying exchange on CAA and antimonates.

Abe and Ito[43,59,78] proposed the following formulae for CAA and AAA:



CAA: $H_2Sb_2O_5(OH)_2$



AAA: $Sb_2O_5 \cdot nH_2O$

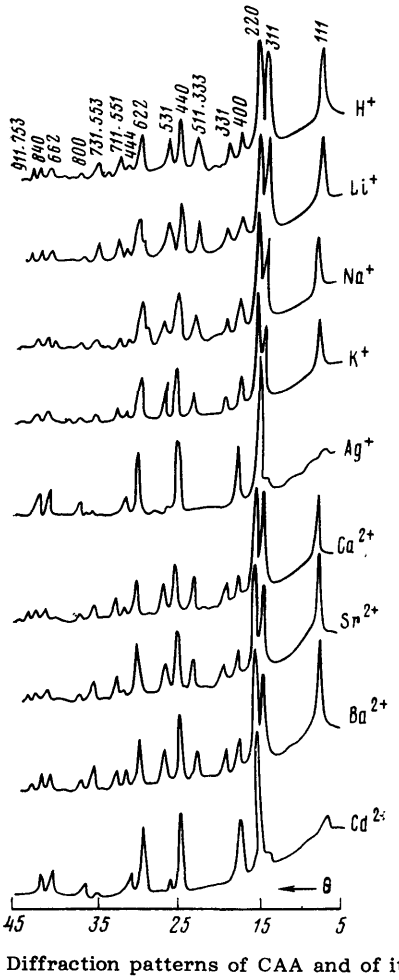


Figure 1. Diffraction patterns of CAA and of its salt forms[13,62].

They showed[59] that the exchangeable H^+ ions (like the Na^+ ions in the $Na[Sb(OH)_6]$ structure) are surrounded by six oxygen atoms. The H^+ ions in this structure can attach

themselves to H_2O, forming H_3O^+ ions. SbOH groups are postulated only in the CAA, following an i.r. spectral study[59] in which absorption bands assigned to Sb—O vibrations (750 cm^{-1}) and to sorbed water (1630 and 3350 cm^{-1}) were observed in all the samples, whereas bands at 1280 and 2430 cm^{-1} (assigned to vibrations of the SbOH group) were found only in the CAA. This conclusion is surprising, since SbOH groups would be expected to appear first in the AAA (the partial condensation product of $H[Sb(OH)_6]$).

The first attempt to correlate the ion-exchange properties and the structural features of CAA was reported in 1968 by Baetsle and Huys[10], who studied partly crystallised samples of CAA. Starting from the composition $Sb_2O_5.4H_2O$ and the experimentally determined density (4.27 g cm^{-3}), and assuming a lattice constant $a = 10.3$ Å, they concluded that the elementary cell contains 14 antimony atoms. They proposed an elementary cell structure of composition $[H_3Sb_3O_5.(OH)_8]_3.H_5Sb_5O_6(OH)_{18}$. This CAA structure accounts for the equality of the maximum exchange capacity to the concentration of Sb, and for the *S*-shaped isotherms (the nine strongly acidic exchange points of the trimers are assumed to be non-equivalent to the five weakly acidic points of the pentamer).

One weakness of the model[10] is its reliance on the measured densities of finely divided materials to calculate the number of Sb atoms in the elementary cell. Experimentally measured densities in these materials are usually lower than the true value (see, for example, Ref.79): this should lead to an erroneously low value of the number of Sb atoms in the elementary cell (14 instead of 16). We note that the CAA structure proposed by Baetsle and Huys[10] is still accepted by many workers[5,80].

In 1969 Novikov and coworkers[13] demonstrated that all the following materials had identical Debye diffraction patterns: the initial CAA, its sodium form, a synthetic sample of $NaSbO_3$ (prepared by heating $Na[Sb(OH)_6]$ at 480 °C), and the product obtained by treating $NaSbO_3$ with acid (i.e. antimonic acid prepared independently from $NaSbO_3$). Diffraction patterns for the hydrogen form and some salt forms of CAA, confirming the conclusions from the Debye patterns, are shown in Fig. 1[62,81–83]. We note the regular decrease in the relative intensity of the odd-order reflections as the scattering power of the counter-ion is increased, and the almost complete disappearance of these reflections for the heaviest counter-ions (Ag^+ and Cd^{2+})#.

All these compounds belong to the pyrochlore structure type ($Fd3m$ space group). According to published data, the Sb(V) atoms in this structure can occupy only the 16(*c*) positions of the elementary cell, and the Sb(III) atoms must be partly or fully accommodated in the 16(*d*) positions[64–67]. Since the maximum exchange capacity for Ag^+ (in mg-atom g^{-1}) is equal to the Sb content (in mg-equiv g^{-1}) we may conclude that the whole of the antimony in CAA is in the Sb(V) form. Using the coordinates of the Sb(V) [16(*c*)] and O atoms (48*f*)[85,86] we constructed a model of the CAA anion skeleton[83]§ consisting of corner-sharing $[SbO_{6/2}]^-$ octahedra

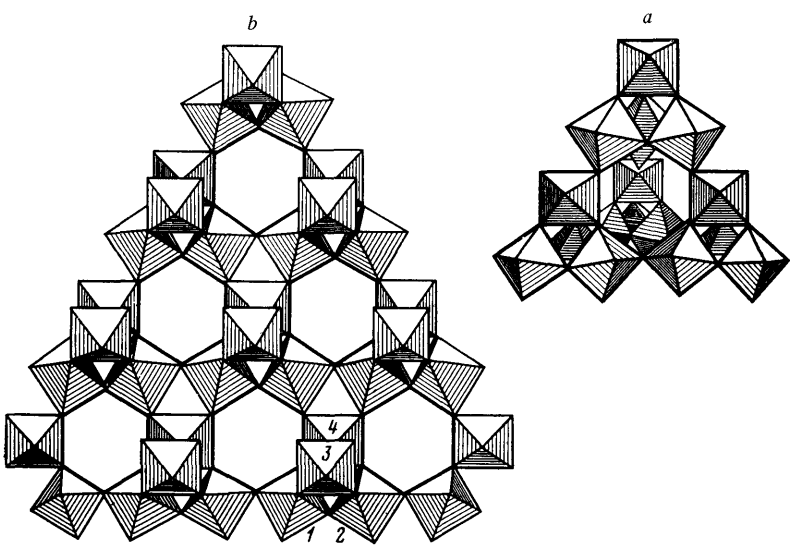


Figure 2. Structure of the anion skeleton of CAA: (*a*) elementary cell, (*b*) schematic representation of two types of (111) plane formed by $[SbO_{6/2}]^-$ octahedra.

The effect of the difference in scattering power between A and B ions in compounds with the pyrochlore structure and in CAA is discussed in Refs. 61 and 84. The similarity between the losses of reflections by ion exchange and by heat treatment[13,69,73,75,76] confirms that the counter-ions and Sb(III) occupy identical positions in the CAA structure.

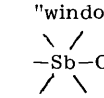
§ The pyrochlore structure was described by Belov[87] as a derivative of the fluorite structure. Interest in compounds with the pyrochlore structure has increased in recent years (see, for example, Refs. 88 and 89). A detailed description of the structure is given in Ref. 90.

carrying an excess of negative charge. This charge is compensated by the exchangeable cations (counter-ions) H^+ (or H_3O^+), Na^+, Sr^{2+}, Ag^+, etc.

The elementary cell of the anion skeleton is shown in Fig.2, with two types of (111) plane. The CAA structure can be built up in different ways. One is to arrange in layers the two types of (111) plane shown in Fig.2*b*. The lower plane forms a system of hexagonal "windows", the upper plane is more open. The next plane is similar to the first, but its "windows" are in a staggered configuration with respect to the lower plane, and so on. The CAA structure can also be built up from layers of parallel columns of octahedra: octahedra *1* and *2* in Fig.2*b* belong to one of these columns, *3* and *4* belong to a column of the next layer. In each layer the columns are perpendicular to those of the next layer. We can choose as the building block the group of four octahedra (*1*, *2*, *3*, and *4* in Fig.2*b*) joined to form an empty octahedron.

As Fig.2 shows, the anion skeleton of CAA has an open-lattice structure. At the centre of the elementary cell we find a hole connected to the neighbouring holes by four hexagonal rings ~3 Å in diameter. Six of the faces of each $[SbO_{6/2}]$ octahedron are in contact with six different holes, the other two with an empty octahedron. The counter-ions and the water can be accommodated at the centre of the hexagonal windows [16(*d*)] or at the centre of the holes [8(*b*)].

By assuming the simplest, uniform distribution of the Sb^{5+} and O^{2-} charges over all the bonds[91] we can calculate the excess of negative charge at the centre of the hexagonal "windows" or at the centre of the holes. Each oxygen bridge

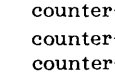


$-Sb-O-Sb-$ contributes an excess charge of $\delta = z_O + n_O\, z_{Sb}/n_{Sb} = -2 + 2(5/6) = -1/3$, where z_O, n_O and z_{Sb}, n_{Sb} are the valence and the coordination number of O and Sb respectively in the anion skeleton. Since each window is formed by six bridges and each bridge contributes to the formation of two windows, each hexagonal ring will carry a charge of -1. On the other hand if we assume that the counter-ions are located at the centre of holes formed by four hexagonal windows (each contributing to two holes) the same calculation gives a charge of -2 for the hole. It follows that singly-charged cations are easily accommodated at the centre of the windows [16(*c*)], as in typical pyrochlores. This leaves room at the centre of the hole [8(*b*)] for the sorbed water. The compositions $NaSbO_3.0.5H_2O$ and $H_3O.SbO_3.0.5H_2O$ are exactly consistent with this distribution of counter-ions on the assumption that H_3O^+ plays the role of a counter-ion. When the skeleton contains doubly charged counter-ions the most suitable locations for these ions are the centres of the holes (as in $RbNbTeO_6$,[90] in which Rb occupies a hole with a charge of -1), or alternatively the M^{2+} ions are randomly distributed at the centres of hexagonal windows, filling alternate windows as in normal pyrochlore structures.

The assumption that H_3O^+ can be treated as a counter-ion in CAA is confirmed by i.r. spectral results[92].

In addition to the strong ν_{Sb-O} absorption band (770 cm^{-1}) the CAA samples give two absorption bands in the region of the OH_n bending vibrations: a wide band with a maximum at 1640 cm^{-1}, assigned to bending vibrations of adsorbed water, and a stronger, narrow band at 1705 cm^{-1}, assigned to H_3O bending vibrations[93]. Deuteration of the CAA shifts both these bands towards lower frequencies (the isotopic shift of the 1705 cm^{-1} band is $\delta(OH)/\delta(OD) = 1.34$). The absorption band at 1705 cm^{-1} is absent in the Na^+ form of CAA, but it reappears when this is converted into the H^+ form. From these results, and from the absence of the absorption bands at 1030–1300 cm^{-1} (assigned to δ_{Sb-OH} vibrations[20,21]), we may conclude that the SbOH group does not exist in CAA and the counter-ions are H_3O^+.[92] Data on the thermal decomposition of antimonic acid are consistent with this conclusion[13].

However, other workers[58,59] failed to observe an absorption band at 1704 cm^{-1} in the i.r. spectra of CAA, and at the same time they found two absorption bands at 1030–1300 cm^{-1} which they assigned to vibrations of the OH group in bridging



Sb–O–Sb groups (1290 cm^{-1}) and to SbOH end-groups (1140 cm^{-1}). Conversion into the Ag^+ form suppresses the 1290 cm^{-1} band, and treatment of the initial CAA sample with hydrofluoric acid suppresses the 1140 cm^{-1} band. From these results the authors conclude[58,59] that the protons of the SbOH bridging groups are responsible for the exchange, and that the SbOH end-groups do not take part in exchange.

Lukina and coworkers[94,95] concluded, from an analysis of i.r. spectra, that both SbOH and H_3O^+ are present in CAA. We must assume that the CAA samples used in that work had an unusual degree of condensation and crystal size, and hence an atypical ratio of surface $[Sb(OH)_{6-x}O_{x/2}]^-$ to bulk $[SbO_{6/2}]^-$ complex groups: this is suggested by the observed i.r. spectra.

The fact that the maximum exchange capacity of AAA and CAA is equal to the Sb content (whatever the degree of condensation or the crystallinity[42]) provides additional evidence that the surface and the bulk complex groups carry a charge of -1, and that the SbOH end-groups do not take part in the exchange: the traditional dissociation of these groups, often invoked to explain the ion-exchange properties of hydroxides, does not apply in this case[42,96].

4. Ion-exchange Properties of Antimonic Acid

The ion-exchange properties of CAA have been fairly fully characterised. Even in acid solutions the exchange capacity for Ag^+, Na^+, Sr^{2+}, Pb^{2+}, and Cd^{2+} ions is already quite high. Thus, the absorption (in mg-equiv g^{-1}) from 0.01 and 0.1 *N* solutions under static conditions (with a 1 : 100 ratio of weight of exchanger to volume of solution) is found to be[13,97]

$$\left.\begin{array}{c} Ag^+ > Na^+ > K^+ > Li^+ > Cs^+ \\ 5.06 \quad 2.22 \quad 1.28 \quad 0.26 \quad 0.04 \\ Pb^{2+} > Cd^{2+} > Sr^{2+} \geqslant Ba^{2+} > Ca^{2+} > Mg^{2+} \geqslant Ni^{2+} \\ 5.10 \quad 3.72 \quad 2.52 \quad 2.42 \quad 1.14 \quad 0.16 \quad 0.10 \end{array}\right\} \text{0.1 } N \text{ solutions},$$

$$\left.\begin{array}{c} Cd^{2+} > Ba^{2+} > Sr^{2+} > Ca^{2+} > Mg^{2+} > Ni^{2+} \\ 3.37 \quad 2.76 \quad 2.05 \quad 0.97 \quad 0.09 \quad 0.07 \end{array}\right\} \text{0.01 } N \text{ solutions}.$$

The absorption of Ag^+ and Pb^{2+} ions under these conditions reaches its maximum value, equal to the exchange capacity (and therefore to the Sb content) of the material.

Since the distribution coefficient (K_d) for the sorption of many cations from dilute solutions can be as high as 10^4, detailed studies of the dependence of K_d on the concentration and nature of the background electrolyte have been carried out (HNO_3, HCl, $HClO_4$, CH_3COOH, NH_4OH, HF, etc.)[10,11,97–99,61].

Exchange isotherms and titration curves give complementary information and offer the fullest description of the ion-exchange properties of CAA. Titration curves for CAA have been obtained with the following solutions: NaOH[6,7,9,13]; KOH, LiOH, $(CH_3)_4NOH$, and CsOH[82]; $Ba(OH)_2$, $Ca(OH)_2$, and $(CH_3)_4NOH$ in the presence of $MgCl_2$ and $NiCl_2$.[83] Isotherms for the exchange of H^+ ions by Na^+,[7,97,100] K^+,[97,100] Li^+,[10,97] Rb^+,[100] Cs^+,[101] Ag^+,[77,97,100] Mg^{2+}, Ni^{2+}, Cd^{2+}, Ca^{2+},[83,97] Sr^{2+},[10,50,101] Ba^{2+},[10,83,97] and La^{3+}[10] have been reported. Isotherms for exchange on CAA in H^+–M^{z+} systems (where $M^{z+} = Ag^+$, Na^+, Li^+, K^+, Mg^{2+}, Ca^{2+}, Sr^{2+}, Ba^{2+}, Cd^{2+}, and Ni^{2+})[97] are compared in Fig.3 for a total concentration of

exchanging ions of 0.1 *N*. Almost all the isotherms are *S*-shaped, intersecting the diagonal of the square at different values of $\gamma_{M^{z+}}$ (the equivalent fraction in the solid phase). Various workers have pointed out that isotherms measured at different total concentrations of exchanging counter-ions are identical[10,101].

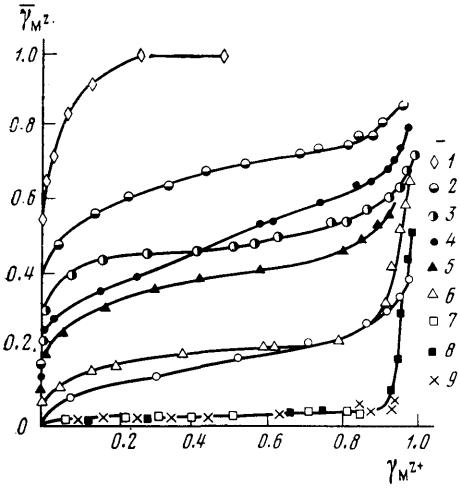


Figure 3. Isotherms for the H^+–M^{z+} exchange on CAA[83,97]: *1*) Ag^+, *2*) Cd^{2+}, *3*) Ba^{2+}, *4*) Sr^{2+}, *5*) Na^+, *6*) K^+, *7*) Ni^{2+}, *8*) Li^+, *9*) Mg^{2+}.

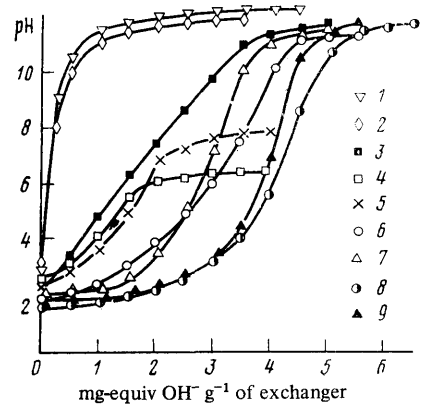


Figure 4. Titration curves of CAA for different solutions[13,82,97]: *1*) CsOH, *2*) $(CH_3)_4NOH$, *3*) LiOH, *4*) $(CH_3)_4NOH$ with Ni^{2+}, *5*) $(CH_3)_4NOH$ with Mg^{2+}, *6*) $(CH_3)_4NOH$ with Ca^{2+}, *7*) KOH, *8*) $Ba(OH)_2$, *9*) NaOH.

Fig.4 shows the titration curves of crystalline antimonic acid with 0.1 *N* solutions of LiOH, NaOH, KOH, CsOH, $Ba(OH)_2$, and $(CH_3)_4NOH$ in the presence of a 1 *N* background of the chloride of the corresponding metal. Since the $(CH_3)_4N^+$ cation is not sorbed (the titration curve for the $(CH_3)_4NOH$ solution being almost identical to the blank titration) we can use this solution for titrations in the presence of 1 *N* $CaCl_2$, $MgCl_2$, and $NiCl_2$, and characterise the sorption of the Ca^{2+}, Mg^{2+}, and Ni^{2+} ions at high pH values (up to the precipitation of the corresponding hydroxide). The titration curves which characterise the ion exchange in the region $2 < pH < 12$ (the non-buffering range of the alkali chosen for the titration and of the acid produced by the exchange) also differ according to the nature of the cation being exchanged. Thus, the titration curve of LiOH suggests that CAA is a polyfunctional cation exchanger, that of NaOH is consistent with a monofunctional cation exchanger, and the *S*-shaped isotherm for the H^+–Na^+ exchange again indicates polyfunctionality of the exchanger.

At first sight polyfunctionality appears inconsistent with the uniform structure of the CAA and with the location of all the counter-ions in identical positions. However, the high charge density of the polymer skeleton¶ and the interconnection between neighbouring holes and six-membered rings through the antimony–oxygen octahedra (see preceding section, p.937, left column) ensure that the replacement of one counter-ion by any other ion affects the bond energy of the other counter-ions. The number of these energetically non-equivalent exchange steps can be estimated by examining the CAA structure (Fig.2). Since each $[SbO_{6/2}]^-$ octahedron of the polymer skeleton contributes to the formation of six windows, at the centre of which the counter-ions are located, the replacement of all the singly charged cations of one kind by singly charged cations of another kind can occur in six energetically non-equivalent stages (each stage having a capacity of $\Gamma^0/6$). If the singly charged cations are replaced by doubly charged cations the number of these non-equivalent stages is three (each corresponding to a capacity of $\Gamma^0/3$). Hence the exchange isotherms (and titration curves) should be interpreted as sums of isotherms (or titration curves) whose shape is determined by the partial exchange constants. The number of these partial exchange constants varies by discrete amounts and depends on the charge of the exchanging cations.

An important aspect of the practical use of CAA is the reversibility and equivalence of the exchange of ions on this material. Contradictory views are held on this problem. Thus, some workers[6,82,83,100,102] find that the exchange is reversible, and that equivalence is preserved. On the other hand complete elution of selectively sorbed ions (Na^+, Sr^{2+}) is difficult or impossible[54,76,103,104]. This problem can be solved by correctly choosing the eluent[98,102]. Thus, Na^+ ions can be eluted by 2 *M* NH_4OH (but not by 10 *N* HNO_3);[98] 1 *M* HNO_3 is recommended for the desorption of Mg^{2+} and Ba^{2+}, and 3 *M* HNO_3 for the desorption of Sr^{2+} and Ca^{2+}.[102] Ag^+ and Pb^{2+} ions are recommended as universal displacers[10], though it is difficult subsequently to remove them from the exchanger (for example, Ag^+ ions can only be removed by converting them into an ammine complex[81]).

No less important is the dependence of the selectivity of CAA and AAA on the preparative conditions and on the degree of crystallinity of the samples[13,42,43,54,60,61,105]. An increase in selectivity and a decrease in the absorption of salts from solutions is observed as the crystallinity is increased from AAA to CAA[43,60,105]. The titration curves of AAA and of its crystallisation products (Fig.5) show a gradual shift from the curve for the monomeric $H[Sb(OH)_6]$ to that for the fully crystallised acid. The maximum exchange capacity (achieved in alkaline solutions) is the same for all the samples, and

¶ In contrast to the aluminosilicates, in which the charge of the anion skeleton is carried by $[AlO_{4/2}]^-$ groups alternating with neutral $[SiO_{4/2}]^0$ groups, in CAA the lattice is composed entirely of charged $[SbO_{6/2}]^-$.

equal to the amount of antimony present, but at lower pH values the capacity for Na^+ of the crystalline samples may be lower than that of the amorphous samples.

Systematic studies of the effect of crystal size on the ion-exchange properties of CAA have not yet been reported. It is stated[68] that the size of the primary crystalline blocks in CAA can vary over wide limits (from 150 to 3200 Å) depending on the preparative conditions. We can expect the sorption properties of small CAA crystals to be more similar to those of the monomeric acid $H[Sb(OH)_6]$ than to those of fully developed crystals. Neglect of the surface groups $[Sb(OH)_{6-x}O_{x/2}]^-$ is justified only when the crystal size is not less than 5×10^2 Å (the size of a cubic crystal containing five elementary cells of the CAA structure along each cube edge).

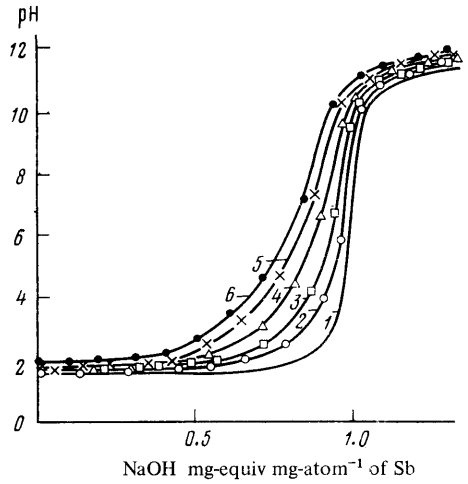


Figure 5. Titration curves of different samples with NaOH solutions: *1*) $H[Sb(OH)_6]$,[18] *2*) freshly prepared AAA and its crystallisation products, *3*) after 5 months, *4*) after 10 months, *5*) after 1.5 year, *6*) after 2 years[42].

Heat treatment of the H^+ form of CAA above 200 °C causes reduction of the Sb(V): as a result, some of the counter-ion sites are occupied by Sb(III), and the exchange capacity decreases. The thermal stability of AAA is lower than that of CAA,[13,105] and therefore samples which have been heat treated (for example, those dried at 270 °C) cannot be said to be identical to samples which have not been heat treated in comparisons of the ion-exchange properties and of the selectivity of these materials. The observed differences in properties suggests useful methods of thermally modifying CAA as an ion exchanger.

III. SYNTHESIS AND PROPERTIES OF MIXED CATION EXCHANGERS DERIVED FROM ANTIMONIC ACID

Ion-exchange properties are found not only in antimonic acid but also in various insoluble oxygen compounds of antimony(V) whose structure includes one or two multivalent elements (P, Si, Zr, Ti, etc.). There is no unique terminology for these materials, but they are often called antimonates. By analogy with the salts of heteropolyacids we shall call them phosphoantimonate, silicoantimonate, titanoantimonate (etc.) cation exchangers, stressing the ability of both constituents (Sb(V) on the one hand and P, Si, Zr, Ti, etc. on the other hand) to form a polymeric skeleton. The role of the second element in the structure of the antimonic acid is not always clear, but there can be no doubt of its influence on the selectivity of the material. At the time of writing, 17 types of these mixed cation exchangers are known.

1. Phosphoantimonate Cation Exchanger (PSb, Phosphoantimonic Acid, Antimony Phosphate)

This cation exchanger was prepared by Abe and Ito by mixing solutions of antimony pentachloride (or pentafluoride) and of phosphoric acid and heating the mixture for 16 h at 80 °C.[106,107] The $\overline{Sb}/\overline{P}$ atomic ratio in the solid phase decreases sharply as the concentration of H_3PO_4 is increased (which also lowers the rate of formation of the precipitate). At H_3PO_4 concentrations of 0.3–0.4 *M* the $\overline{Sb}/\overline{P}$ ratio is approximately 2, and a glassy product is obtained[108]. Glassy materials with different $\overline{Sb}/\overline{P}$ ratios can be prepared also by adding NH_4OH to a mixed solution of $SbCl_5$ and H_3PO_4 in hydrochloric acid[109–112]. Changes in the Sb/P ratio in solution from 0.5 to 8 give samples with $\overline{Sb}/\overline{P}$ ratios between 1.31 and 9.3.[112] Increasing the amount of phosphorus in solution during the synthesis does not yield an even greater concentration of phosphorus in the solid phase. Instead of NH_4OH, we can use NaOH, NH_4Cl, or HNO_3 as precipitants[113,114]. Phosphoantimonate cation exchangers have been prepared with reagents of various concentrations: 8 *M* $SbCl_5$,[113,114] 1 *M* and 10 *M* H_3PO_4,[109] 1 *M* and 0.01 *M* H_3PO_4,[114] and 0.25–4.0 *M* H_3PO_4.[113]

A granular product is obtained either by drying the precipitate in a thermostat[106–113] or by freezing it (at −10 °C[114] or at −6 °C[115]). When the dried material is mixed with water the larger granules disintegrate into smaller granules[108,109], but if the sample is first stored for 1 week in air at room temperature and then in a desiccator it can be mixed with water without change in granule size[108].

A series of papers by Lefebvre and coworkers[116–121] describes a detailed study of the products of the interaction of $SbCl_5$ and H_3PO_4, and of the properties of the resulting compounds.

The phosphoantimonate cation exchanger consists of transparent, heavy (density 2.66–3.22 g cm^{-3} for samples with an atomic ratio $\overline{Sb}/\overline{P} = 1.3–9.3$[112]), glassy granules[108,109] which can be amorphous to X-rays[111,112] or show a crystalline structure[115] (for $\overline{Sb}/\overline{P} \geq 2$).

The ion-exchange properties of phosphoantimonate cation exchangers have been characterised by potentiometric titration curves[106,109–115,122,124], by measurements of the absorption of cations bearing different charges[97,111,112], by isotherms for the exchange of hydrogen ions by alkali metal[97,112,125,126], alkaline-earth[97,112,125], and cadmium ions[127], and by the distribution coefficients of alkali metal ions[114,128] and of barium and lanthanum[97]. Studies of the rate of ion-exchange processes are described in Refs. 112, 114, and 122.

The high chemical stability of PSb cation exchangers in solutions of acids and salts has been stressed[97,108]. Partial dissolution of the samples occurs in hot water[108] and at pH > 8;[97] it is pointed out[108] that the materials are more stable in NH_4OH solutions than in NaOH solutions. The chemical stability depends markedly on the drying temperature of the sample: samples dried at 60 °C are more soluble than those dried at 100 °C.[108]

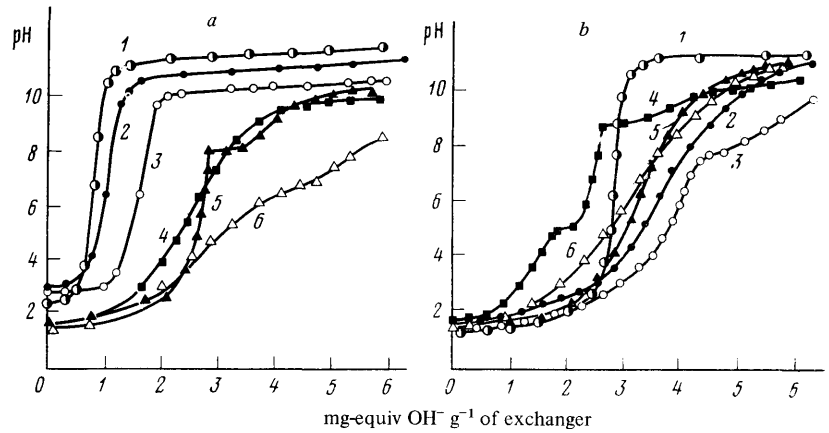


Figure 6. Titration curves of PSb for different solutions: *1*) $Ba(OH)_2$, *2*) $Sr(OH)_2$, *3*) $Ca(OH)_2$, *4*) LiOH, *5*) NaOH, *6*) KOH; (*a*) sample of composition $\overline{Sb}/\overline{P} = 1.35$, (*b*) sample of composition $\overline{Sb}/\overline{P} = 6.8$.

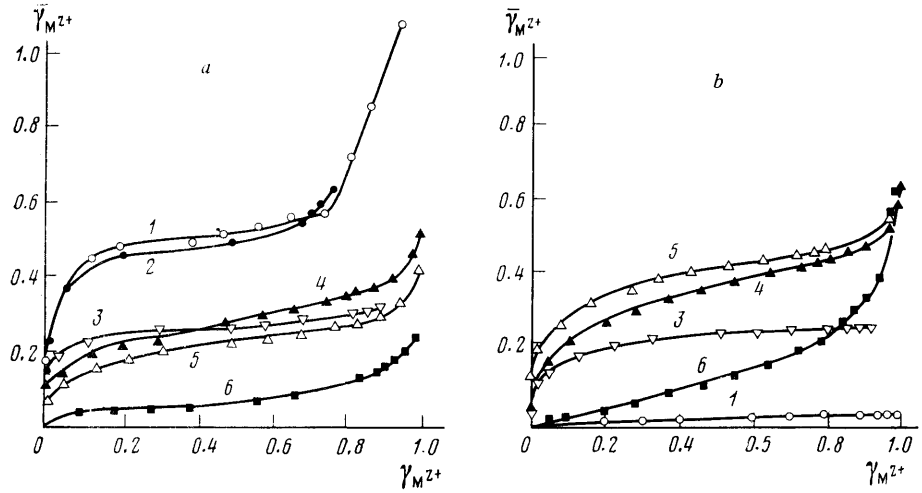


Figure 7. Isotherms for the H^+–M^{z+} exchange on PSb:[97,125] (*a*) sample with $\overline{Sb}/\overline{P} = 6.73$, (*b*) sample with $\overline{Sb}/\overline{P} = 1.64$; *1*) Ca^{2+}, *2*) Sr^{2+}, *3*) Cs^+, *4*) Na^+, *5*) K^+, *6*) Li^+.

Drying the gels at 100 and 200 °C shortens the time needed to prepare these materials without significantly affecting their ion-exchange properties[122]. Increasing the drying temperature of the granules lowers the ion exchange capacity, by a negligible amount for temperatures up to 140 °C[108] but more markedly in the range 100–260 °C (depending on the $\overline{Sb}/\overline{P}$ ratio in the sample), with complete loss of exchange capacity at 800 °C.[122] Hence there must be some doubt about the claim[123] that PSb samples with good exchange capacity can be prepared by drying the gel at 300–700 °C.

The most detailed study of the ion-exchange properties of PSb samples as a function of the $\overline{Sb}/\overline{P}$ ratio is described in Refs.112, 124, and 125. The titration curves of PSb samples with different alkalis and a constant 1 *N* salt background are shown in Fig.6 (for LiOH, NaOH, KOH, $Ca(OH)_2$, $Ba(OH)_2$, and $Sr(OH)_2$). We see that the shape of the curve and its distance from the pH axis depend not only on the nature of the exchanging cation (as in the case of CAA) but also on the $\overline{Sb}/\overline{P}$ ratio of the sample.[112,124] For each sample we can distinguish a number of pH regions of different selectivity. As a result, statements of the functionality of PSb cation exchangers (monofunctional or multifunctional) may be contradictory[106,115]. The type and shape of the exchange isotherms (Fig.7) also depend on the nature of the cation and on the $\overline{Sb}/\overline{P}$ ratio. The titration curves and the exchange isotherms (as well as the absorptions of different ions from 0.1 *N* solutions of their chlorides or of $AgNO_3$) can be used to demonstrate the effect of the phosphorus content on the selectivity of PSb.[97,111,112] Samples in which the P content is relatively small ($\overline{Sb}/\overline{P} = 9.3$) are like CAA in absorbing Ca^{2+} and Sr^{2+} more selectively than Mg^{2+}, Ni^{2+}, Co^{2+}, and triply charged or singly charged ions. High phosphorus contents ($\overline{Sb}/\overline{P} = 1.3$) favour selectivity towards singly charged cations, and the absorption of doubly or triply charged cations becomes negligible[111,112].

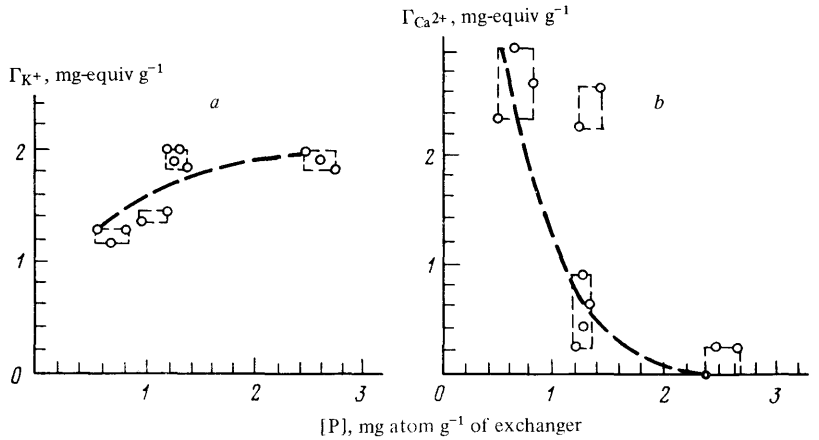


Figure 8. Plots of the absorption Γ_{K^+} (*a*) and $\Gamma_{Ca^{2+}}$ (*b*) against the phosphorus content of PSb samples[112]. Sorption from 0.1 *N* solutions of the chlorides. Data for PSb samples synthesised from nominally identical solutions are indicated by the rectangles.

A closer study of the dependence of the absorption (ΓM^{z+}) on the phosphorus content (Fig.8) shows that this is the predominant (but not the only) effect on the selectivity of the material. Other factors tending to influence ΓM^{z+} include the number of functional groups in the sample (which is equal to the concentration of antimony), and their accessibility to the counter-ions. This structural characteristic of the PSb samples can be evaluated qualitatively from differential thermal analysis results[112]. This method can be used to calculate the amount of free water and of structural water in the PSb sample and to highlight differences between samples of similar composition ($\overline{Sb}/\overline{P}$) prepared under identical conditions[112]. The combined effect of all three factors determines the position of the sample within the rectangles arbitrarily drawn in Fig.8 as well as the relative positions of the rectangles.

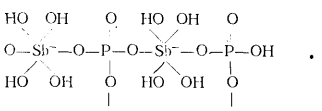
The highest affinity of the phosphoantimonate cation exchangers is for silver ions[97,108,110–112,118,126]. The selectivity of the PSb increases as the loading of the exchanger phase with metal ions decreases[112,125] and as the concentration of the solution decreases[97,112,114]. Several workers report high values of the distribution coefficients of alkali metal ions[114,128] and of Ba[97].

A study[108] of the reversibility of ion exchange in a PSb sample ($\overline{Sb}/\overline{P} = 2$) showed that both sorption and displacement go to completion in the H^+–NH_4^+, K^+–NH_4^+, and Ag^+–NH_4^+ systems. The hydrogen ions are quantitatively replaced by potassium ions; the sorbed K^+ ions are not washed out by 3 *N* solutions of HCl or HNO_3, but they are easily eluted by 1 *M* NH_4NO_3.[108]

Oxidation–reduction processes can take place on PSb cation exchangers. Treatment of PSb samples with a 0.2 *N* solution of $SnCl_2$ in 1 *N* HCl produces sorption of Sn^{2+}, accompanied by conversion of some of the Sb(V) in the solid phase into Sb(III) with formation of Sn(IV).[129] A Mössbauer study[129] of the Sn forms revealed the presence of two types of Sn(II), differing in the ionicity of their bond with the ionogenic group (52% and 26% respectively). The appearance of Sb(III) in the cation exchanger causes a decrease in the total exchange capacity for Na^+ ions and in the absorption of doubly and triply charged cations[129].

Abe and Ito believe[106] that antimony-containing, strongly acidic groups analogous to $H[Sb(OH)_6]$ are responsible for the ion-exchange properties of PSb.

Studies of phosphoantimonate cation exchangers by ion exchange, differential analysis, and i.r. spectroscopy[111,112,130] have led to the following structure, in which the polymer chains consist of interconnected antimony–oxygen octahedra (the building blocks of CAA) and phosphorus–oxygen tetrahedra:



The hydrogen ions which compensate the charge on the $[SbO_{x/2}(OH)_{6-x}]^-$ octahedra and the hydrogen ions of the phosphate groups are involved in the ion exchange process[112,130]. The dependence of the selectivity of the phosphoantimonate cation exchangers on the phosphorus content stems from the decrease in the density of fixed charges produced by the phosphorus, which enters the structure as the non-exchanging $\equiv PO_4$ group[111,112].

More recently, Lefebvre and coworkers[119,120] proposed a PSb structure in which the basic elements are groups of three $[SbO_{6/2}]^-$ octahedra associated with one $\equiv PO_4$ (or $=HPO_4$) tetrahedron and which is consistent with all the above considerations.

In contrast, Tikavyi and Bratennikova[115] suggest that the phosphorus in the PSb structure is present as HPO_4^{2-} and $H_2PO_4^-$ groups, but Astaf'eva and coworkers[113] support the $=HPO_4$ structure.

2. Silicoantimonate Cation Exchanger (SiSb, Silicoantimonic Acid, Antimonosilicic Acid, Antimonosilicic Cation Exchanger)

The SiSb cation exchanger is prepared by joint polycondensation of the hydrolysis products of $SbCl_5$ and Na_2SiO_3[62,131–133]. The resulting gel is allowed to remain in the mother liquor for 1–2 days before being washed and dried. In contrast to PSb, in SiSb the $\overline{Sb}/\overline{Si}$ ratio can be varied over wide limits (0.29–17.67).[133] The diffraction patterns of SiSb are similar to those of CAA, but the peaks are more diffuse in the case of SiSb. Raising the temperature (to 150 °C) and increasing the drying time (to 200 h) has no effect on

the degree of crystallinity. The similarity between the diffraction patterns of SiSb and CAA suggests that the structure of SiSb is determined by the antimony[62,133].

Unlike the normal CAA material, SiSb does not form a powder but consists of mechanically strong white granules of irregular shape. Its chemical stability is very high, as shown by the absence of any indication of dissolution during the measurement of titration curves or of exchange isotherms. SiSb is decomposed only by concentrated HCl at the boiling point.

Samples of SiSb can be characterised by the absorption from 0.1 *N* or 0.01 *N* solutions of various salts[97,134], by their exchange isotherms (H^+–Li^+, Na^+, K^+, Ba^{2+}, Sr^{2+}, Cd^{2+}),[97, 135,136] and by titration curves obtained with different alkalis (KOH, LiOH, NaOH, $Ba(OH)_2$)[135]: the equivalence and the reversibility of the exchange have been demonstrated. Over a wide range of pH values and of solution compositions the exchange capacity (as in CAA) is correlated only with the antimony content of the samples. Increasing the pH raises the exchange capacity to its maximum value, corresponding to the amount of Sb in the sample. At pH 9–10 the SiSb titration curves show a second horizontal section, corresponding to weakly acid groups[135,136].

The exchange isotherms for samples with low concentrations of silicon ($\overline{Sb}/\overline{Si} = 13.8$) are almost indistinguishable from those for CAA[97,135,136]. On the other hand in samples with $\overline{Sb}/\overline{Si} = 2.34$ and 0.51 (Fig.9*a* and 9*b*) the isotherms are shifted within the $\bar{\gamma}_M = f(\gamma_M)$ square. The selectivity towards Ca^{2+}, Sr^{2+}, and Ba^{2+} is improved, especially at low concentrations, and there is a small increase in the absorption of Li^+, Mg^{2+}, and Ni^{2+} ions (whose absorption is very slight on CAA), but the shape of the H^+–Cd^{2+} exchange isotherms is almost unaffected.

By comparing the diffraction patterns, exchange isotherms, and titration curves of CAA and SiSb we conclude that the silicon may be present as $[SiO_{4/2}]^0$ or $[SiO_{6/2}]^{2-}$ groups. In the former case the silicon should not contribute to the exchange capacity, but in the second case the exchange capacity of the sample should be greater than the antimony content. By using Pauling's electrostatic valency rule we can show[134–136] that in the first case the bond between the proton and the oxygen bridges in the SiSb structure should be weaker (i.e. the acidic properties should be enhanced), and in the second case the bond should be stronger (the strength of the residual O^{2-} bond in the $-\overset{\backslash/}{\underset{/\backslash}{Sb}}-O-\overset{|}{\underset{|}{Si}}-$ and $-\overset{\backslash/}{\underset{/\backslash}{Sb}}-O-\underset{/\backslash}{\overset{\backslash/}{Si}}-$ groups should be 1/6 and 1/2 respectively, as compared with 1/3 for the $-\underset{/\backslash}{\overset{\backslash/}{Sb}}-O-\underset{/\backslash}{\overset{\backslash/}{Sb}}-$ group in CAA).

Since the ion-exchange properties of SiSb also indicate a slight weakening of the bond between the polymer skeleton and the H^+ counter-ion, and a small increase in capacity in the alkaline region, it has been suggested[133,135] that the $[SiO_{4/2}]^0$ and $[SiO_{6/2}]^{2-}$ groups can exist together in SiSb.

Further studies of SiSb cation exchangers are reported in Refs.99, 137, and 138. Super-equivalent sorption on SiSb was observed in a study of the sorption of Na^+ (using radioactive tracers) in the pH range 0–1.5, and of the sorption of Na^+, Sr^{2+}, Cd^{2+}, and Hg^{2+} from nitric acid solutions at pH 3.5.[99,137,138]. There is a report of irreversible sorption of the Sr^{2+} ion[99], which cannot be eluted from SiSb either by 7–10 *N* HNO_3 or by concentrated salt solutions. The protonogenic groups in SiSb are thought to be[138] "the hydroxyl

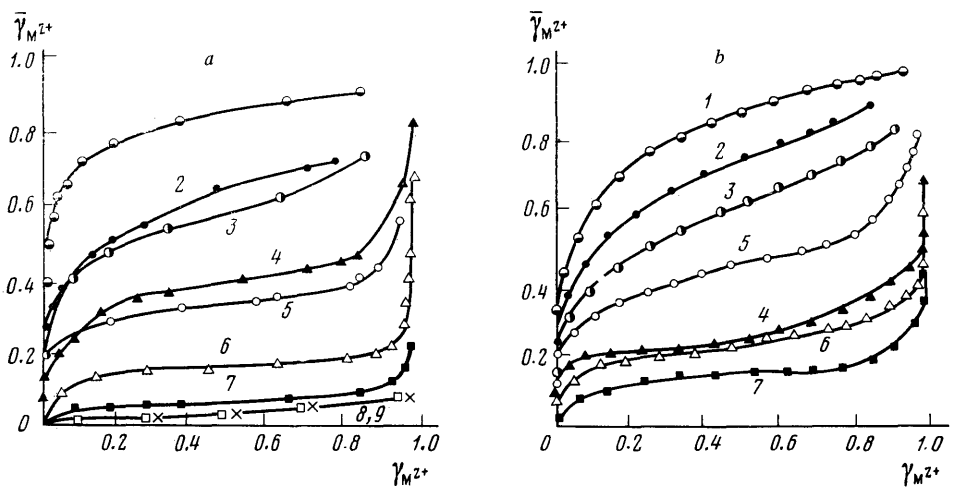


Figure 9. Isotherms for the H^+–M^{z+} exchange on SiSb[97,135,136]: (*a*) sample with $\overline{Sb}/\overline{Si} = 2.43$, (*b*) sample with $\overline{Sb}/\overline{Si} = 0.51$; *1*) Cd^{2+}, *2*) Sr^{2+}, *3*) Ba^{2+}, *4*) Na^+, *5*) Ca^{2+}, *6*) K^+, *7*) Li^+, *8*) Ni^{2+}, *9*) Mg^{2+}.

groups in –SbOH and –SiOH, and also H_2O molecules attached by coordination bonds to neighbouring SbO_6 octahedra".

Since many of the published papers[99,137,138] fail to state exactly the conditions under which the samples were prepared, and to describe the methods of analysis and the methods of measuring exchangeable and non-exchangeable sorption, it is not easy to discuss the discrepancies between their results and ours.

3. Silicophosphoantimonates (SiPSb, Phosphoantimonosilicate (PASC) Cation Exchangers)

The samples are prepared by mixing solutions of $SbCl_5$, Na_2SiO_3, and H_3PO_4; the precipitate is washed with water to pH 4–6 or with acetone, dried in a thermostat at 60 °C, converted into the hydrogen form by treating it with 1 *N* HCl, washed with water until free from Cl^- ions, and air-dried[139–143]. Approximately 50 samples were prepared in our laboratory[143], and used to investigate the relationship between the composition of the solid phase and that of the solutions used for the synthesis. In each sample the combined phosphorus and silicon contents were found to be strictly determined, and directly proportional to the concentration of antimony in the sample[143] (Fig. 10*a*). The concentrations of silicon and phosphorus vary in opposite senses (Fig. 10*b*).

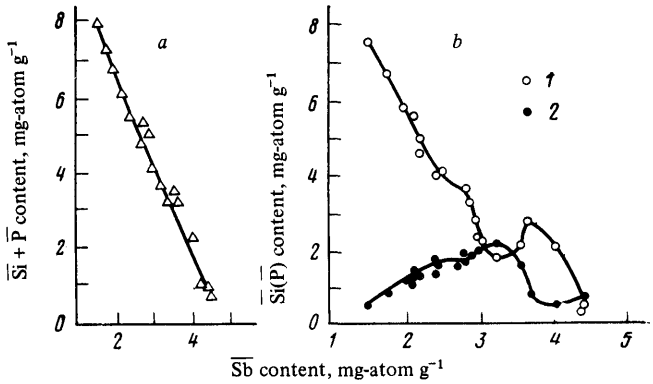


Figure 10. Variation of the $\overline{Si}(\overline{P})$ and $(\overline{Si} + \overline{P})$ content with amount of $\overline{Sb}$ in SiPSb samples[143]: (*a*) $\overline{Si} + \overline{P}$; (*b*), *1*) $\overline{Si}$, *2*) $\overline{P}$.

The compositions of the SiPSb samples and those of the samples in the binary systems (SiSb and PSb) were plotted in a composition triangle[143] (see Fig. 11). We can see that the concentration of silicon in the SiPSb samples can vary over wide limits, but the phosphorus concentration can vary only over a narrow range, and both these ranges apply to the binary systems as well. The SiPSb samples consist of mechanically strong granules of irregular shape and density between 2.0 and 3.2 g cm^{-3} (measured pyknometrically in CCl_4 at 20 °C).[143]

The SiPSb cation exchangers are chemically very stable[143]. According to the potentiometric titration curves obtained with different alkalis, these exchangers are polyfunctional[144].

The variation of the absorption of M^{z+} (at different pH values) with composition suggests that in the acid and the neutral region the H^+–M^{z+} exchange takes place at the antimony–oxygen ionogenic groups, whereas in the alkaline region (pH ≥ 9) phosphorus-containing groups are involved (as well as the antimony–oxygen groups) in the exchange of singly-charged ions. The silicon–oxygen groups take part in the exchange of doubly charged cations[144].

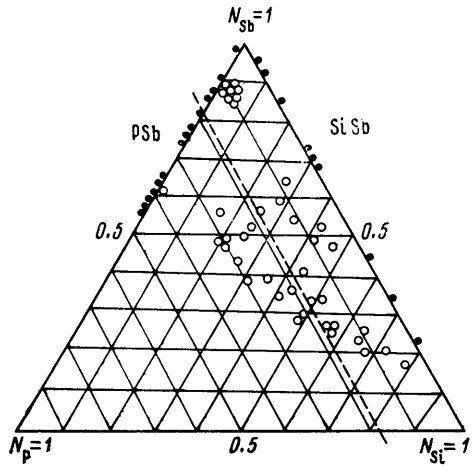


Figure 11. Composition triangle for SiPSb, SiSb, and PSb samples[143]. *N* is the atom fraction of the element in the solid phase (the ratio of the concentration in mg-atom g^{-1} of one of the components $\overline{Sb}$, $\overline{Si}$, or $\overline{P}$ to the sum of the concentrations).

Like the other types of antimony-containing cation exchanger the SiPSb samples are most selective towards Ag^+ ions, and the Γ_{Ag^+} value corresponds to the antimony content. Addition of silicon favours the sorption of doubly and triply charged cations, whereas an increase in the concentration of phosphorus has the opposite effect. Above a critical phosphorus concentration (1.5–2.0 mg-atom g^{-1}, shown in Fig. 11 as a broken line) the sorption of multiple-charged cations decreases, and below this concentration multiple-charged cations can be sorbed (but Γ_M depends on the concentration of antimony and silicon: an increase in the concentration of antimony favours the sorption of Sr^{2+} and Cd^{2+}, and an increase in the concentration of silicon favours the sorption of La^{3+}).[145,146]

The sorption of ions on SiPSb samples takes place by an ion exchange mechanism in which equivalence is preserved[145,146]. The shape of the exchange isotherms (as in the case of the related SiSb and PSb samples) depends on the composition of the material and on the nature and charge of the counter-ion[127,146] (Figs. 12*a* and 12*b*).

Non-equivalent sorption of singly charged and doubly charged cations has been observed[47,94,99,147,148] in a study of SiPSb (Sb : P = 8 : 1; 4.5 wt.% Si).

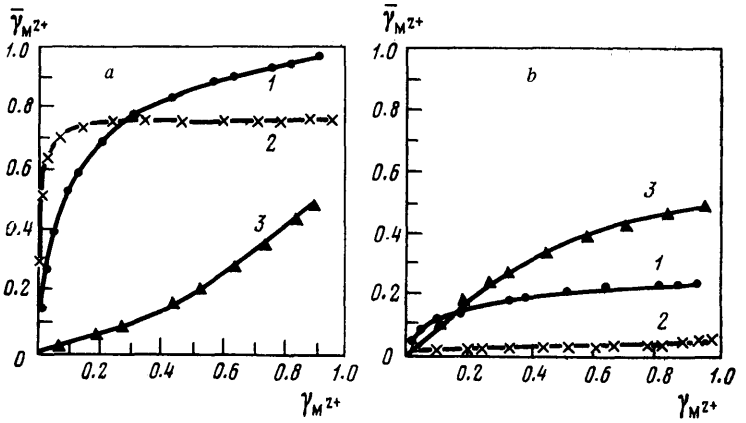


Figure 12. Isotherms for the H^+–M^{z+} exchange on SiPSb samples[127,146]: (*a*) sample with $\bar{Sb} : \bar{Si} : \bar{P} = 2.18 : 4.49 : 1.24$, (*b*) sample with $\bar{Sb} : \bar{Si} : \bar{P} = 3.52 : 2.17 : 1.71$; *1*) Sr^{2+}, *2*) La^{3+}, *3*) Na^+.

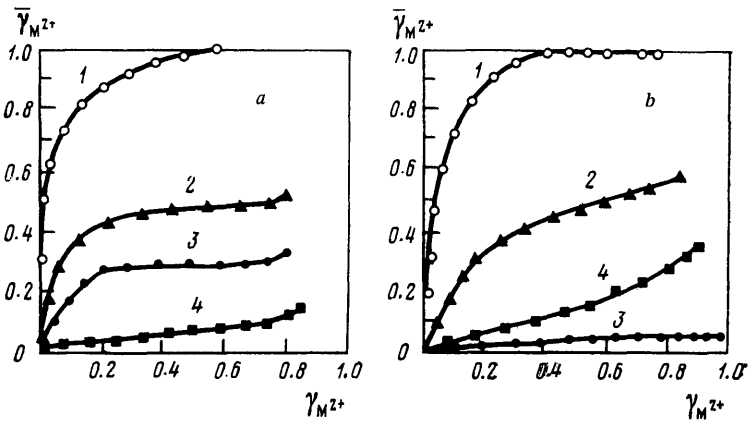


Figure 13. Isotherms for the H^+–M^{z+} exchange on TeSb[151]: (*a*) sample with $\bar{Sb}/\bar{Te} = 5.76$, (*b*) sample with $\bar{Sb}/\bar{Te} = 1.93$; *1*) Ag^+, *2*) Na^+, *3*) Sr^{2+}, *4*) Li^+.

4. Telluroantimonate Cation Exchanger (TeSb)

The exchanger was prepared by mixing solutions of 1 *M* $SbCl_5$ (in 3 *M* HCl) and 0.5 *M* H_2TeO_4.[149–151] Varying the Sb/Te ratio in solution during the synthesis allows the ratio in the solid samples to be varied in the range $\bar{Sb}/\bar{Te} = 1.93$–6.23, but the total concentration of tellurium and antimony is almost constant in all the samples (4.98–5.19 mg-atom g^{-1})[151]. The selectivity is again greatest towards Ag^+ ions, and the sorption of Ag^+ is practically equal to the concentration of antimony in the sample. As the tellurium concentration increases the absorption values for alkali metal ions (Li,Na, K) increase somewhat, but those for the alkaline earth metals (Mg, Sr, Ba) and for Cd fall off sharply, reaching zero at tellurium concentrations Te ≥ 1 mg-atom g^{-1}. Triply charged ions are not sorbed on the majority of these samples[127,150,151]. Thus the effect of tellurium on the selectivity is similar to that of phosphorus, but it can be observed at much lower concentrations[151].

Measurements of the exchange isotherms in the H^+–Ag^+, H^+–Li^+, H^+–Na^+, and H^+–Sr^{2+} systems revealed that—depending on the composition of the sample (i.e. on $\bar{Sb}/\bar{Te}$) and on the nature of the exchanging counter-ion—the sorption of M^{z+} can be predominant over the whole range of solution compositions (in the H^+–Ag^+ system), or the sorption of H^+ can be predominant (in the H^+–Li^+ system, and also in the H^+–Sr^{2+} system for the $\bar{Sb}/\bar{Te} = 1.93$ sample), or a selectivity reversal can take place, with an *S*-shaped exchange isotherm (H^+–Na^+ on both samples and H^+–Sr^{2+} on the sample with $\bar{Sb}/\bar{Te} = 5.73$, see Figs. 13*a* and 13*b*).[151]

The potentiometric titration curves obtained with 0.1 *N* solutions of NaOH and KOH showed that as the pH increases from 2 to 12 the capacity of the samples (Γ, mg-equiv M^+ g^{-1}) varies from 2.3 to 4.6 for the H^+–Na^+ exchange and from 2 to 4.5 for the H^+–K^+ exchange: $\Gamma_{K^+} < \Gamma_{Na^+}$ for all samples[151]. At high pH values (>10) the capacity for Na^+ of all samples exceeds the antimony content, the difference increasing with the tellurium content[151].

This work led to the conclusion that both the antimony and the tellurium are accommodated in the cation exchanger structure with six oxygen atoms as nearest neighbours. The tellurium replaces antimony isomorphously, and the structure is similar to that of polymeric antimonic acid. The protons which compensate the charge on the antimony–oxygen

octahedra and those of the tellurium-containing groups are both involved in the ion exchange process[150,151].

5. Zirconium Antimonate (ZrSb)

The ZrSb samples were prepared by adding an NH_4OH solution to a mixed solution of $ZrOCl_2$ and $SbCl_5$ in hydrochloric acid[152-155], or by mixing solutions of zirconium oxide chloride and of potassium pyroantimonate[156,157] or of antimonic acid prepared by ion exchange[156]. Samples with the following $\overline{Sb}/\overline{Zr}$ ratios were obtained: 2,[152] 0.53–4.1,[154] and 0.99–1.14.[157]

The most detailed studies of the preparation, structure, and of the physicochemical and ion-exchange properties of the ZrSb cation exchanger were reported by Lapitskii and Tikavyi[154,155,158-161]. The ZrSb samples consist either of white, glassy granules, suitable for operation in a column[154,157], or of friable, chalky particles[154]. The chemical stability of ZrSb was studied in several laboratories[152,154,157]. Raising the drying temperature of the samples lowers their ion-exchange capacity[153,157], and when ZrSb is heated to 300 °C its selectivity towards singly charged cations increases[155,159].

The cation exchange capacity of ZrSb increases with the antimony content[154,157,161]. Samples with $\overline{Sb}/\overline{Zr}$ ratios of 0.53 and 0.55 showed anion exchange properties: their capacity towards chlorine, determined from the potentiometric titration curves, was 0.75 and 0.95 mg-equiv g^{-1} respectively.[154]

The kinetics of the exchange of H^+ ions by Cs^+ and Rb^+ ions have been studied in detail[162] on a sample with an $\overline{Sb}/\overline{Zr}$ ratio of 1.03. The rate-determining step in the exchange of these ions was found to be diffusion in solution (in the case of 0.02 *M* and 0.05 *M* solutions) and diffusion in the grains for solution concentrations ≥ 0.1 *M*.[162] The kinetics of ion exchange on ZrSb are discussed also in Refs. 154 and 157.

The unusual alkali metal selectivity sequence ($Na^+ > Rb^+ > K^+$) of a sample with $\overline{Sb}/\overline{Zr} = 2$ was first noted by Phillips and Kraus[152]. Abe and Ito point out[156] that a more conventional selectivity sequence is obtained with samples in which the ratio is $\overline{Sb}/\overline{Zr} < 1$, whereas samples with $\overline{Sb}/\overline{Zr} > 1$ contain enough antimonic acid to display an abnormally high selectivity towards Na^+ ions. Similar explanations are given in Refs. 155 and 158. The following selectivity sequence is given[157] for a ZrSb sample with $\overline{Sb}/\overline{Zr} = 1.03$:

	Ba^{2+}	$>Ca^{2+}\geqslant$	$Mg^{2+}\simeq$	Na^+	$> K^+ >$	$NH_4^+\simeq$	Li^+
Γ, mg-equiv g^{-1}	1.85	1.24	1.21	1.20	1.09	0.74	0.73

Exchange isotherms have been measured in H^+–M^+ systems ($M^+ = Li^+$, Na^+, K^+, Rb^+, Cs^+, NH_4^+, Ag^+, Tl^+) with three ZrSb samples ($\overline{Sb}/\overline{Zr} = 0.55$, 3.05, and 4.1).[155,158] The selectivity of the cation exchanger towards these ions was found to increase as the antimony content increases and as the equivalent fraction of the ions in the exchanger decreases. The sample with the ratio $\overline{Sb}/\overline{Zr} = 4.1$ had the highest affinity for the Ag^+ and Tl^+ ions.

Contrasting views have been expressed on the structure and on the functional groups of ZrSb.[155,163] Mathews and Tandon[163] describe zirconium antimonate as the polymeric condensation product of antimony and zirconium hydroxides. On the basis of DTA and TGA data they assign to the $\overline{Sb}/\overline{Zr} = 1.03$ sample the formula $ZrO_2.0.5Sb_2O_5.5.1H_2O$. The number of water molecules shown in this formula describes the total content of water of crystallisation and water of constitution. The formula weight contains only one exchangeable proton (in the Sb–OH hydroxyl group[163]). Singly charged ions (Rb^+ and Cs^+) are sorbed by an ion exchange mechanism, unlike the doubly and triply charged ions (whose sorption is thought[157,163] to involve a more complicated mechanism).

From these results, and using the criteria for the monofunctionality of the cation exchanger discussed above, the authors conclude[162,163] that ZrSb is polyfunctional, either because it contains more than one type of functional group or because the single functional group $[Sb(OH)_6]^-$ is connected to the exchanger skeleton in different ways. However, no data on the structure of the ZrSb exchanger or on the constitution of the $[Sb(OH)_6]^-$ group are given in these papers.

Lapitskii and Tikavyi[155,160,161] treat zirconium antimonate as a polymeric compound of variable composition, consisting of $[SbO_6]^-$ antimony–oxygen octahedra attached to zirconium atoms. By comparing the i.r. spectra of antimony and zirconium hydroxides with those of the hydrogen and the sodium form of ZrSb (whose absorption bands are assigned according to Balicheva and Roi[57,58]) these workers conclude that the cation exchanger structure includes bridging hydroxyl groups



(Sb–O–Zr) whose proton can be exchanged reversibly for different counter-ions[155,161]. It is suggested[155] that, in addition to the proton from the bridging hydroxyl groups, oxonium ions H_3O^+ are also involved in ion exchange on ZrSb, but their absorption band (1710 cm^{-1} according to Yukhnevich[93]) does not appear in the spectra reported by these workers[155,160].

6. Tin Antimonate (Sn(II)Sb, Sn(IV)Sb)

An ion exchanger containing Sb(V) and Sn(II) was synthesised by Abe and Ito[164] by mixing solutions of stannous chloride and potassium pyroantimonate. Increasing the Sb/Sn(II) ratio in the solution increases the $\overline{Sb}/\overline{Sn}$(II) ratio in the samples from 0.25 to 5. All the samples are stable towards water and mineral acids, but only the samples with a high $\overline{Sb}/\overline{Sn}$ ratio are stable in alkaline solutions. The potentiometric titration curves suggest weakly acidic properties. As we have shown[129], reduction of Sb(V) to Sb(III) with formation of Sn(IV) can be expected in the Sn(II)–Sb(V) system.

Several papers on the preparation and ion-exchange properties of tin(IV) antimonate have been published[156,165,166,167]. The Sn(IV)Sb samples were prepared by mixing $SnCl_4$ solutions with solutions of $SbCl_5$[165] or of potassium pyroantimonate[166], or of antimonic acid[166]. The samples obtained by precipitation with antimonic acid are found to have a higher exchange capacity and greater mechanical strength than those prepared by precipitation with potassium pyroantimonate[166].

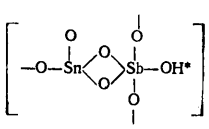
The exchanger is stable in water and in mineral acids (less so in hydrochloric than in nitric and in sulphuric acid), and its stability in these media is higher than that of TiSb.[165] When these samples are heated their capacity decreases: by 21.6% at 100 °C and by 50% at 500 °C.[165] Studies of the chemical and thermal stability of these materials are reported also in Ref. 166.

The capacity of an Sn(IV)Sb sample with $\overline{Sb}/\overline{Sn}$(IV) = 5.10 towards NH_4, alkali metal, and alkaline earth metal ions decreases in the sequence[166]

$NH_4^+ >$	$Ba^{2+} >$	$Na^+ \geqslant$	$Ca^{2+} >$	$Mg^{2+} >$	$K^+ >$	$Li^+ >$	$Rb^+ >$	Cs^+	
1.94	1.76	1.60	1.55	1.18	1.09	0.88	0.72	0.56	

Measurements of the distribution coefficient have shown that this exchanger has a high affinity for the Hg^{2+}, Pb^{2+}, and Ag^+ ions[166]; the cations Zr^{4+}, Hf^{4+}, Th^{4+}, La^{3+}, Ce^{3+}, Y^{3+}, Sm^{3+}, Nd^{3+}, and Pr^{3+} are fully sorbed at pH 0–6.[165]

Qureshi and coworkers[165] treat Sn(IV) antimonate as an individual compound for which they propose the formula



The hydrogen ion of the Sb–OH group, indicated by an asterisk, takes part in ion exchange.

On the other hand, Mathew and Tandon[166] consider their cation exchanger as a mixture of oxides in which Sb–OH groups only can take part in exchange. They point out that only Rb^+ and Cs^+ are sorbed by an ion exchange mechanism: other ions (Tl^+, Ca^{2+}, Zn^{2+}, Tl^{3+}) are sorbed by a different mechanism[166].

7. Titanoantimonate Cation Exchanger (TiSb, Titanium Antimonate)

This exchanger is prepared by adding a solution of NH_4OH to a solution of $TiCl_4$ and $SbCl_5$ in hydrochloric acid[168–170], or by mixing solutions of titanium tetrachloride and of potassium pyroantimonate (or of hexahydroxoantimonic acid).[171] Samples with different Sb/Ti ratios have been obtained (0.3–3.6,[168,169] 1.0–1.10,[171] and 0.16–4.7[170]), some of which showed weak crystallinity while others were amorphous to X-rays.

The material consists of mechanically strong, semi-transparent granules suitable for packing in columns[168–171]; however, the TiSb samples obtained from solutions of potassium pyroantimonate are less suitable for column operation and have a lower capacity than the samples prepared from antimonic acid solutions[171].

The TiSb cation exchanger is chemically stable in solutions of mineral acids and alkalis[97,168–172]. Its stability is higher than that of TiAs, TiMo, and TiSe, and it is also more thermally stable than these compounds[4,172], retaining its exchange capacity up to 300 °C.[171] The properties of TiSb (with $\overline{Sb}/\overline{Ti} = 1.04$) are unaffected by a dose of 4×10^7 Rad of γ-radiation[171]. The exchange of ions bearing different charges (Cs^+, Hg^{2+}, Tl^+) on TiSb obeys the law of mass action[173].

Fairly large differences in exchange capacity are reported by different workers for samples of similar composition: for $\overline{Sb}/\overline{Ti} = 1$, $\Gamma_{Na^+} = 0.73$,[169] for $\overline{Sb}/\overline{Ti} = 1.04$, $\Gamma_{Na^+} = 1.71$,[171] and for $\overline{Sb}/\overline{Ti} = 1.4$, $\Gamma_{Na^+} = 1.5$ mg-equiv g^{-1}.[170]

The selectivity of TiSb varies between samples of the same material[168–171]. Qureshi and Kumar[168] ascribe this variation to holes of different size, whose relative numbers are determined by the precipitation conditions rather than by the composition ($\overline{Sb}/\overline{Ti}$) of the sample.

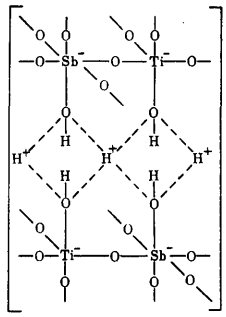
According to some workers[168–171] the potentiometric titration curves of TiSb samples are typical of a monofunctional cation exchanger. On the other hand, other workers[97,124,170] consider TiSb to be a bifunctional exchanger, its potentiometric titration curves (for a 0.1 *N* NaOH solution and samples of different $\overline{Sb}/\overline{Ti}$ composition) lying between those of CAA and titanium hydroxide[124].

The ion-exchange capacity of TiSb samples towards ions with different charges increases with pH.[170] The sorption of silver ions is good on all the TiSb samples. However, unlike other cation exchangers containing antimony (such as PSb,[97,111] SiPSb,[144] TeSb[151]), this material has a capacity for Ag^+ ions not equal to its antimony content[170].

The selectivity towards cations carrying multiple charges increases with the titanium content of the samples[170]:

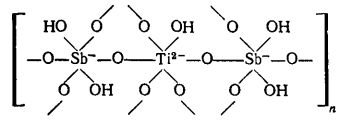
$\overline{Sb}/\overline{Ti} = 2.4$, $Ag^+ > Ba^{2+} > Na^+ > La^{3+}$;
$\overline{Sb}/\overline{Ti} = 1.4$, $Ag^+ > Na^+ > Ba^{2+} > La^{3+}$;
$\overline{Sb}/\overline{Ti} = 0.16$, $Ag^+ > La^{3+} > Na^+ > Ba^{2+}$.

Contradictory results have been published on the structure and on the functional groups of the titanoantimonate cation exchanger. Qureshi and Kumar[168] treat the material as the product of simultaneous condensation of titanium and antimony hydroxides, and they propose a structural formula in which Sb and Ti have oxygen coordination numbers of 5 and 4 respectively. However, in their next paper[169] they assign to the Sb atom its characteristic coordination of 6, but the Ti atom has a coordination of 5:



Gill and Tandon[174] propose the formula $TiO_2 \cdot \frac{1}{2}Sb_2O_5 \cdot 4H_2O$, and they conclude from the i.r. spectra of as-prepared and of baked samples that OH^- groups are responsible for the ion-exchange properties of the material (without specifying whether those groups are attached to Sb or Ti atoms).

Using the concepts on the structure of inorganic cation exchangers developed in Ref. 96 we can describe TiSb as a polymer consisting of alternate $[SbO_{x/2}(OH)_{6-x}]^-$ and $[TiO_{y/2}(OH)_{6-y}]^{2-}$ [124,170] (or $[TiO_{y/3}(OH)_{6-y}]^{-(2-y/3)}$) octahedra:

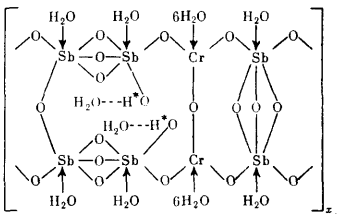


The hydrogen ions which compensate the charge on these octahedra take part in the exchange of counter-ions.

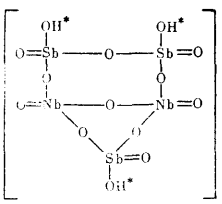
8. Other Mixed Cation Exchangers

Other mixed ion exchangers based on oxygen compounds of antimony have been prepared, mainly by Qureshi and coworkers: NiSb and CoSb,[175] AlSb,[176] FeSb,[165,177,178] CrSb,[179,180] CeSb,[173,174,181] ThSb,[165,182,183] TaSb,[184] NbSb,[185,186] AsSb,[187] and WSb[188]. However, these compounds (described as antimonates of the stated metals) have not been studied as fully as the sorbents discussed above. By mixing solutions of M^{z+} salts and of $SbCl_5$, or potassium pyroantimonate, orantimonic acid, samples with different $\overline{Sb}/\overline{M^{z+}}$ ratios have been prepared. Like the other sparingly soluble antimony compounds, these are found to be chemically very stable. Their capacity decreases as the drying temperature is increased, and increases with the pH of the solution. Each sorbent has a characteristic selectivity towards certain ions: for example, CeSb[181] has a high affinity for Hg^{2+} ions, and NbSb[185] for Mg^{2+} ions.

When the structure of these compounds and the functional groups responsible for their exchange properties are mentioned it is usually assumed that the exchangeable ions are the protons of hydroxyl groups, without specifying whether these groups are attached to Sb or to M atoms[174,184]; alternatively, Qureshi and his coworkers rely on the analogy between antimony and phosphorus compounds, and they suggest the following formulae: for NiSb and CoSb,[185] $M(OH)_2M_3(HSb_2O_7)$; for FeSb,[165] $FeSbO_4.\frac{3}{4}H_2O$; for CrSb,[179] $Cr_2O_3.3Sb_2O_5.22H_2O$, i.e.



and for NbSb[185]



The protons of the SbOH groups (labelled with an asterisk) take part in ion exchange on NbSb and CrSb.

These formulae are unacceptable, since it is well known that antimony differs from phosphorus in not forming tetrahedral oxygen groupings either in solid compounds or in solutions (see, for example, the recent work on the stereochemistry of antimony compounds[86], on the state of antimony in solutions[18,28-35,38], and on the i.r. spectra of antimony compounds[20,21,57,58,130,155,160,162,163]).

9. Modified Sorbents

The term "modified" refers to sorbents supported or precipitated on an inert carrier. The preparation and ion-exchange properties of phosphoantimonic acid (PSb) supported on silica gel have been described[189], and also those of the same exchanger supported on SKT and BAU active carbons[190-192]. The silica gel (or carbon) is steeped in a hydrochloric acid solution of $SbCl_5$ (or a mixed solution of $SbCl_5$ and H_3PO_4), and the resulting material is hydrolysed with water or NH_4OH solution. By baking the finely ground inorganic sorbent (for example, CAA, SiSb, or SiPSb) with polytetrafluoroethylene at 375 °C porous blocks are obtained: these are very convenient for use in columns[193,194]. The capacity (referred to antimony content) is somewhat decreased by this treatment, and the selectivity is slightly affected, but the kinetic characteristics of the material are greatly improved.

A method for preparing heterogeneous compositions from a suspension in acetone of finely divided cation exchanger and the F-26 soluble fluorine-containing polymer has been developed[110,124,195]. By varying the geometric shape of the composition (membranes, tubes, filaments, gauzes, etc.) it is possible to vary the conditions of the sorption process over wide limits, to achieve high flow rates, to control the free volume of the column, to apply an electric field, etc.

Modification of the exchangers yield granulated materials, convenient for column operation, with improved kinetic characteristics and enhanced dynamic exchange capacity, without (as a rule) significant loss of selectivity.

IV. APPLICATIONS OF CATION EXCHANGERS

The high selectivity of sorbents based on oxygen compounds of Sb(V) defines the practical applications of these materials. The most widely used so far is "hydrated antimony pentoxide", marketed by the Italian firm Carlo Erba; the use of the silicoantimonate cation exchanger as a medicinal preparation has also been described. The application of the other sorbents described in this review is still at the stage of practical recommendations by the authors, based on laboratory tests. These recommendations include the possible applications listed below.

CAA: to purify highly radioactive acid solutions from decay products, and to separate ^{137}Cs and ^{90}Sr;[10] to remove Sr^{2+} from dilute nitric acid solutions[50]; to separate alkali[98,196] and alkaline-earth metal ions[197]; to purify lithium chloride solutions from sodium and potassium[198]; to separate Cd^{2+} (or Sr^{2+}, Ba^{2+}) from Ca^{2+} (or Mg^{2+}, Ni^{2+}), and Ca^{2+} from Mg^{2+} (or Ni^{2+}), and for the selective concentration of elements to be sorbed (Cd^{2+}, Sr^{2+}, Ba^{2+}, Ag^+)[13,63,97]; to extract Na radioisotopes from biological samples during neutron activation analysis[11,103,199-203]. The use of antimonic acid activated at 150 and 500 °C in gas chromatography (for the separation of n-butane, n-pentane, n-hexane, n-heptane, and n-octane) has been described[204]. Antimonic acid supported on silica gel or active carbon[104,191,192] is recommended for the removal of Na^+ from solutions of mineral acids[104], and for purifying Li^+, K^+, and Cs^+ salts from Na^+ impurities[190].

SiSb: for the extraction of Cd^{2+}, Sr^{2+}, and Ba^{2+} ions from mixed solutions[134], and for the separation of Cd^{2+} (or Sr^{2+}, Ba^{2+}) ions from Ca^{2+} (or Mg^{2+}, Ni^{2+}), and of Ca^{2+} ions from Mg^{2+} (or Ni^{2+})[134]; SiSb is known as the medicinal preparation "Polisur'min", used in cases of contamination with radiostrontium[205-207].

PSb: for the chromatographic separation of alkali metal ions[128]; to separate the short-lived sodium isotope from large quantities of magnesium and aluminium[208]; to extract strontium from natural waters[209]. Membranes made of PSb have a high electrical conductivity[110,124], and have been used to partition the cathode space in the electrolytic refining of metals[210]; filaments made from PSb have been used for sorbing potassium from biological fluids[195,211].

Because of their high specificity towards Cd^{2+} the cation exchangers SiSb, PSb, and SiPSb have been recommended[127] for the medical treatment of poisoning by cadmium salts. A method of using modified sorbents (CAA, SiSb, SiPSb) for the rapid extraction of sodium from the condensate of boiling water reactors[194] and in the analysis of effluent waters from atomic power stations[193] has been developed.

ZrSb: for the separation of alkali metal ions[152,156]; for the separation of Hg^{2+} from Zn^{2+}, Cd^{2+}, Pb^{2+}, and Bi^{3+}; of Ca^{2+} from Mg^{2+}; of Sr^{2+} from Rb^+, Cs^+, and Ba^{2+}; of Ba^{2+} from La^{3+}; of In^{3+} from Fe^{3+}, Ga^{3+}, and La^{3+}; of Ag^+ from Tl^+.[157]

SnSb: for the following separations. Mg^{2+}–Sr^{2+}, Cd^{2+}, Cu^{2+}, Al^{3+}, La^{3+};[165] Zn^{2+}–Cd^{2+}, Hg^{2+}–Bi^{3+}, Cs^+–UO_2^{2+}, UO_2^{2+}–ZrO_2^{2+}; Th^{4+}–La^{3+}; Th^{4+}–ZrO_2^{2+}; Mn^{2+}–Fe^{3+}; Mg^{2+}–Ca^{2+}; Zn^{2+}–Hg^{2+}–Cd; Al^{3+}–Fe^{3+}–UO_2^{2+}.

TiSb: for the separation of various cations[168,169]. The material can be used to fabricate ion-exchange membranes[124]; filaments made from TiSb compositions are recommended for

the sorption of calcium from complex solutions including biological fluids[212].

Separations of various ions on the following sorbents have been reported:

$NbSb^{185}$: Mg^{2+} — Sr^{2+}, Ba^{2+}, Hg^{2+}, Al^{3+}, Ga^{3+}, Fe^{3+}, La^{3+}, Th^{4+}.

$FeSb^{177}$: Mg^{2+} — Sr^{2+}, Al^{3+} — Ga^{3+}, Y^{3+} — La^{3+}, Th^{4+} — Sm^{3+}, Mg^{2+} — Cd^{2+} — Sm^{3+}.

$AlSb^{176}$: Th^{4+} — UO_2^{2+}, Mg^{2+} — Ca^{2+}, Mg^{2+} — Sr^{2+}, Ni^{2+}—Cu^{2+}—Ag^{+}, Mo^{6+}—Ti^{4+}—W^{6+}.

$CeSb^{181}$: Hg^{2+}—Cd^{2+}, Zn^{2+}, Pb^{2+}, Tl^{+}; Cu^{2+}—Mn^{2+}, Fe^{3+}—Al^{3+}, Zr^{4+}—Th^{4+}.

$ThSb^{183}$: Mg^{2+}—Zn^{2+}, Mg^{2+}—Cd^{2+}, Mg^{2+}—Cu^{2+}, Zn^{2+}—Cd^{2+}, Ni^{2+}—Cu^{2+}, Co^{2+}—Cu, Mn^{2+}—Cu^{2+}.

$TaSb^{184}$: VO^{2+}—Fe^{3+}—Ti^{4+}, VO^{2+}—Al^{3+}—Ti^{4+}, UO_2^{2+} — Ti^{4+}.

$NiSb^{175}$: Bi^{3+}—Cu^{2+}, Cd^{2+}, Al^{3+}, Fe^{3+}, Hg^{2+}, Zn^{2+}, Mn^{2+}, VO^{2+}, Mg^{2+}, Ba^{2+}, Ca^{2+}, Sr^{2+}, Co^{2+}, Pb^{2+}, Y^{3+}.

The high affinity of CrSb for the following ions has been stressed[180]: Ag^{+}, Tl^{+}, Hg^{2+}, Co^{2+}, Pb^{2+}, Ca^{2+}, Sr^{2+}, Fe^{3+}, Bi^{3+}, Al^{3+}, La^{3+}, and Zr^{4+}.

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To conclude this review we should point out that cation exchangers based on antimony(V) compounds are scientifically important as well as having great practical value. Crystalline antimonic acid is one of the few "hydrated oxides" for which a simple correlation between composition, structure, and ion-exchange properties has been demonstrated.

Antimony also plays a structure-determining role in many mixed cation exchangers: when symptoms of crystallinity are detected in these materials the X-ray reflections are usually those of CAA. However, the structure of mixed cation exchangers and the role of the second element (added to the antimonic acid polymeric skeleton during the synthesis) are still the subject of debate. The structures proposed by some workers for the mixed sorbents are incompatible with modern views on the crystal chemistry of the oxygen compounds of antimony(V). For example, the coordination number of Sb(V), which is almost invariably 6, is taken[168] to be 5, and by analogy with phosphorus the group $-\underset{|}{\overset{|}{Sb}}=O$ is postulated[175,186]; the soluble form of antimonic acid is written[175] $H_4Sb_2O_7$, and so on. Differences in the coordination number of Sb(V) lead to different interpretations of the nature of the active groups: either in terms of the dissociation of the SbOH groups[168,180,186], which is not typical of the chemistry of antimony, or in terms of exchange with the outer-sphere ligands of the $[SbO_{6/2}]^-$ complex groups[96]. Hence, structural studies of Sb-containing compounds (including those of variable composition) are still needed.

Because of the discrepancies between the ion-exchange characteristics of sorbents of the same type studied in different laboratories, greater attention must be paid to the state of the starting materials in the solutions from which the sorbent is synthesised, especially in the preparation of mixed sorbents, for which it is not always clear whether the product is a single-phased or a multi-phased (micro-heterogeneous) system.

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