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Sorption Mechanism of Metal Ions on the Salts of Heteropoly Acids

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Published data on the sorption properties of insoluble salts of heteropoly acids (HPA) are discussed in terms of recent views on the structure of HPA salts and on the tendency of ions to form heteropoly compounds, and a classification of ions which can be sorbed on HPA salts is proposed. The special features of the sorption mechanism of specific groups of ions are discussed, and sorption on HPA salts is shown to be a complex process, influenced by properties of the ions such as radius, ionic potential, state of the ion in solution, and tendency to form complexes. The sorption of ions which can form heteropoly compounds is a multi-step process, accompanied by interaction of the sorbed ions with the molybdophosphate anion. 111 references.

CONTENTS

I.	Introduction	793
II.	Structural properties of the HPA salts used as inorganic sorbents	794
III.	Sorption of metal ions able to form salts with HPA anions	795
IV.	Sorption of ions able to act as the central atom in heteropoly compounds	798
V.	Sorption of ions able to form the co-ordination sphere of heteropoly compounds	802

I. INTRODUCTION

The ion-exchange properties of the salts of heteropoly acids (HPA) were discovered by Baxter and Griffin in 1905 when washing with potassium salt solutions a precipitate of ammonium molybdophosphate (AMP) used for the gravimetric determination of phosphorus[1]. However, this phenomenon was not widely used until the late 1950's and early 1960's, when it was applied to the concentration and separation of alkali metal ions[1-26], and to the determination of caesium in sea water and in effluents[27-30] and in biological materials[31-33]. It was then realised that insoluble HPA salts are valuable inorganic ion exchangers: they are cheap, readily available, and easily prepared in any laboratory. They can be used in theoretical studies of ion exchange processes[8] because they are monofunctional when suitably prepared and, like zeolites, they do not swell significantly in aqueous solutions.

Together with the experimental papers began to appear papers on the mechanism of sorption processes HPA salts[7,8,13-20,34-43] as well as review articles[1,2,4,44]. However, the most interesting of these reviews[1] is already more than 10 years old, and more recent reviews are either too sketchy[2,4] or inaccessible[44].

Furthermore, all the reviews published so far adopt a formal classification of the sorbed ions into univalent, bivalent, and multivalent to describe the mechanism of sorption processes. Univalent and bivalent ions have almost identical sorption mechanisms, and the substantial differences in sorption behaviour of the other ions are not revealed by classifying them all as "multivalent". We have therefore attempted to develop a more rational description of the sorption mechanism of various ions on HPA salts by combining two types of information: published data on the structure, formation conditions, and stability of the heteropoly compounds of different

elements, and observations on the sorption properties of HPA salts.

II. STRUCTURAL PROPERTIES OF THE HPA SALTS USED AS INORGANIC SORBENTS

Insoluble salts of heteropoly acids are inorganic sorbents with a fairly complex crystal structure[1-4]. The structural features of the initial heteropoly compounds (HPC) are responsible for the complexity of the processes at the sorbent–solution interface, and they should not be overlooked when the experimental results are analysed. We shall therefore examine the structure of a range of heteropoly compounds before attempting to describe the mechanism of ion exchange on HPA salts.

Of the many sparingly soluble HPA salts, ammonium molybdophosphate is most widely used as a sorbent. It is a HPC of the 12th series[45], having the Keggin structure[46-48]. Ammonium molybdophosphate is precipitated from aqueous solutions as fine yellow crystals of the neutral salt $(NH_4)_3.PMo_{12}O_{40}\cdot nH_2O$ or of the acid salt $(NH_4)_2HPMo_{12}O_{40}\cdot nH_2O$ (depending on the ratio of molybdophosphoric acid to ammonium salt)[49].

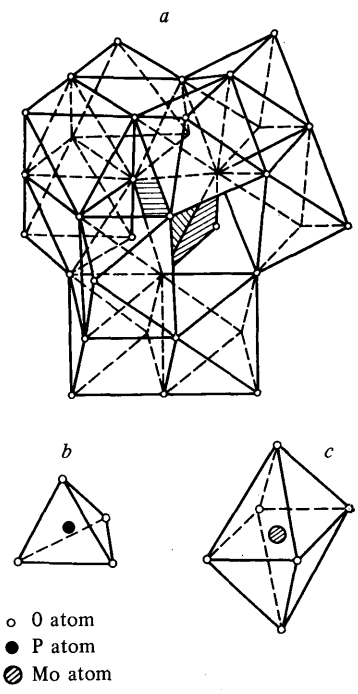


Figure 1. Structure of the $PMo_{12}O_{40}^{3-}$ ion[46]: (*a*) overall shape of the anion, (*b*) PO_4 tetrahedron, (*c*) MoO_6 octahedron.

Heteropoly compounds differ from ordinary coordination compounds in not having discrete ligands coordinated to a central atom. Therefore the coordination sphere of the HPC can be treated as a single complex ligand. At the centre of a ligand anion having the Keggin structure we find a PO_4 [46-48] tetrahedron (Fig. 1), surrounded by twelve MoO_6 octahedra arranged in four groups of three: within each triplet the octahedra are edge-sharing, and the triplets are interconnected by sharing corners. Because of the electrostatic interaction between the atoms the octahedra are distorted, with different Mo–O distances. The structure is characterised by the presence of twelve Mo=O double bonds (oxygen end-atoms), and twelve almost linear and twelve angular Mo–O–Mo bridging bonds (bridging oxygen atoms). The HPA anion as a whole is an almost spherical particle with a negative charge (–3) on its surface. In the crystalline state there is no direct bond between the anions: the structure is stabilised by hydrogen bonds, or by the cations. All HPC can form a variety of crystal hydrates, in which the amount of water is often difficult to determine exactly[47,48]. Heteropoly acids and their salts with a Keggin structure crystallise in the cubic system[46,50]. The HPA anions retain their high symmetry in aqueous solutions[48,51]. In the crystalline salts the cations are accommodated in the spaces between anions, and they can exchange with cations in solution if their size allows[1,48].

Heteropoly compounds with the Keggin structure have the general formula[48] $E^{x+}M_{12}O_{40}^{x-8}$, where M is usually Mo or W, and E = B, Si, P, As, Cr, Mn, Fe, Co, Cu, Zn, Ti, Zr, Ga.

In addition to the simpler heteropoly compounds, a whole series of mixed HPC (in which one or more molybdenum atoms are replaced by Tungsten, vanadium, or another metal) has been synthesised[48]. The formation of mixed compounds is due to the general tendency of these ions to combine in polymeric structures, giving compounds which in most cases can be classified as complexes with the Keggin structure.

Triple complexes[48] are formed when highly charged ions (for example, Zr^{IV}, Ti^{IV}, Th^{IV}, Nb^{V}) are added to heteropoly acids in solution. The i.r. spectra of the solid complexes[52,53] show that zirconium, titanium, and thorium can replace molybdenum in the coordination sphere, forming mixed heteropoly complexes. Under these conditions the Keggin structure is retained.

Furthermore, we know from the chemistry of heteropoly compounds[48,54] that addition of alkali to a solution of (say) 12-tungstophosphoric acid produces an 11-tungstophosphate. These "unsaturated" compounds, for example the anion $EW_{11}O_{39}^{n-}$, have an incomplete Keggin structure in which one tungsten atom and one oxygen end-atom are missing[55]. The charge on the anion is always increased by four units. Some lanthanide and actinide ions can form stable complexes with unsaturated heteropoly complexes: the formation of these complexes with thorium[56], cerium[55], and other elements[57] has been reported.

Thus, several variants of the interaction of sorbed ions with ammonium molybdophosphate or other sparingly soluble salts of a HPC of the 12th series are possible.

1. As stated above, the cations in the salt structure are located in the spaces between the anions, and they can (if their size allows it) exchange with cations in the bulk of the solution[1]. Therefore, one variant of the interaction is the replacement of cations from the outer sphere of the sorbent by sorbed ions (i.e. the normal ion exchange reaction).

2. Since the HPA anions are not inert as a matrix, the sorption of ions tending to form mixed complexes with the molybdenum or tungsten of the coordination sphere can cause replacement of molybdenum or tungsten atoms by the corresponding metal atom.

3. Another possible variant is the adsorption of a metal ion on the surface of the anion in a geometrically favourable position, due to interaction with an oxygen end-atom. This interaction should be enhanced by the partial decomposition of the 12th-series HPA anion at high pH, giving a small amount of 11th-series HPA anions.

The most frequently used sorbents are sparingly soluble salts of 12th-series heteropoly acids with a Keggin structure: on these materials differences in sorption properties, and hence also in the possibility of separating various ions, are

determined mainly by the properties of the ions being sorbed, both physical (ionic radius, ionic potential) and chemical (state of the ion in solution, tendency to form complexes in general, and formation of heteropoly compounds in particular).

On the basis of their ability to form heteropoly compounds the inorganic ions can be classified into three groups.

I. The first group includes the ions which cannot normally act as complex-forming hetero-atoms, or form the coordination sphere of HPA, but which form salts with heteropoly acid anions. These are the ions of the alkali and alkaline-earth metals, many doubly charged ions such as Zn^{2+}, Cu^{2+}, Co^{2+}, Ni^{2+}, Mn^{2+}, and Cd^{2+}, and some triply charged ions. These ions, if their size allows it, can exchange with the cations of sparingly soluble HPA salts, which behave towards them as ordinary strongly acidic cation exchangers.

II. The second group consists of ions which can act as the central atom in HPC. They include Ge^{IV}, Ti^{IV}, Zr^{IV}, Th^{IV}, Ce^{IV}, Te^{IV}, Se^{IV}, Ga^{IV}, Cr^{III}, Fe^{III}, Co^{II}, etc. Typical complex-forming ions with a high charge and a small radius, such as Ti^{IV}, Zr^{IV}, Th^{IV}, Ce^{IV}, Te^{IV}, etc., can interact with the anionic part of the sorbent by an addition reaction, especially in the presence of structural defects on the surface (partial degradation of the 12th-series HPA with formation of unsaturated compounds). The sorption of ions such as selenium, able to form highly stable HPC, can lead to reconstruction of the whole surface structure of the sorbent. However, all these ions can also take part in exchange in the outer sphere of the HPA salts as one of the steps in the sorption process.

III. The third group consists of ions able to form the coordination sphere of heteropoly compounds, such as molybdenum(VI), tungsten(VI), vanadium(V), and chromium(VI). Sorption of these ions by HPA salts is often accompanied by the formation of mixed heteropoly compounds.

This classification is not absolute, because some ions could be assigned to two of the groups with equal justification. For example, in the case of iron(III), salt formation with HPA anions has been reported[45] as well as the formation of heteropoly complexes in which the iron is the central atom[48]. Niobium can act as the central atom, forming molybdenum–niobium HPA,[48] but it can also form heteropoly compounds by entering the coordination sphere[47]. We should also note that in real systems it is rare to find one of the above types of interaction in a pure form: sorption process on HPA salts are usually complex. This statement is consistent with a large volume of recently published work.

III. SORPTION OF METAL IONS ABLE TO FORM SALTS WITH HPA ANIONS

Many salts of heteropoly acids have been described[45]. In the case of molybdophosphoric acid (MPA) and tungstophosphoric acid (TPA) the salts of the alkali and alkaline earth metals, and those of silver, thallium, and mercury(I) are known, as well as those of manganese, cobalt, nickel, cadmium, copper(I), iron(III), and zinc. All these ions can be assumed to undergo exchange, to varying extents, on the insoluble salts of heteropoly acids. For the separation and concentration of ions the product of the interaction of the sorbed ion with the initial, sparingly soluble HPA salts must also be insoluble, i.e. the ammonium ions in the AMP structure can be exchanged to a significant extent only for metal ions which form HPA salts insoluble in water[7].

Healy's work[49,58,59] is highly relevant to the identification of the range of ions which can form sparingly soluble salts with HPA anions: he prepared and analysed the neutral and the acid salts of the alkali metals, silver, thallium(I), mercury(I), and barium, and also some mixed salts of alkali metals and of barium with aluminium, iron(III), and some rare-earth elements, with the anions of MPA, TPA, and tungstosilicic acid. Healy concludes from a study of the solubility of these salts[59] that mixed salts prepared by exchange of ions in the outer sphere of HPA are sparingly soluble if two of the three hydrogen atoms in the MPA or TPA are replaced by a heavy alkali metal, while the third hydrogen atom can be replaced by a light ("soluble") or a heavy ("insoluble") alkali metal. For example, the salts $K_2LiW_{12}O_{40}$ and $K_2RbW_{12}O_{40}$ have a very low solubility in water. Salts of the alkaline-earth metals are more soluble in water(and even more so in acids) than the salts of the heavy alkali metals, and therefore they are not absorbed by tungstophosphates at acidities above 0.3 M, though they can be easily removed from solutions at pH 1–4.[59]

From the point of view of solubility the most effective use of the ammonium salts of HPA is exchange with heavy alkali metal ions such as K^+, Rb^+, and Cs^+, or with the Tl^+, Ag^+, and Hg_2^{2+} ions, which form the least soluble salts with HPA.[49] For this reason HPA salts were first used as ion exchangers in the concentration and separation of heavy alkali metal ions[5–9]. A large amount of experimental information on the exchange of alkali metal ions on MPA and TPA salts is now available, and the mechanism of these processes has been studied in detail.

Smit and coworkers[5–8] carried out one of the first and most fundamental studies of this problem by synthesising the ammonium salts of various HPA,[7] calculating the distribution coefficients of several alkali metal anions, and analysing the results[7,8]. They established[7] that for a given HPA salt the distribution coefficient increases with the atomic number (or ionic radius) of the alkali metal, i.e. in the same order as in the case of strongly acidic organic ion exchangers. The higher distribution coefficients of Ag^+ and Tl^+ (as compared to alkali metal ions of the same size) are ascribed by Smit to the partial covalency of the bond between Ag^+ or Tl^+ ions and the HPA anions. The separation factors for pairs of alkali metal ions (defined as the ratio of the distribution coefficients under similar experimental conditions) are much higher for the ammonium salts of HPA than for the Dowex-50 resin. The selectivity of AMP towards heavy alkali metals is so great that small amounts of the larger alkali metal ions (Cs^+ and Rb^+) can always be selectively adsorbed from solutions containing amounts of the smaller alkali ions several times greater than the maximum capacity of the column[8]. Thus, 19 mg of Rb^+ can be quantitatively separated from 600 mg of K^+ on a column containing 1 g of AMP and 0.5 g of asbestos. The first attempt at relating the cation exchange properties of AMP and other HPA salts to their crystal structure was reported by Smit.

The basic parameter which determines the exchange of a univalent cation on AMP is, according to Smit, the ionic radius. The large alkali metal cations can be stably accommodated in the holes of the lattice and lower the lattice energy sufficiently to form sparingly soluble salts. It is suggested[7] that because of the pore structure of the HPA salts ion exchange can take place over the whole of the crystal lattice, and not just on the surface of the crystals. However, large organic cations cannot move freely through the lattice, and they are exchanged on the crystal surface only.

The validity of the law of mass action for exchange processes on MPA has been tested[8] by a study of the Rb^+–NH_4^+ exchange. By analysing the elution curves it was shown that not all the ammonium ions in AMP can be exchanged: ~60% of the ammonium ions can be replaced by caesium, and ~80% by rubidium. Smit explains this observation by postulating that caesium ions (and, to a lesser extent,

rubidium ions) can block the channels of the ions exchanger, thus hindering the diffusion of ions in the lattice.

However, subsequent work on the exchange properties of HPA salts has shown that the sorption of alkali metal is a more complex process. Thus, Krtil established[13-19,36] that in most cases the results apply to the acid salts of HPA. When the initial salts have the composition $(NH_4)_{2.67}H_{0.33}(PW_{12}O_{40})\cdot 9.8H_2O$ or $(NH_4)_{2.95}H_{0.05}(PMo_{12}O_{40})\cdot 11.6H_2O$ treatment with acid causes exchange of NH_4^+ ions by hydrogen ions, with formation of a more acid salt[9]. Later work showed[13,15,36] that the sorption of alkali metal ions on the salts of heteropoly acids can involve three independent processes: a) exchange of ammonium ions by alkali metal ions, b) exchange of hydrogen ions from the sorbent by alkali metal ions, c) exchange of ammonium ions from the sorbent by hydrogen ions from the acid solution.

The equilibrium constant for all these processes have been determined[36], and it has been shown that the exchange of alkali metal ions on HPA salts obeys the law of mass action. Mathematical treatment of sorption data using this law can be carried out relatively simply only when the sorbed ion is present in trace amounts (as compared with the ammonium ion or the acidic hydrogen of the sorbent[1]). In this case the plots of $\lg D$ against pH and $\lg D$ against $[NH_4]$ should be straight lines of unit slope. This expectation has been confirmed experimentally in studies of the sorption of alkali metal ions on HPA salts[5-36].

Table 1. Distribution coefficients D of different cations on AMP in 0.1 M NH_4NO_3.[34]

Cation	Li+	Na+	K+	Rb+	Cs+	Ag+	Tl+	H_3O^+
r, Å	0.60	0.95	1.33	1.48	1.69	1.26	1.40	—
D	0.57	0.78	4.7	266	4024	54	3939	0.84
θ_{max} %	20.9	26.4	48.7	53.6	45.3	64.8	45.8	—

Though the general features of the sorption of alkali metal ions on HPA salts are generally agreed, different workers report different experimental values of the distribution coefficients D and of the maximum extent of exchange of the ammonium ion in HPA salts by alkali metal ions. Thus, Krtil[18] determined the maximum sorption capacity of AMP and ammonium tungstophosphate (ATP) towards caesium: the results (1.0 and 0.66 mg-equiv Cs g^{-1} respectively) indicate the formation of the dicaesium salt of the HPA in both cases. On the other hand, measurements of the maximum extent of exchange (θ_{max}) of the ammonium ions by alkali metal ions under dynamic conditions[34] did not give values of 33.3 and 66.6%, corresponding to the exchange of one or two ammonium ions (Table 1). The differences between the D values obtained by different workers[8,15,18,34,36] can be ascribed to different experimental methods and different procedures for the preparation of the sorbent.

A detailed study[18] of the sorption of caesium and rubidium on normal and on acid ammonium and thallium salts of MPA and TPA revealed some interesting features: thus, caesium in weakly acidic solutions (0.01 M HNO_3) has a lower affinity for the acid salt than for the normal salt. A possible explanation is that in normal ammonium salts of HPA the caesium can be exchanged only by ammonium ions, whereas in acid salts it can be exchanged by NH_4^+ and H^+ ions. Measurements of the pH dependence of the sorption of caesium on acid salts at constant concentration of ammonium ions have shown that the process is influenced by hydrogen ions only at acidities ≥1 M (in HNO_3). Hence, caesium can exchange with hydrogen ions only in strongly acid solutions.

Attempts have been made[34,35] to relate the sorption of alkali metal ions to various physicochemical characteristics of AMP and of the sorbed ions. Thus, it has been shown[35], by analysing the solubilities of the corresponding HPA salts and their crystal lattice energies, that the separation of alkali metal ions on AMP is possible in principle. The affinity series obtained from that work, $Cs^+ > Rb^+ > K^+$, is consistent with the more general sequence[34]

$$Cs^+ = Tl^+ > Rb^+ > Ag^+ > K^+ > H^+ > Na^+ > Li^+,$$

shown in Table 1. Furthermore, we note a linear relationship between $\lg K'$ (where K' is the equilibrium constant of the exchange reaction) and ΔH (the energy of hydration) for Cs^+, Rb^+, and K^+, whereas the smaller ions Na^+ and Li^+ have unexpectedly high values of $\lg K'$. It is suggested[34] that the smaller alkali metal ions undergo exchange in a partially hydrated form (Fig.2). By applying the law of mass action to the experimental exchange isotherms for the alkali metal ions an isotherm equation valid over a wide range of concentration has been obtained[34]. It assumes that the activity of the ammonium ions in the crystal is equal to the mole fraction of exchangeable ammonium ions, and that the ions in the solid phase are in an ideal solution. Thus, the equation is an analogue of the Langmuir isotherm[60]. The agreement between experimental and calculated results is satisfactory.

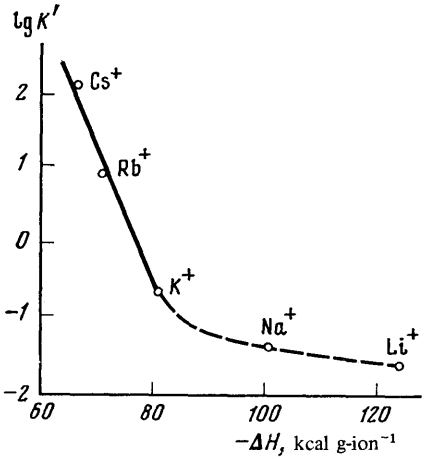


Figure 2. Logarithm of the equilibrium constant of the exchange reaction against hydration energy of the alkali metal ions[34].

One of the early publications[6] suggested the following mechanism for the exchange of bivalent ions (in particular, barium) on AMP:

$$Ba^{2+} + H_2O \rightleftarrows Ba(OH)^+ + H^+ \quad (1)$$

$$RNH_4 + Ba(OH)^+ \rightleftarrows RBa(OH) + NH_4^+ \quad (2)$$

where R is a molybdophosphate anion. The evidence for this conclusion was that only large univalent cations are readily exchanged with the ammonium ions of AMP, and the ion $Ba(OH)^+$ satisfies both conditions (univalence, and large crystallographic radius). Furthermore, this reaction scheme

explains the dependence of the sorption of barium on the concentration of ammonium ions as well as on the acidity of the medium.

More recent work[14,27,61] in different laboratories on the sorption of ^{90}Sr on various HPA salts led to the conclusion[14] that $\lg D$ for strontium varies linearly with pH at pH < 3, with a slope of −2 (i.e. one strontium ion is exchanged for two hydrogen ions). These experimental facts cannot be explained by Smit's mechanism[18]. Healy[59] critically examined Smit's mechanism, and pointed out that a species such as $Ba(OH)^+$ is highly unstable, and very unlikely to exist in bivalent cation salt solutions under the conditions used for sorption on AMP. Smid himself came to the same conclusion in a later paper[62]. Referring to Stockdale's results[63], Smit pointed out that even in weakly acid solutions the sorbent is in the form of an acid salt of MPA, of composition intermediate between the doubly and the triply substituted salt. The pure doubly substituted salt can be prepared by washing the exchanger with acid[58,63]. Smit concluded from these observations that bivalent ions are sorbed reversibly on AMP by exchanging with ammonium ions or with the oxonium ions remaining in the AMP precipitate in spite of thorough washing with ammonium nitrate:

$$2\,(NH_4)_2\,(H_3O,\,NH_4,\,Na\ \text{ etc.})\,MP + Ba^{2+} \rightleftarrows \rightleftarrows [(NH_4)_2\,MP]_2\,Ba + 2\,(H_3O^+,\,NH_4^+,\,Na^+\ \text{etc.}) \qquad (3)$$

This reaction scheme is consistent with the dependence of the sorption of bivalent ions on pH and on the concentration of ammonium ions, and also with the slope of the plots of $\lg D$. Furthermore, it is clear that the exchange mechanisms of univalent and bivalent ions on HPA salts must be similar, and there are no grounds for involing specific mechanisms in the two cases as is often done in the literature[1,6,62,64]. However, there is a difference in the sorption and elution conditions of the two types of ion, and this difference has been used in the separation of ^{137}Cs and ^{90}Sr.[6,14,27,36,61,62] It is probably associated with the differences in solubility of the exchange products in water and in acid solutions[49,58,59].

Table 2. pH of the equilibrium solutions before (pH_1) and after (pH_2) contact with AMP.[64]

M^{2+}	Mg^{2+}	Ca^{2+}	Sr^{2+}	Ba^{2+}	Mn^{2+}	Co^{2+}	Ni^{2+}	Cu^{2+}	Zn^{2+}	Cd^{2+}
pH_1	5.89	6.20	6.30	6.54	6.37	6.19	6.33	4.88	5.37	6.14
pH_2	3.87	3.55	3.41	3.03	3.74	3.50	3.49	3.26	3.48	3.53

The sorption of Be^{2+}, Mg^{2+}, Ca^{2+}, Sr^{2+}, Ba^{2+}, Mn^{2+}, Co^{2+}, Ni^{2+}, Cu^{2+}, Zn^{2+}, and Hg^{2+} has been studied[64] under both static and dynamic conditions. The D values are independent of acidity at pH > 3 for practically all the listed ions, and in more strongly acidic solutions they increase with pH. The variation of $\lg D$ with $\lg [NH_4NO_3]$ is a straight line of unit slope. From these observations the authors conclude[64] that the exchange with ammonium ions involves a singly charged particle, possibly $M(OH)^+$: in other words, they revert to the Smit mechanism[6], described by Eqns.(1) and (2). Though the $M(OH)^+$ complexes are unstable for most of these ions, it is suggested[64] that the equilibrium of their formation reaction (1) is shifted towards the right by the sorption of $M(OH)^+$ particles on the AMP. The observed decrease in pH of the equilibrium solutions during sorption of bivalent ions on AMP (Table 2) is quoted[64] as evidence for the validity of Eqns.(1) and (2).

However, a lowering of the pH of the equilibrium solution can be produced also by the exchange mechanism corresponding to Eqn.(3) if the sorbent is an acid salt of MPA. The authors[64] had worked with a normal salt, and therefore they excluded the possibility of exchange by the mechanism (3). However, they controlled the composition of their sorbents by determining the AMP content alkalimetrically rather than by determining the ammonia content. Because of the large molecular weight of the molybdophosphate anion (as compared to NH_4^+, and even more so as compared to the hydrogen ion) this approach cannot give accurate results. The most convincing argument in favour of exchange by Eqns.(1) and (2) is the slope of the plots of $\lg D$ against $\lg [NH_4NO_3]$, and also the pH value of the solutions before sorption (greater than 5 in every case, see Table 2). The $M(OH)^+$ particles may be relatively stable under these conditions.

Table 3. Distribution coefficients of trace amounts of doubly charged cations on AMP in 0.1 M NH_4NO_3 solution[64].

M^{2+}	D	M^{2+}	D	M^{2+}	D
Mg^{2+}	0.81	Mn^{2+}	1.34	Cu^{2+}	1.92
Ca^{2+}	1.48	Co^{2+}	1.38	Zn^{2+}	4.28
Sr^{2+}	1.34	Ni^{2+}	1.77	Cd^{2+}	2.21
Ba^{2+}	3.68				

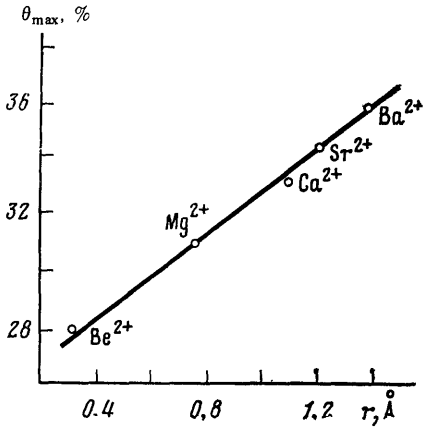


Figure 3. Maximum exchange (θ_{max}) of alkaline-earth ions against ionic radius[64].

The stoichiometry of the exchange was tested[64] by a series of dynamic experiments aimed at determining the maximum capacity of the column for different bivalent cations: the result was that different cations can replace different amounts of ammonium ions in AMP. For example, in the exchange of Hg^{2+} ions ~10% of the ammonium ions are replaced, as compared to 27% in the exchange of Zn^{2+}, 23.5% in the exchange of Co^{2+}, etc. These values differ very substantially from the values (33.3 and 66.6%) corresponding to the stoichiometric exchange of one or two ammonium ions. With the alkaline-earth metal ions a direct proportionality is found between the maximum degree of exchange and the ionic radius (Fig.3), but not with other ions.

The distribution coefficients for trace amounts of bivalent[64] and univalent ions[34] have also been determined (under otherwise identical conditions). We note (Table 3) that the distribution coefficients for bivalent ions are much smaller than those for the heavy univalent ions. From the experimental results the bivalent ions can be arranged in the following affinity series:

$$Zn^{2+} > Ba^{2+} > Cd^{2+} > Cu^{2+} > Ni^{2+} > Ca^{2+} > Mn^{2+} \sim Sr^{2+} \sim Co^{2+} > Mg^{2+}.$$

IV. SORPTION OF IONS ABLE TO ACT AS THE CENTRAL ATOM IN HETEROPOLY COMPOUNDS

This is the most extensive group of ions in our classification. As was pointed out in Section II, it includes the typical complex-forming ions, such as Ce^{III}, Y^{III}, Sc^{III}, Fe^{III}, Cr^{III}, Ti^{IV}, Zr^{IV}, Th^{IV}, Ce^{IV}, Te^{IV}, Ga^{IV}, Nb^{V}, U^{VI}, U^{IV}, Np^{IV}, etc. Many of these ions carry a high charge and have a small radius, i.e. they have a high ionic potential, which explains their highly developed tendency to form complexes. All these ions can act as the central atom in heteropoly compounds. The heteropoly complexes of Ti^{IV}, Zr^{IV}, Cr^{III}, and Fe^{III} have the Keggin structure[48,65].

Hexamolybdenum and hexatungsten compounds with octahedral coordination of the central atom, of general formula $E^{x+}M_6O_{24}^{x-12}$, are formed by ions such as Te^{IV}, Al^{III}, Cr^{III}, Fe^{III}, Ga^{III}, etc.[48,66,67]

The structure of the heteropoly complexes of Ce^{IV}, Th^{IV}, U^{IV}, and Np^{IV} has been described[48,68-71]. It has one special feature: the central atom has icosahedral surroundings. This structure is now called the Dexter–Silverton structure[72], and the anion has the general formula $E^{4+}M_{12}O_{42}^{8-}$. "Triple" heteropoly complexes have been described for many ions of this group. They have been used in the spectrophotometric determination of titanium[73-77], thorium[78,79], zirconium[80], niobium[81,82], hafnium[83], yttrium[84], nickel[85], and other elements. Opinions as to the location of the second hetero-atom in such a structure have varied. The earlier papers[73-75,80,81,83] suggested that the third component occupies a special place in the coordination sphere rather than replacing molybdenum, thus acting (with the phosphorus) as a second central atom. More recently the most generally held view has been that the triple complexes are mixed heteropoly compounds, in which some of the molybdenum is replaced by another element[48].

On the other hand, some of the ions listed above can also form salts with HPA anions. In particular, Healy[59] has described the formation of mixed cerium–caesium $[(Cs_2PW_{12}O_{40})_3Ce]$, aluminium–caesium $[(Cs_2PW_{12}O_{40})_3Al]$, and iron–caesium $[(Cs_2PW_{12}O_{40})_3Fe]$ salts of tungstophosphoric acid. The same paper describes the formation of mixed salts of ammonium and caesium with cerium, praseodymium, and europium during the sorption of the latter elements on precipitated ammonium and caesium molybdophosphates.

The cations do not occupy a fixed position in the structure of the heteropoly acid salts[47,48,86], and they are merely accommodated in the space between the anions. If their size allows, they can be exchanged for cations from the external solution[1,7,8]. Hence, the first step in the sorption of cations on sparingly soluble heteropoly acid salts is diffusion into the crystal and exchange with the cations of the salt. In the first group of cations, discussed in Section II of this review, these steps conclude the process, and mixed salts of the appropriate HPA are formed. On the other hand when the sorbed ions can act as the hetero-atom in an HPA it can also (under suitable conditions) interact further with the anion, which can no longer be treated as an inert matrix (as in the exchange of alkali or alkaline-earth metals).

Before discussing the possible types of interaction between the sorbed ions and the anions of HPA salts we should examine the experimental information on the sorption of these ions on molybdophosphates and tungstophosphates. The sorption of ions in this group has been studied for many years merely from the standpoint of separating these ions from alkali metal ions (for example, in the preparation of radiochemically pure caesium-137 [6,11,17,19,22] or potassium-42.[24]) Krtil[36] and Smit[62] were among the first to study the sorption mechanism of tervalent ions.

Krtil believes[36] that the interaction of yttrium(III) and cerium(III) with ammonium tungstophosphate is based on ion exchange with the ammonium or hydrogen ions of the sorbent. At nitric acid concentrations of 0.2–1 M Krtil observed a linear relationship between $\lg D$ and $\lg c_{HNO_3}$, with a slope of 3, from which he concluded that yttrium and cerium(III) are exchanged for three hydrogen ions at these acidities. The bond between the sorbed ions and the sorbent is relatively weak, since these ions can be displaced by hydrogen ions. The pH for maximum sorption is ~1. Furthermore, Krtil suggests that the sorption of these ions (in contrast to the sorption of alkali metal ions) does not depend on diffusion of sorbate into the sorbent lattice, since all the processes are confined to the surface of the sorbent.

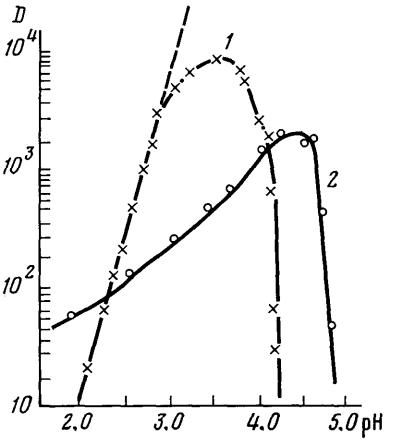


Figure 4. Distribution coefficient of yttrium from 0.1 M NH_4NO_3 solution against acidity of the medium[62]: *1*) on AMP, *2*) on ATP.

Smit[62] studied the pH dependence of the sorption of yttrium on AMP and ATP. Like Krtil[14], he found a fairly complex dependence (Fig. 4), the slope in the pH region 2–3 (curve *1*) being 2.72 instead of the expected 3.0. The distribution coefficients were determined after stirring the yttrium solution with the sorbent for 10–12 h. As Fig. 4 shows, when the pH of the equilibrium solution is increased above 3 the sorption of yttrium on AMP falls off sharply. By comparing these results with those of dynamic experiments Smit discovered some interesting discrepancies. In the dynamic experiments some of the yttrium sorbed at pH < 4 can be eluted (together with strontium) by a 1 M solution of NH_4NO_3, whereas elution of the remainder requires a solution

of 1 M NH_4NO_3 + 1 M HNO_3. On the other hand, after sorption on AMP from an acetate buffer solution at pH 4.5 the whole of the yttrium is in a form which cannot be eluted by 1 M NH_4NO_3. This can be exploited for the separation of strontium from yttrium. The process is not easily reversible: rapid elution of the yttrium requires at least a 0.5 M solution of HNO_3. Smit believes that the yttrium which cannot be eluted by NH_4NO_3 is adsorbed on an unusual type of exchange centre, or by a special mechanism, so that the ion exchange reaction is complicated by some additional interaction in this case. It is suggested[62] that complex formation between the sorbed ions and various decomposition products of the heteropoly anion (or even the 12th series HPA themselves, structurally modified) can occur in the solid phase.

As stated, in Smit's experiments the equilibrium sorption fell off steeply at pH > 3, which at first sight cannot be reconciled with the results of dynamic experiments. However, it was shown that if the equilibrium experiments at pH > 3 are carried out in 1 min rather than 10–12 h the D values no longer decrease with increase of pH, but lie on an extension of the left-hand branch of curve *1* in Fig.4 (broken line). The decrease in the distribution coefficients of yttrium at high pH values after relatively long equilibration times is ascribed[62] to complex formation between ytrrium in the aqueous phase and the soluble decomposition products of the 12-AMP (which may include the 11-molybdophosphate anion).

Unfortunately, kinetic sorption curves for yttrium are not given in Ref.62, but the results of the following experiment are quoted. A sample of AMP was left overnight in contact with a 0.1 M solution of NH_4NO_3 in a pH 4.5 buffer (sodium acetate). The water phase (which had developed a yellow colour) was then separated, a trace of yttrium was added to it, and the solution was allowed to contact a fresh portion of AMP for 1 min. Under these conditions practically no sorption of yttrium was observed. On the other hand, when the first sample of AMP was immersed for 1 min in a fresh buffer solution (at pH 4.5) containing a trace of yttrium unusually high D values for yttrium were obtained.

It is suggested[62] that this experiment demonstrates the formation of water-soluble complexes which cannot be adsorbed on AMP. X-Ray diffraction patterns of AMP samples exposed for 20 h to a pH 4.5 buffer solution are taken as evidence that the AMP samples are unchanged. The present writers find this evidence unconvincing, since one of the most likely decomposition products of 12-molybdophosphate is the 11th series anion, which consists (see Section 1) of an incomplete Keggin structure with a missing molybdenum atom and oxygen end-atom[55]. The presence of a few structural defects of this type on the sorbent surface can hardly be detected by X-ray diffraction analysis. Therefore, we believe that the type of interaction between yttrium and the molybdophosphate anion in the solid phase is still an open question.

As regards the other ions of this group, the sorption of titanium, thorium, uranium, neptunium, zirconium, niobium, selenium, and tellurium on various heteropoly acid salts has been investigated[37–43,87–93]. Sorption processes involving these elements may be even more complex than with yttrium, because these multiply charged ions tend to hydrolyse in aqueous solutions as well as forming many types of complex with anions of different acids. Allowance for all these factors (in addition to the possible interactions with the anionic part of the sorbent) must be made in studies of the sorption processes for these ions.

Thus, in a study of the behaviour of uranium(VI) during sorption on AMP the hydrolysis of the ion and the formation of nitrato and sulphato complexes had to be allowed for[38]. At low concentrations of HNO_3 (<10^{-2} M) and NH_4NO_3 (<5 × 10^{-3} M) the distribution coefficient of the uranyl ion on AMP ($\lg D$) was found[38] to be independent of the concentration of HNO_3 and NH_4NO_3, but at higher concentrations a linear relationship with a slope of unity was observed. These results led to the conclusion[38] that in the ion exchange reaction a univalent ion replaces an ammonium ion, the most probable exchanging particle in this case being UO_2OH^+. Exchange of the $UO_2NO_3^+$ particle is said to be impossible, because its formation occurs at higher concentrations of nitric acid than those used in this work (0.01–0.25 M). The sorption mechanism of the UO_2OH^+ ion is equated[38] to that of alkali metal ions, an ammonium or hydrogen ion in the AMP being replaced by the UO_2OH^+ ion. The law of mass action was shown to apply to exchange equilibria involving uranyl ions present in solution in different forms. The sorption of uranium is reversible: under dynamic conditions the uranium is sorbed from a 10^{-3} M solution of nitric acid and eluted in 100% yield by a 1 M solution of the acid.

The sorption of elements such as zirconium and niobium has been studied for many years merely with the aim of optimising their separation from caesium-137.[17,19,22,36] It was shown[17,36] that the behaviour of zirconium and niobium differs very substantially from that of the other fission products. Though the plot of $\lg D$ against $\lg c_{HNO_3}$ is linear, its slope is fractional. Krtil suggests[36] that in this case molecular sorption of neutral complexes or hydrated forms of the elements must be taking place. Because of the low solubility of zirconium phosphates he concludes that the anomalous behaviour of zirconium and niobium is due to chemisorption. Under the conditions used for the sorption of alkali metal ions the sorption of zirconium and niobium is partially irreversible. If the initial solution contains hydrofluoric acid, the elements are converted into fluoro complexes and are sorbed with difficulty: only 0.01% of a ^{95}Zr–^{95}Nb mixture is extracted under these conditions[19]. Solutions containing tartaric acid[22] as well as HF are recommended to minimise the sorption of these isotopes.

In a more recent paper[89] the same workers describe in detail the sorption mechanism of zirconium and niobium, allowing for the formation of hydrolysed and polymerised forms of these elements in aqueous solutions. Both elements give rise, in acid solutions, to chemical forms which can be sorbed on AMP both by ion exchange (cations) and by adsorption (neutral molecules, and colloidal particles). Addition of neutral salts was found to affect the sorption of zirconium and niobium on MPA, the distribution coefficients increasing with the concentration of ammonium and sodium ions, whereas under ion exchange conditions ammonium ions lower the sorption coefficients by taking part in the exchange equilibrium. Hence, the sorption of trace quantities of zirconium and niobium on AMP involves adsorption of hydrolysed or polymeric forms of these elements rather than ion exchange (as in the case of caesium). Complexing agents decrease the sorption of both elements by hindering the formation of strongly sorbed polymeric forms. The effect of complexing agents on the sorption of ^{95}Zr increases in the sequence $NO_3^- \ll$ tartrate ≅ citrate ≅ $SO_4^{2-} < F^- \cong$ oxalate, and for ^{95}Nb the series is citrate ≅ tartrate ≅ $NO_3^- \ll SO_4^{2-} < F^-$ ≅ oxalate.

The sorption of microgramme quantities of niobium on the caesium and ammonium salts of MPA was first studied[87] with the aim of separating niobium from a large excess of titanium. As in the case of trace amounts of ^{95}Nb,[89] the niobium is not desorbed by solutions of mineral acids, but it can be eluted quantitatively by 40 ml of a solution of NH_4F (0.2 M) at pH 2. Hence, and also in view of the considerable sorption of niobium from acid solutions and of the failure of ammonium

and sodium ions to influence the sorption, the interaction of niobium with HPA salts cannot be purely by ion exchange. Titanium is less strongly held by caesium molybdophosphate: it is not sorbed at an acidity >0.5 M HCl, and it can be desorbed quantitatively by a 5 M solution of HCl. The differences in behaviour of niobium and titanium can be used to separate these isotopes[87].

The sorption of thorium on ammonium molybdophosphate was first described by Ganzerli-Valentini and coworkers[37]. Their measurements (under static conditions at room temperature) included the effect of factors such as the concentration of nitric acid, time, and the concentration of ammonium nitrate on the distribution coefficient of thorium (D_{Th}) on AMP. By studying the dependence of D_{Th} on the time of shaking the solution with the sorbent it was found that equilibrium in solutions 10^{-3} M and 0.7 M with respect to HNO_3 is reached in 12 and 8 h respectively. The plot of $\lg D_{Th}$ against concentration of nitric acid is fairly complex (Fig.5): at nitric acid concentrations below 0.3 M the dependence is non-linear, but the experimental points for 0.3–1 M HNO_3 lie on a straight line of slope −3.7. The maximum value of D_{Th} is 13500. The linearity of the plot of $\lg D_{Th}$ against $\lg [HNO_3]$ denotes that in this region of $[HNO_3]$ values of Th^{4+} ion is replacing the acidic hydrogen of AMP by an ion exchange mechanism. The deviation of the slope from an integral value was first ascribed[37] to experimental error, but in view of the reproducibility of the measurements the authors then concluded that the activity of thorium in solution may be affected by the concentration of nitric acid through the formation of nitrato complexes.

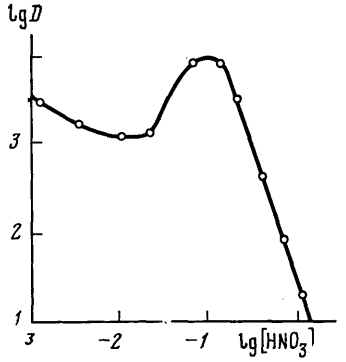


Figure 5. Distribution coefficient of thorium on AMP against the acidity of the medium[37].

The authors[37] do not reach a firm conclusion on the sorption mechanism of thorium for $[HNO_3] < 0.3$ M, though they suggest the possibility of formation of thorium hydrolysis products, or of complexes of thorium with molybdophosphoric acid or its decomposition products. It is not stated whether these complexes are formed in the liquid phase or in the ion exchanger, but nevertheless the slow equilibration in a 10^{-3} M HNO_3 solution (as compared with 0.7 M HNO_3) is ascribed to the formation of these complexes.

The following dependence of $\lg D_{Th}$ on the concentration of ammonium nitrate was observed (Fig.6): between 5×10^{-3} and 1.5×10^{-2} M NH_4NO_3 the plot is linear, with a slope of −4, confirming that the interaction of thorium with AMP is by an ion exchange mechanism, but for $[NH_4NO_3] > 1.5 \times 10^{-2}$ M there is a change in slope which the authors[37] ascribe (as in the case of nitric acid) to a change in the activity of thorium ions in solution. In all the equilibrium experiments the pH was measured in the initial solutions as well as at equilibrium. In every case the pH of the equilibrium solution was found to be lower by ~0.1 pH unit, confirming that the acidic hydrogen of the sorbent is involved in the exchange.

With thorium, uranium, and neptunium the experiments under dynamic conditions show a hysteresis effect[40] which had been briefly mentioned in Ref.37. Whereas thorium is sorbed on AMP from 10^{-3} M HNO_3, its removal from the column begins at a concentration of 0.5 M HNO_3, and does not go to completion. A mixture of 1 M HNO_3 + 1 M NH_4NO_3 removes 70% of the thorium, and a 2 M HNO_3 + 1 M NH_4NO_3 solution removes 90%. Increasing the concentration of ammonium nitrate has little effect on the elution of the thorium, but by increasing the concentration of acid we can remove the thorium from the column quantitatively (at 8 M HNO_3). If sulphuric acid is used as the eluent the thorium can be washed out of the column at a lower concentration of the acid.

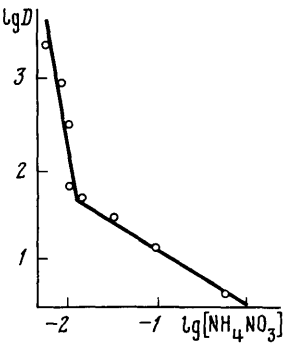


Figure 6. Distribution coefficient of thorium on AMP against concentration of NH_4NO_3 (in 0.1 M HNO_3). [37]

Np(IV) behaves in many ways like Th(IV) during sorption on AMP. The shift of the linear portion of the $\lg D_{Np}$ against $\lg [HNO_3]$ plot towards acidities greater than in the case of thorium is explained[39] by a higher tendency towards hydrolysis. In the region of 0.5–2.5 M HNO_3 the slope of the linear portion denotes exchange of a Np(IV) particle. However, at lower acidities the sorption of Np(IV) is no longer described by an ion-exchange reaction. Experiments under dynamic conditions[40] have shown that the sorption of Np(IV) on AMP is even more irreversible than that of thorium: even 14 M nitric acid cannot elute more than 87% of the neptunium.

It has been confirmed experimentally[40] that thorium, neptunium, and (to some extent) uranium can form complexes with molybdophosphate or its decomposition products under the conditions needed for the sorption of these elements on AMP. It is not stated[40] whether these complexes are formed in the solid or in the liquid phase. However, it is suggested that the AMP lattice may be distorted by the small size and high charge of the Np(IV) and Th(IV) ions, causing an increase in the rate of decomposition of the AMP, but the influence of these changes on the distribution coefficients of the sorbed ions is not made clear.

The maximum in the plot of the sorption of neptunium(IV) against time of contact between the phases (Fig.7) is explained[39] by postulating that the Np(IV) ions initially adsorbed on the AMP surface can form complexes with the heteropoly anions which are then returned (in part) to the solution. The possibility of complex formation in the solid phase is specifically mentioned in order to explain the difference between the slope (−2) of the plot of $\lg D_{Np}$ against $\lg [NH_4NO_3]$ and the expected value (−4), and also the almost total irreversibility of the sorption of Np(IV) under dynamic conditions[40].

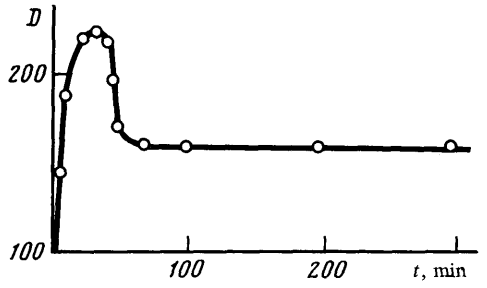


Figure 7. Distribution coefficient of neptunium(IV) on AMP against time of contact between the phases[39].

In an attempt to clarify the treatment of the sorption mechanism of thorium on AMP the writers have shown[43] that the dominant process at pH 0–1.15 is ion exchange of the thorium for the ammonium or the acidic hydrogen of the sorbent. Further evidence for this conclusion comes from the dependence of the distribution coefficient of thorium on AMP on the concentration of phosphate and molybdate ions in solution at pH 0.7: the phosphate ions have almost no effect on the sorption of thorium, whereas addition of molybdate ions to the solution gives a lower value of D_{Th}. This can be explained by postulating the formation by thorium in aqueous solutions of molybdenum–thorium heteropoly complexes of an anionic type[69], which cannot be sorbed in the outer sphere of the AMP.

Simultaneously present phosphate and molybdate ions have a more marked effect than molybdate ions alone. The measurements were made at pH 0.7, which corresponds to the optimum conditions for the formation of the soluble thorium–phosphorus–molybdenum triple complex[78] (of the anionic type). Since under the present conditions the triple complex is more stable than the double (thorium–molybdenum) complex, the sorption of thorium on AMP is almost totally suppressed by the presence of the phosphomolybdate reagent. Hence, the sorption of thorium on AMP is hindered by the formation of heteropoly complexes in the aqueous phase. From the sorption isotherms on AMP at different temperatures[43] we find that the sorption of thorium on AMP increases with temperature, in contrast to the behaviour of true ion exchange systems. This effect sets in at high concentrations of thorium.

Thus, the ion exchange process is complicated by the interaction of thorium with the anionic part of the sorbent. In order to establish whether molybdenum is displaced from the coordination sphere of the AMP, or whether the metal is adsorbed on the anion surface as a result of interaction with an oxygen end-atom, the equilibrium solutions were analysed for molybdenum and phosphorus during the measurement of the isotherms. No correlation between the amount of sorbed thorium and the amount of molybdenum in solution could be found, and therefore any interaction between the thorium and the anionic part of the sorbent can only be of the addition type.

As was stated above, an increase in pH favours the decomposition of heteropoly compounds of the 12th series with formation of compounds of the 11th series[48,54]. Thorium can form relatively stable compounds with the latter[56]. Therefore we cannot exclude the possibility of an equilibrium between 11th- and 12th-series compounds on the surface of the sorbent in contact with the solution, the presence of the 11th-series compounds enabling the thorium to form complexes with the anionic part of the sorbent.

In the case of selenium and tellurium—the next members of this group of ions—kinetic measurements have shown[41] that sorption is accompanied by chemical interaction with the anionic part of the sorbent. The experimental results obey the equation for diffusion within the grain. In order to identify the rate-limiting step unequivocally the activation energies for the sorption of Se(IV) and Te(IV) on AMP were calculated (18.4 and 7.7 kcal $mole^{-1}$ respectively). These values confirm that diffusion in the grain is the slowest step in the process. When the chemical interaction between the ions and the sorbent is unhindered (small ionic radii, high concentration of sorbed ions, and long contact times between the sorbent and the solution) the kinetic curves no longer obey the diffusion equations. The presence of chemical interactions between the anion of the sorbent and the sorbed ion is confirmed by the lack of dependence of the rate of sorption of Se(IV) on the nature of the cation of the sorbent and on the concentration of electrolyte.

Studies of the sorption of Se(IV) and Te(IV) on AMP under equilibrium conditions have shown[42] that the hydrogen ions in the sorbent can contribute to the ion exchange process if the acidity of the solution is high enough. At higher pH values the value of D is unaffected by changes in acidity, suggesting chemical interaction between the sorbed ion and the sorbent matrix.

The exchange constants and thermodynamic exchange functions have been calculated from the sorption isotherms. The change in the thermodynamic Gibbs potential ($\Delta\Phi$) is negative for both Se(IV) and Te(IV), indicating that the sorption of both elements is selective on AMP. This is due mainly to the increase in the entropy of the system, since the enthalpy factor is unfavourable in this case ($\Delta H > 0$). The conditions for optimum sorption of selenium and tellurium coincide with the existence region[94–97] of the known double and triple complexes of Se(IV) and Te(IV) with molybdate and molybdophosphate: therefore, the concentrations of molybdenum and phosphorus in the equilibrium solutions were determined[42] during the measurement of the sorption isotherms under equilibrium conditions in order to clarify the interaction between these ions and the sorbent matrix. As the concentration of Te(IV) on the sorbent is increased, the amount of Mo(VI) and P(V) in solution is unchanged, but in the sorption of selenium it increases in proportion to the concentration of Se(IV), the average P : Mo ratio in solution being 1 : 12, i.e. the sorption of selenium is accompanied by a reconstruction of the sorbent matrix, leading to the transfer of molybdophosphate ions into the solution. Thus, published data on the mechanism of sorption lead to the conclusion that the sorption of ions of the second group on heteropoly acid salts is a multi-step process[42,43,98].

Step 1. Penetration of the sorbed ions into the macropores of the sorbent grain and ion exchange with a cation or acidic hydrogen of the sparingly soluble HPA salt.

Step 2. Sorption of the ions on the surface through interaction with the oxygen end-atoms of the anion structure, giving E–O–Mo bonds. This step is most marked when the sorbed ion has a strong tendency to form heteropoly acids. By comparing HPA stability data[69,99–102] with the conditions conducive to sorption of the corresponding ions[37–43,62,87–89,93,103] we arrive at the following affinity series:

$$Y^{III} < UO_2^{II} < Th^{IV} \simeq Ce^{IV} < Te^{IV} < Ti^{IV} < Zr^{IV} < Nb^{V}.$$

Step 3. In the case of ions with a high ionic potential the chemical interaction with the surface results in the removal of some of the molybdophosphate ions from the surface [as in the sorption of Se(IV)].

V. SORPTION OF IONS ABLE TO FORM THE COORDINATION SPHERE OF HETEROPOLY COMPOUNDS

Very little has been published on the sorption of molybdenum(VI), tungsten(VI), vanadium(V), and chromium(VI) ions on HPA series. However, we know[48] that these ions (in solutions) have a strong tendency to combine into polymeric structures, giving "mixed" heteropoly compounds. The best known of these are the mixed HPA of vanadium and molybdenum[104–107] and those of molybdenum and tungsten[108,109]. Some indirect information was obtained in studies of the coprecipitation of vanadium(V) with ammonium molybdophosphate[110,111]. The dependence of the extent of coprecipitation of vanadium on the amount of coprecipitant was found to vary with the concentration of vanadium in solution, i.e. to depend on the vanadium to phosphorus ratio. The incorporation of vanadium(V) into the precipitate is a maximum only when the conditions in the solution (acidity, excess of molybdate ions) are favourable to complex formation between phosphate, vanadate, and molybdate. Tsyganok and coworkers[111] have shown, by the molar ratio and isomolar series method, that a complex with a ratio of P : V = 1 : 1 is formed in solution during coprecipitation. Hence they concluded that the co-crystallisation process plays a dominant role in this system, since the replacement of one molybdenum atom by vanadium does not affect the structure of the heteropoly anion. The $PMo_{12}O_{40}^{3-}$ and $PMo_{11}VO_{40}^{4-}$ anions are isomorphous. The coprecipitation of vanadium on a pre-existing AMP precipitate has also been studied, and found to be less complete than coprecipitation during formation of the precipitate.

Thus, published data on the sorption mechanism of various ions on HPA salts lead us to conclude that more comprehensive studies of complex formation between the sorbed ions and the HPA anions are needed, under different conditions and in the presence of the components found in real mixtures, before the application of heteropoly acid salts in the separation and concentration of radioactive or stable isotopes can be further extended.

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