

ION-EXCHANGE PROPERTIES OF AMMONIUM SALTS OF HETEROPOLY-ACIDS

VII. SORPTION OF ^{137}Cs AND ^{86}Rb ON ACID AND NORMAL AMMONIUM AND THALLOUS SALTS OF PHOSPHOTUNGSTIC AND PHOSPHOMOLYBDIC ACID

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Data on Cs(Rb) sorption on thallos salts of HPA* have been particularly concerned with the separation under dynamic conditions^{1,2}. A considerably greater number of papers deal with the sorption of Cs and Rb on ammonium salts of HPA (e.g. refs. 3-10), however there is little published information concerning the mechanism of sorption. SMIT and coworkers¹¹ measured the distribution coefficient of the alkali metals in 0.1 M NH_4NO_3 on ammonium salts of different HPA and the validity of the mass-action law has been checked for the sorption of Rb on NH_4PMo^6 . In another paper¹², the characteristics of Cs sorption on ammonium phosphotungstate and phosphomolybdate were described. HEALY¹³⁻¹⁵ dealt with the preparation and composition of different salts of HPA and discussed the exchange properties of the salts prepared. He found that $(\text{NH}_4)_2\text{HPMo}$ and $(\text{NH}_4)_2\text{HPW}$ sorbed caesium less than the normal salts; and the sorption of rubidium was higher than that of caesium on these sorbents.

Our work aimed at finding the connections between sorption and sorbent composition, the constants characterizing Cs and Rb sorption, and at the interpretation of the mechanism of Cs and Rb sorption on these sorbents.

EXPERIMENTAL

Preparation of sorbents

Ammonium and thallos salts of phosphomolybdic and phosphotungstic acids were prepared by precipitating the commercial HPA (Lachema, C.P. grade) with ammonium and thallos nitrate solutions. The procedure involved dissolution of weighed amounts (40 g) of the HPA in a certain volume (300 ml) of nitric acid. Two kinds of salts were prepared, *viz.* the tertiary (normal) and the secondary (acid) ones. For the preparation of the tertiary salts, the acidity was 0.1 M HNO_3 while for the

* The following abbreviations are used in the article: HPA = Heteropolyacid (in general); $(\text{NH}_4)_3\text{PW}$ = tri-ammonium phosphotungstate; $(\text{NH}_4)_3\text{PMo}$ = tri-ammonium phosphomolybdate; $(\text{NH}_4)_2\text{HPW}$ = di-ammonium phosphotungstate; $(\text{NH}_4)_2\text{HPMo}$ = di-ammonium phosphomolybdate. Thallos salts ($\text{Tl}_3\text{PW}(\text{Mo})$, $\text{Tl}_3\text{HPW}(\text{Mo})$), caesium salts, or mixed salts are denoted similarly.

preparation of the secondary salts, a higher acidity of 3 M HNO₃¹³ was chosen. Clear solutions of HPA were precipitated either by an excess of ammonium (thallous) nitrate in the case of the normal salts, or by the stoichiometric amount of it in the case of acid salts, the nitrates being dissolved in nitric acid of the same concentration (30 ml in volume). The molar ratios of NH₄(Tl):HPA equalled 6:1 when the normal salts were prepared and 1.7–2.0:1 when the acid salts were precipitated, according to literature^{13,14}. The precipitates formed of ammonium (thallous) salts were separated from the mother liquor by centrifuging and they were washed three times with nitric acid of the same concentration as that from which the salts were precipitated. After washing, the precipitate was dried at 60° and analyzed for ammonium ion (thallium), phosphorus, molybdenum, tungsten, and water. Ammonium ion was determined colorimetrically by means of the Nessler reagent¹⁶; the phosphorus in the heteropolyacids containing molybdenum was determined colorimetrically as phosphomolybdo vanadic acid^{16,17}, while in heteropolyacids containing tungsten it was also determined colorimetrically but as the phosphotungsto vanadic acid¹⁷; tungsten and molybdenum were determined gravimetrically by means of oxine and after annealing to oxides¹⁸; thallium was determined as chromate¹⁸; the water of crystallization by drying at 164° for the phosphomolybdate and at 271° for the phosphotungstate.¹⁹

The results of the analyses are summarized in Tables I and II.

The results of the analyses of the salts prepared show that the composition of the synthesized compounds differs from the theoretical only negligibly and that the

TABLE I

RESULTS OF THE ANALYSES OF AMMONIUM SALTS OF PHOSPHOMOLYBDIC AND PHOSPHOTUNGSTIC ACIDS

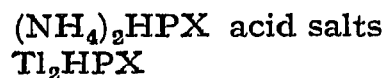
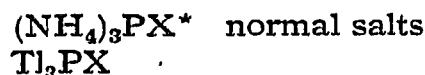
| <i>Ion exchanger</i> | % NH ₄ | | % P | | % Mo | | % W | | % H ₂ O | |
|--------------------------------------|-------------------|---------------|--------------|---------------|--------------|---------------|--------------|---------------|--------------------|---------------|
| | <i>Found</i> | <i>Theor.</i> | <i>Found</i> | <i>Theor.</i> | <i>Found</i> | <i>Theor.</i> | <i>Found</i> | <i>Theor.</i> | <i>Found</i> | <i>Theor.</i> |
| (NH ₄) ₃ PMo | 2.66 | 2.80 | 1.59 | 1.61 | 59.2 | 59.0 | | | 2.7 | 2.7 |
| (NH ₄) ₂ HPMo | 1.59 | 1.85 | 1.56 | 1.59 | 58.2 | 59.0 | | | 4.4 | 4.4 |
| (NH ₃) ₃ PW | 1.45 | 1.28 | 0.99 | 0.99 | | | 72.0 | 70.5 | 6.2 | 6.2 |
| (NH ₄) ₂ HPW | 1.13 | 1.17 | 1.00 | 1.01 | | | 71.0 | 72.1 | 5.1 | 5.1 |

TABLE II

RESULTS OF THE ANALYSES OF THALLOUS SALTS OF PHOSPHOMOLYBDIC AND PHOSPHOTUNGSTIC ACIDS

| <i>Ion exchanger</i> | % Tl | | % P | | % Mo | | % W | | % H ₂ O | |
|----------------------|--------------|---------------|--------------|---------------|--------------|---------------|--------------|---------------|--------------------|---------------|
| | <i>Found</i> | <i>Theor.</i> | <i>Found</i> | <i>Theor.</i> | <i>Found</i> | <i>Theor.</i> | <i>Found</i> | <i>Theor.</i> | <i>Found</i> | <i>Theor.</i> |
| Tl ₃ PMo | 24.1 | 24.4 | 1.27 | 1.23 | 47.0 | 45.6 | | | 3.2 | 3.2 |
| Tl ₂ HPMo | 16.7 | 17.0 | 1.31 | 1.29 | 48.5 | 47.8 | | | 7.2 | 7.2 |
| Tl ₃ PW | 16.5 | 17.2 | 0.87 | 0.87 | | | 62.3 | 62.1 | 2.0 | 2.0 |
| Tl ₂ HPW | 12.4 | 12.0 | 0.89 | 0.90 | | | 63.4 | 65.0 | 3.7 | 3.7 |

deviations are within the limits of experimental error. Hence, the following salts were prepared:



The sorption of ^{137}Cs and ^{86}Rb was studied with the above-mentioned thallos and ammonium salts under static conditions. The experiments were arranged so that the weighed amounts of the sorbent (0.10 g) were shaken with 6.00 ml solution of ammonium nitrate, thallos nitrate, or a mixture of ammonium nitrate and nitric acid, which contained carrier-free amounts of ^{137}Cs and ^{86}Rb (10^{-10} – 10^{-11} M). On establishing the equilibrium (5 h shaking is sufficient), the contents of the test tubes were centrifuged twice at 4000 r.p.m. and samples for activity measurement were taken from the centrifugate. The partition of caesium (rubidium) between both phases was determined by comparing the activities of the centrifugate and a standard measured under the same geometric conditions. The sorption was evaluated by means of the distribution coefficient K_d , which was defined as

$$K_d = \frac{{}^{137}\text{Cs} ({}^{86}\text{Rb}) \text{ activity in 1 g of the sorbent}}{{}^{137}\text{Cs} ({}^{86}\text{Rb}) \text{ activity in 1 ml of the solution at equilibrium}}$$

All relationships were studied at room temperature. All chemicals used were of A.R. grade.

RESULTS AND DISCUSSION

(a) Dependence of ^{137}Cs sorption on time of shaking

In order to reach equilibrium, sufficient time of contact of solid and liquid must be secured. Therefore, the dependence of $K_{d(\text{Cs})}$, as a function of the time of contact with both phases was studied. The results obtained for normal ammonium as well as thallos salts of phosphomolybdic acid are summarized in Fig. 1.

With the ammonium salt, the $K_{d(\text{Cs})}$ values practically did not vary with time and the equilibrium was established almost immediately, while with the thallos salt, constant values of K_d were obtained only after an hour's shaking. This difference is evidently connected with the bond strength between thallium, caesium, ammonium, and the heteropolyanion¹⁵. On the basis of the data plotted in Fig. 1, 5 hours' contact with both phases was chosen for all experiments.

(b) Dependence of ^{137}Cs sorption on ammonium nitrate concentration

The effect of the presence of ammonium ions in the solution on caesium sorption was investigated with ammonium as well as thallos salts of both heteropolyacids. The NH_4NO_3 concentration range chosen was 0.1–2.0 M for all sorbents. The results are plotted in Fig. 2.

From the course of most relationships for $\log K_d = f(\log [\text{NH}_4^+])$, which are

* X denotes Mo or W.

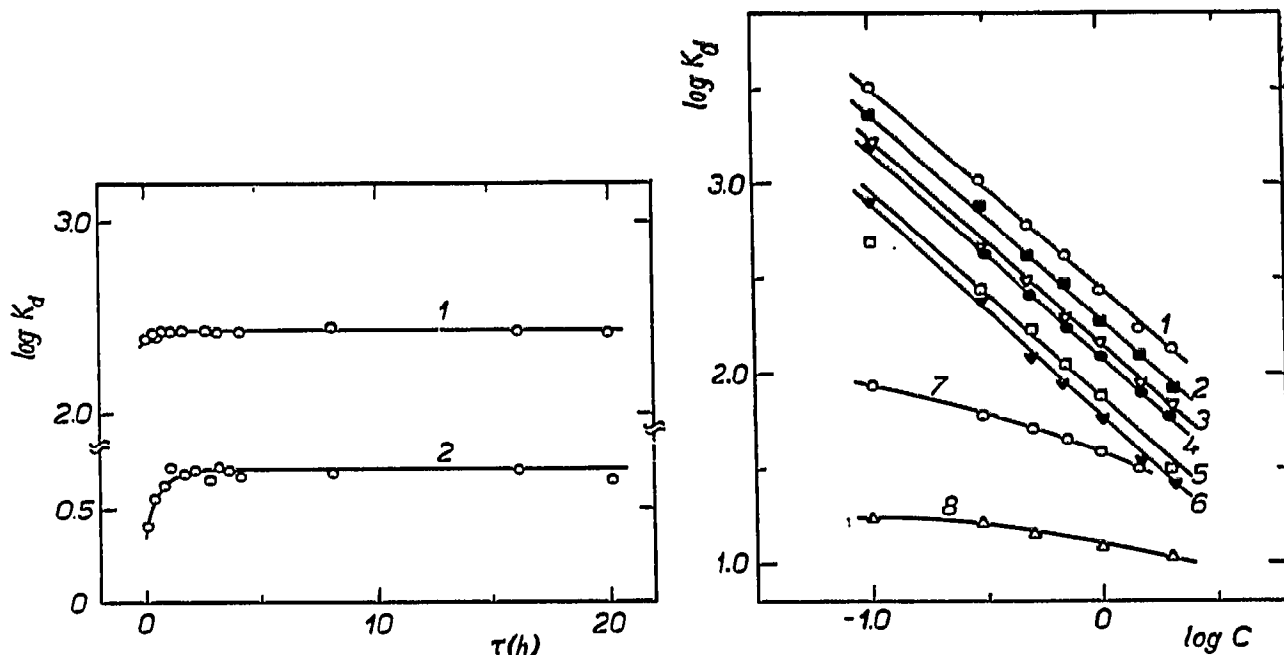


Fig. 1. Dependence of distribution coefficient K_d for Cs on time of contact with both phases. K_d = Distribution coefficient (ml/g); τ = time of contact with phase (h). 1 = $(\text{NH}_4)_3\text{PMo}$; $[\text{NH}_4\text{NO}_3] = 1.0 \text{ M}$; 2 = Tl_3PMo ; $[\text{TlNO}_3] = 0.01 \text{ M}$; $[\text{HNO}_3] = 0.01 \text{ M}$.

Fig. 2. Dependence of distribution coefficient K_d for Cs on ammonium nitrate concentration. K_d = Distribution coefficient (ml/g); C = molar concentration of NH_4NO_3 . 1 = $(\text{NH}_4)_3\text{PMo}$; 2 = $(\text{NH}_4)_3\text{PW}$; 3 = $(\text{NH}_4)_2\text{HPMo}$; 4 = Tl_2HPW ; 5 = Tl_2HPMo ; 6 = $(\text{NH}_4)_2\text{HPW}$; 7 = Tl_3PW ; 8 = Tl_3PMo ; $[\text{HNO}_3] = 0.01 \text{ M}$.

linear, one may expect that the exchange of Cs ions for NH_4 ions will be controlled by the law of mass action. From the value of the slope (-1), one may further suggest that one Cs^+ ion will replace one NH_4^+ ion, and vice versa. From this it follows that caesium is bonded to the sorbents studied by an ion-exchange mechanism.

The caesium-ammonium exchange may be, in our case, expressed by the equation:



In equilibrium, we obtain

$$K_{\text{Cs}/\text{NH}_4} = \frac{[\text{Cs}^+]_s [\text{NH}_4^+]_L}{[\text{Cs}^+]_L [\text{NH}_4^+]_s} \quad (2)$$

If Cs is a microcomponent, $[\text{NH}_4^+]_L \doteq [\text{NH}_4^+]_{\text{init}}$ and $[\text{NH}_4^+]_s = \text{const.}$ After modification, we obtain

$$\log K_d = \log (K_{\text{Cs}/\text{NH}_4} \cdot Q) - \log [\text{NH}_4^+]_L \quad (3)$$

where $[\text{Cs}^+]_s/[\text{Cs}^+]_L = K_d$, $[\text{NH}_4^+]_s \doteq Q$ is the total capacity of the sorbent, which corresponds to the maximum number of exchangeable ammonium ions of the sorbent.

When comparing relation (3) and the relationship shown in Fig. 2, agreement is

apparent and therefore the hypothesis of Cs ion exchange on ammonium and thallos salts of heteropolyacids is well-founded. For the calculation of the selectivity coefficient values, the maximum capacity of the sorbent, Q , must be known. The capacity was determined under static conditions for $(\text{NH}_4)_2\text{PW}$, as well as for $(\text{NH}_4)_2\text{PMo}$. The results are shown in Table III.

TABLE III

DETERMINATION OF MAXIMUM SORPTION CAPACITY FOR CAESIUM ON $(\text{NH}_4)_3\text{PMo}$ AND $(\text{NH}_4)_3\text{PW}$ 0.1 g $(\text{NH}_4)_3\text{PMo}$ (52 μmoles) and 0.1 g $(\text{NH}_4)_3\text{PW}$ (33 μmoles) were shaken in 6.00 ml 0.3 M NaNO_3 and 0.01 M HNO_3 .

| [CsNO_3] _{init} (M) | % S | | Mequiv. Cs/g | | g atoms Cs/mole P | |
|--|-----------------------------|----------------------------|-----------------------------|----------------------------|-----------------------------|----------------------------|
| | $(\text{NH}_4)_3\text{PMo}$ | $(\text{NH}_4)_3\text{PW}$ | $(\text{NH}_4)_3\text{PMo}$ | $(\text{NH}_4)_3\text{PW}$ | $(\text{NH}_4)_3\text{PMo}$ | $(\text{NH}_4)_3\text{PW}$ |
| 5.0×10^{-3} | 98.8 | 97.4 | 0.29 | 0.29 | 0.57 | 0.88 |
| 1.0×10^{-2} | 80.5 | 60.3 | 0.48 | 0.36 | 0.92 | 1.09 |
| 2.0×10^{-2} | 49.5 | 35.2 | 0.59 | 0.43 | 1.14 | 1.31 |
| 3.0×10^{-2} | 39.5 | 26.4 | 0.71 | 0.48 | 1.40 | 1.56 |
| 4.0×10^{-2} | — | 25.0 | — | 0.60 | — | 1.82 |
| 5.0×10^{-2} | 28.9 | 21.9 | 0.87 | 0.66 | 1.67 | 2.06 |
| 7.0×10^{-2} | 33.3 | — | 0.98 | — | 1.88 | — |
| 9.0×10^{-2} | 19.0 | 12.5 | 1.02 | 0.68 | 1.96 | 2.12 |

From Table III it follows that the maximum capacity of $(\text{NH}_4)_3\text{PMo}$ equals 1.0 mequiv. Cs per 1 g of sorbent, and that of $(\text{NH}_4)_3\text{PW}$ equals 0.66 mequiv. Cs per 1 g sorbent, which corresponds, in both cases, to the formation of a dicaesium ammonium salt of the type $\text{Cs}_2\text{NH}_4\text{PMo(W)}$. This statement is in agreement with that published by HEALY¹⁵. The Q values for Cs exchange on thallos salts of HPA were taken from ref. 15 where the formation of Tl_2CsPW is described.

The selectivity coefficient values, calculated from relation (2) under the above-mentioned presupposition are summarized in Table IV.

TABLE IV

SELECTIVITY COEFFICIENT VALUES $K_{\text{Cs}/\text{NH}_4}$ FOR EXCHANGE IN AMMONIUM AND THALLOS SALTS OF PHOSPHOMOLYBDIC AND PHOSPHOTUNGSTIC ACIDS AT A HNO_3 CONCENTRATION OF 0.01 M

| Ion exchanger | $K_{\text{Cs}/\text{NH}_4}$ |
|------------------------------|-----------------------------|
| $(\text{NH}_4)_3\text{PMo}$ | 2.8×10^2 |
| $(\text{NH}_4)_3\text{PW}$ | 2.9×10^2 |
| $(\text{NH}_4)_2\text{HPMo}$ | 1.5×10^2 |
| $(\text{NH}_4)_2\text{HPW}$ | 8.7×10^1 |
| Tl_2HPMo | 3.1×10^2 |
| Tl_2HPW | 2.8×10^2 |

The results show first that, in the presence of ammonium ions, caesium is sorbed equally well on the normal ammonium and acid thallos salts of both HPA. Further, one can see that caesium has a lower affinity to the acid than to the normal ammonium salts. In this respect, our results agree with those published by HEALY¹⁵. The reason for this difference in caesium sorption on acid and normal ammonium salts of HPA

may be sought in the different nature of the caesium bond. In the normal ammonium salts, caesium can be exchanged only for ammonium ion of the sorbent. In the case of acid ammonium salts, we can assume that the caesium can be exchanged for the ammonium ion or for the acid hydrogen ion of the sorbent. In order to elucidate the mechanism of caesium sorption on acid ammonium salts, the sorption of ^{137}Cs was investigated as a function of the concentration of hydrogen ions at constant concentration of ammonium (sodium) ions (Fig. 3).

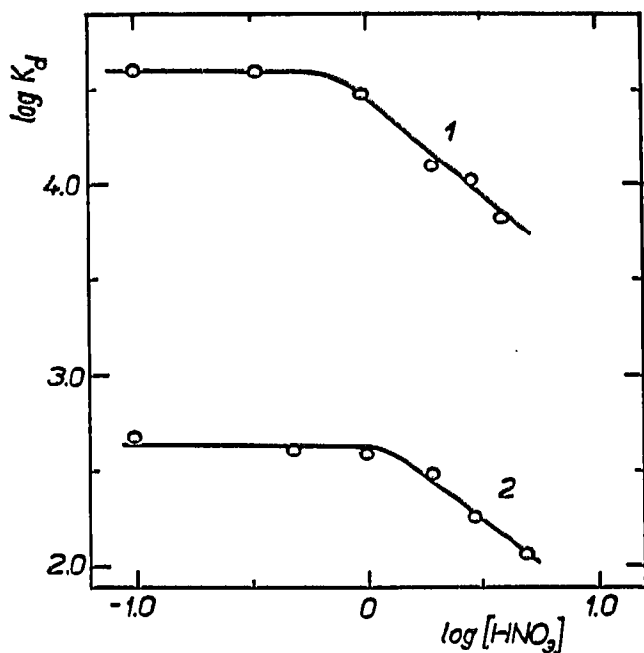


Fig. 3. Dependence of distribution coefficient K_d for Cs on nitric acid concentration. K_d = Distribution coefficient (ml/g); $[\text{HNO}_3]$ = molar concentration of HNO_3 . Sorbent: $(\text{NH}_4)_2\text{HPMo}$. 1 = 0.3 M NaNO_3 ; 2 = 0.5 M NH_4NO_3 .

From the course of the relationship: $\log K_d = f(\log [\text{HNO}_3])$ it follows that the sorption of ^{137}Cs on $(\text{NH}_4)_2\text{HPMo}$ does not depend on the acidity up to $[\text{HNO}_3] \ll 1 M$ (see curve 2). The effect of HNO_3 appears only at higher acidities when $\log K_d$ decreases linearly with a slope of -1 . This means that caesium is exchanged by acid hydrogen only at higher acidities and that 1 Cs^+ is exchanged again for 1 H^+ , and vice versa. Curve 1, where the experiments were performed in the presence of Na-ions instead of NH_4 -ions, has the same character.

In our former case (Fig. 2), the acidity of the solutions, from which caesium was sorbed, was 0.01 M, and therefore ^{137}Cs was exchanged for ammonium ion of the sorbent. The results show that the K_d as well as the $K_{\text{Cs}/\text{NH}_4}$ values are lower for acid ammonium salts, and from this we can conclude that ammonium ions in the ammonium salts of HPA are bonded by different strengths and that caesium is apparently very easily exchanged for the first, but less easily for the second ammonium ion. These conclusions are drawn for the exchange of microamounts of ^{137}Cs and they are not necessarily valid for macroconcentrations, or for the formation of salts precipitated from their components. The above mentioned conclusions are supported also by some solubility data published in the literature¹⁵.

The $K_d^{11, 12, 15}$ and K_{CS/NH_4}^{12} values presented in the literature when compared with our results differed very much. This is obviously caused by different methods of sorbent preparation, and composition¹¹.

With thalious salts of HPA, a difference exists between the sorption properties of acid and normal salts when sorbing caesium in the presence of ammonium salts because acid thalious salts sorb caesium far more. The explanation of this difference can be sought in an exceptionally strong bond between thallium and heteropoly-anion¹⁵. With the normal salts, thallium occupies all of the three hydrogen atoms of the HPA and therefore the substitution of thallium of the sorbent by caesium does not proceed readily and only to a far smaller extent. The K_d values consequently are low. Higher sorption of caesium on Tl_2HPW and Tl_2HPMo can be explained provided that caesium is bonded to the sorbent instead of the acid hydrogen. However, at higher ammonium ion concentrations in the solution, the formation of the dithalious ammonium salt can be supposed, by which caesium is sorbed by exchange for ammonium. The hypothesis of caesium exchange for the ammonium of the sorbent is more acceptable, it corresponds to the experimental results and the exchange of caesium for thallium. With acid thalious salts of HPA, the exchange of caesium for ammonium is controlled by the mass-action law and the K_{CS/NH_4} values are comparable with the K_{CS/NH_4} values for ammonium salts of HPA.

(c) *Dependence of ^{86}Rb sorption on ammonium nitrate concentration and the separation factor for Cs and Rb*

The dependence of ^{86}Rb sorption on ammonium nitrate concentration is shown in Fig. 4 for ammonium and thalious salts of HPA.

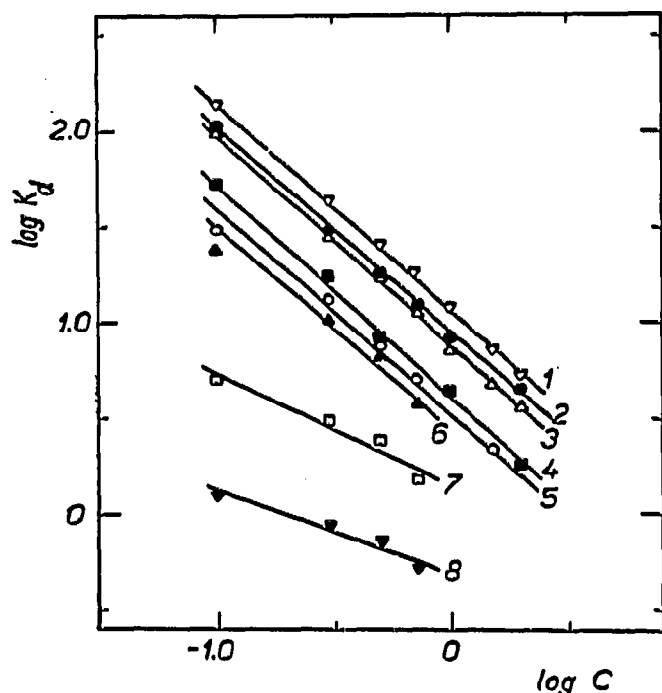


Fig. 4. Dependence of distribution coefficient K_d for Rb on ammonium nitrate concentration. K_d = Distribution coefficient (ml/g); C = molar concentration of NH_4NO_3 . 1 = $(NH_4)_3PMo$; 2 = $(NH_4)_3PW$; 3 = $(NH_4)_3HPMo$; 4 = $(NH_4)_2HPW$; 5 = Tl_2HPMo ; 6 = Tl_2HPW ; 7 = Tl_3PW ; 8 = Tl_3PMo ; $[HNO_3] = 0.01 M$.

The curves for $\log K_d = f(\log [\text{NH}_4^+])$ have the same character as those for the sorption of caesium, and rubidium may be therefore assumed to be sorbed by the same mechanism as caesium. The relations derived for caesium can be used for rubidium and, provided that finally the dirubidium ammonium salt is formed when sorbing an excess of rubidium, the selectivity coefficient values can be calculated for the exchange of rubidium with ammonium. The results are presented in Table V.

TABLE V

SELECTIVITY COEFFICIENT VALUES $K_{\text{Rb}/\text{NH}_4}$ FOR EXCHANGE IN AMMONIUM AND THALLOUS SALTS OF PHOSPHOMOLYBDIC AND PHOSPHOTUNGSTIC ACIDS AT A HNO_3 CONCENTRATION OF 0.01 *M*

| <i>Ion exchanger</i> | $K_{\text{Rb}/\text{NH}_4}$ |
|------------------------------|-----------------------------|
| $(\text{NH}_4)_3\text{PMo}$ | 12.2 |
| $(\text{NH}_4)_3\text{PW}$ | 13.7 |
| $(\text{NH}_4)_2\text{HPMo}$ | 8.1 |
| $(\text{NH}_4)_2\text{HPW}$ | 6.0 |
| Tl_2HPMo | 9.3 |
| Tl_2HPW | 10.0 |

HEALY¹⁵ suggests that, for acid salts, $K_{d(\text{Rb})} > K_{d(\text{Cs})}$, our results show that acid as well as normal salts of heteropolyacids sorb heavy alkali metals in the order $\text{Cs} > \text{Rb}$. The K_d values published in the literature for phosphomolybdate differ from those measured in this work by more than the K_d values for phosphotungstate^{6, 20, 15}.

The same conclusions as those for the sorption of caesium are valid for the sorption of rubidium on thallos salts of HPA, though caesium is sorbed more than rubidium on thallos salts of heteropolyacids.

The differences between the sorption of ¹³⁷Cs and that of ⁸⁶Rb show that there is a possibility of using these sorbents for the separation of these elements. The values of the separation factors (defined as a ratio of $K_{d(\text{Cs})}/K_{d(\text{Rb})}$, or $K_{\text{Cs}/\text{NH}_4}/K_{\text{Rb}/\text{NH}_4}$) in ammonium salts medium are presented in Table VI for both ammonium and thallos salts of HPA.

TABLE VI

SEPARATION FACTOR VALUES $\alpha_{\text{Cs}/\text{Rb}}$ FOR SORPTION ON THALLOUS AND AMMONIUM SALTS OF HETEROPOLYACIDS WHEN USING AMMONIUM SALTS AT A HNO_3 CONCENTRATION OF 0.01 *M*

| <i>Sorbent</i> | $\alpha_{\text{Cs}/\text{Rb}}$ |
|------------------------------|--------------------------------|
| $(\text{NH}_4)_3\text{PMo}$ | 23.4 |
| $(\text{NH}_4)_3\text{PW}$ | 21.3 |
| $(\text{NH}_4)_2\text{HPMo}$ | 18.2 |
| $(\text{NH}_4)_2\text{HPW}$ | 14.5 |
| Tl_2HPMo | 33.3 |
| Tl_2HPW | 28.0 |

Table VI shows that there is less possibility of separating rubidium from caesium on acid ammonium salts of heteropolyacids than on normal salts. The separation factor data presented in literature are, on the whole, in agreement^{6, 20, 21} with our

values. The values of the separation factors, $\alpha_{Cs/Rb}$, measured for acid thallos salts of heteropolyacids are higher than those for ammonium salts, which means that the separation of rubidium from caesium would proceed better and more completely with the acid thallos salts.

In an ideal case, the separation factor $\alpha_{Cs/Rb}$ should represent the exchange constant $K_{Cs/Rb}$, which would mean the exchange of ^{137}Cs for rubidium ions of the sorbent should be accomplished in the presence of macroconcentrations of Rb in the solution. In our experiments, we sorbed microamounts of ^{137}Cs on ammonium salts of HPA in the presence of macroamounts of rubidium and thus we introduced, to a certain extent, an error due to the change in the sorbent composition. The results of the experiment made with two ammonium salts of HPA are summarized in Fig. 5.

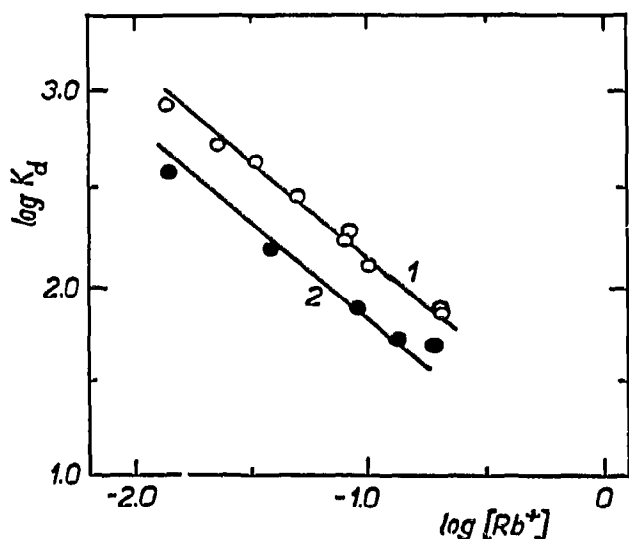


Fig. 5. Dependence of distribution coefficient K_d for caesium on rubidium nitrate concentration. K_d = Distribution coefficient (ml/g); $[Rb^+]$ = molar concentration of $RbNO_3$. 1 = $(NH_4)_3PMo$; 2 = $(NH_4)_3PW$; $[HNO_3] = 0.01 M$. In the plot, equilibrium Rb concentrations are shown, supposing that $Rb_2NH_4PMo(W)$ salt is formed.

The course of the relation: $\log K_{d(Cs)} = f(\log [Rb^+])$ is linear for both sorbents studied, the slope of the straight line being -1 . If we calculate the $K_{Cs/Rb}$ values, with the presupposition presented in part (a), *viz.* that the dicaesium rubidium salt will be formed when sorbing an excess of caesium (see Table VII, column (a)), we obtain the $K_{Cs/Rb}$ values that are approximately half the $\alpha_{Rb/Cs}$ values. This disagreement may be explained obviously by a change in the sorbent composition caused by the action of rubidium ions. In the limiting case, the Rb_2NH_4PX salt can be formed, by which

TABLE VII

COMPARISON OF SELECTIVITY COEFFICIENT VALUES $K_{Cs/Rb}$ WITH SEPARATION FACTORS $\alpha_{Cs/Rb}$ AT A HNO_3 CONCENTRATION OF $0.01 M$

| Ion exchanger | $K_{Cs/Rb}$ (a) | $K_{Cs/Rb}$ (b) | $\alpha_{Cs/Rb}$ |
|---------------|-----------------|-----------------|------------------|
| $(NH_4)_3PMo$ | 13.4 | 26.7 | 23.4 |
| $(NH_4)_3PW$ | 11.7 | 23.4 | 21.3 |

caesium is sorbed. Caesium can be exchanged either for ammonium of the sorbent or for both ammonium and rubidium of the sorbent. The exchange of caesium for ammonium seems to be the most acceptable for interpretation of the results. In the presence of an excess of Cs, the formation of dirubidium caesium salt may be presumed and, in this case, the $K_{Cs/Rb}$ values agree with the $\alpha_{Rb/Cs}$ values. (Table VII, column (b).)

(d) Sorption of ^{137}Cs and ^{86}Rb on ammonium and thalious salts of heteropolyacids in the presence of thalious ions

The curves of K_d for ^{137}Cs and ^{86}Rb sorption on ammonium and thalious salts of HPA in the presence of thalious ions are plotted in Figs. 6 and 7.

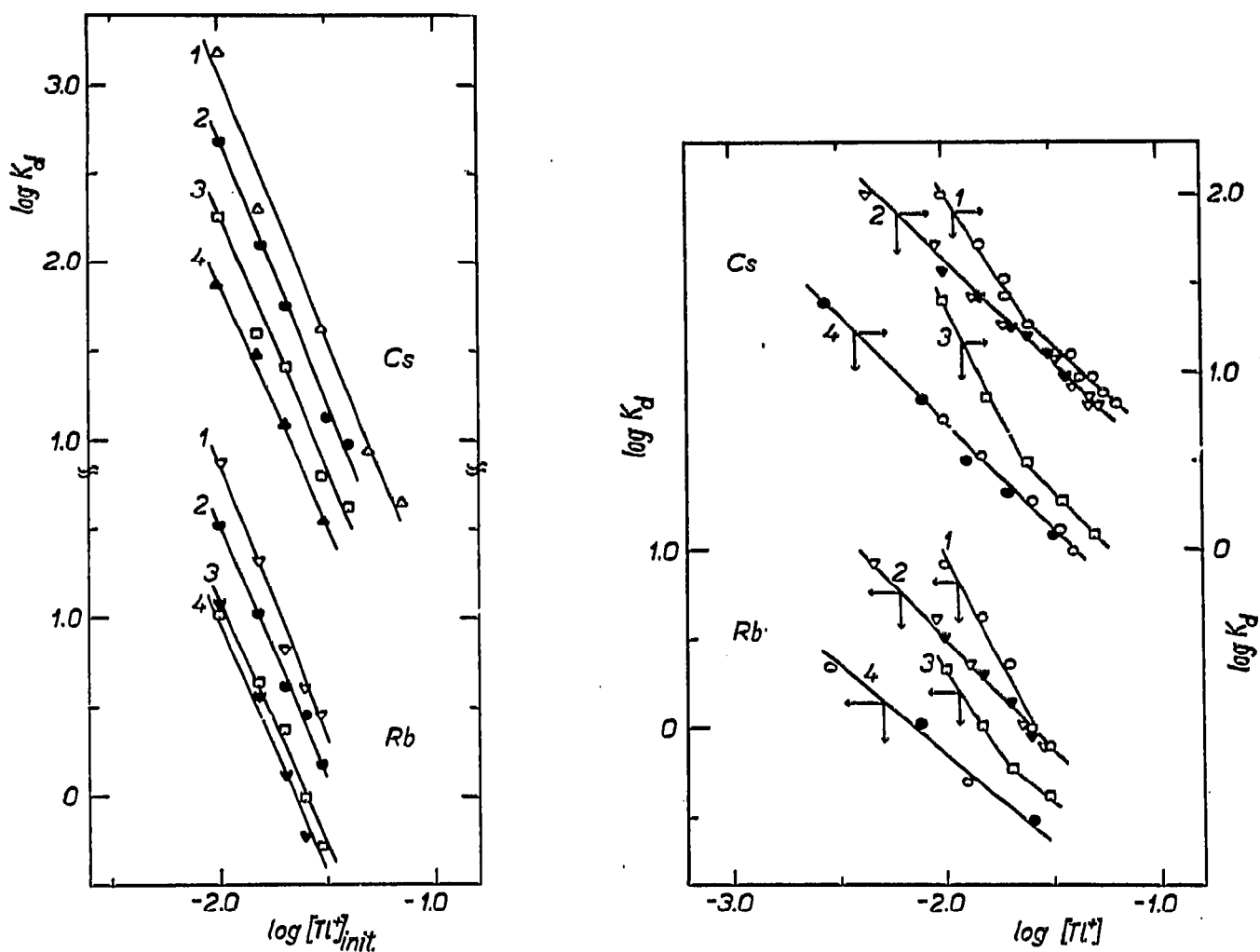


Fig. 6. Dependence of distribution coefficient K_d for Cs and Rb on thalious nitrate concentration. K_d = Distribution coefficient (ml/g); $[Tl^+]_{init}$ = molar concentration of Tl in initial solution. 1 = $(NH_4)_3PMo$; 2 = $(NH_4)_3PW$; 3 = $(NH_4)_3HPMo$; 4 = $(NH_4)_3HPW$; $[HNO_3] = 0.01 M$.

Fig. 7. Dependence of distribution coefficient K_d for Cs and Rb on Tl ion concentration in solution. K_d = Distribution coefficient (ml/g); $[Tl^+]$ = molar concentration of $TlNO_3$. 1 = Tl_3HPW ; 2 = Tl_3PW ; 3 = Tl_3HPMo ; 4 = Tl_3PMo ; $[HNO_3] = 0.01 M$. \blacktriangle Equilibrium concentrations of Tl, assuming that $Tl_3PW(Mo)$ salt is formed.

Thalious ions greatly affect the sorption of caesium and rubidium on ammonium and thalious salts of HPA. Considerable depression of caesium and rubidium sorption is caused by the high affinity of thallium to the sorbent¹⁵. The course of the relation: $\log K_d = f(\log [Tl^+]_{init})$ is somewhat unusual, which is true also for the slope, the value of which is -3^* . This is obviously caused by the fact that the condition of $[Tl^+]_{init} \doteq [Tl^+]_{equilibrium}$ is valid neither for ammonium nor thalious salts of HPA and a change in the sorbent composition may occur. The exchange of ¹³⁷Cs may be regarded as a result of two reactions on thalious ions. They are, on the one hand, the exchange of Tl⁺ for NH₄⁺ of the sorbent and the competitive exchange of Tl⁺ for Cs⁺ on the other. As it is difficult to find to what extent the sorbent composition has changed, we cannot describe the sorption of Tl on NH₄ salts of HPA quantitatively.

The situation when sorbing Cs and Rb on thalious salts of HPA is somewhat clearer. The dependence of $\log K_{d(Cs,Rb)} = f(\log [Tl^+])$ gives a straight line with a slope of -1 for normal thalious salts of HPA, while for acid salts, $\log K_d$ decreases at the beginning with a slope of -2 , and only later with a slope of -1 . This course of the sorption dependence is obviously connected with the change in the sorbent composition and, consequently, with a change in the concentration of free thallium in the solution. If one assumes that an excess of thallium causes the formation of the normal salt of the HPA from the acid thalious salt, we also obtain a linear course for the sorption dependence for acid thalious salts of HPA, which is coincident with the dependence for normal thalious salt. This means that acid thalious salts of HPA are not stable in the presence of thalious ions and give normal salts. The values of the selectivity coefficients of the exchange of Cs⁺ and Rb⁺ ions for Tl⁺ are presented in Table VIII together with the separation factors $\alpha_{Cs/Rb}$ supposing the formation of, at most, dithalious caesium (rubidium) salt.

TABLE VIII

VALUES OF SELECTIVITY COEFFICIENTS $K_{Cs/Tl}$, $K_{Rb/Tl}$, AND SEPARATION FACTORS $\alpha_{Cs/Rb}$ FOR EXCHANGE IN THALIOUS SALTS OF HPA

$[HNO_3] = 0.01 M$.

| <i>Ion exchanger</i> | $K_{Cs/Tl}$ | $K_{Rb/Tl}$ | $\alpha_{Cs/Rb}$ |
|----------------------|-------------|-------------|------------------|
| Tl ₂ HPW | 1.43 | 0.12 | 11.9 |
| Tl ₃ PW | 1.43 | 0.12 | 11.9 |
| Tl ₂ HPMo | 0.13 | 0.02 | 7.2 |
| Tl ₃ PMo | 0.13 | — | — |

The selectivity coefficient values for Cs are very low and they indicate, on the one hand, the great affinity of thallium to the sorbent and, on the other, allow us to use Tl salts for the desorption of sorbed caesium (rubidium). The separation factors obtained are considerably lower than those obtained with ammonium salts, and therefore Tl salts do not seem to be useful for a more complete separation of rubidium and caesium, even when the trivalency of Tl will certainly play a role in this separation.

* While experimenting with the Tl⁺-ions, we did not expect them to change to Tl³⁺ ions, according to the literature data available²².

(e) Sorption of ^{137}Cs and ^{86}Rb from alcoholic-aqueous medium and their separation factors

The sorption of ^{137}Cs (^{86}Rb) from an alcoholic-aqueous medium was studied with the $(\text{NH}_4)_3\text{PMo}$ and $(\text{NH}_4)_2\text{HPMo}$ pair of sorbents. Methyl alcohol and ethyl alcohol were chosen. The dependence of ^{137}Cs (^{86}Rb) sorption on the percentage of alcohol in the aqueous phase is plotted in Fig. 8.

The K_d values for ^{137}Cs as well as for ^{86}Rb increase with increasing alcohol concentration. A number of factors obviously play their role under these conditions, as for example, the decrease in solubility of the sorbent and the salts formed, etc., and one of them is also the increased dissociation of NH_4^+ ions to their components in alcoholic medium: $\text{NH}_4^+ \rightleftharpoons \text{NH}_3 + \text{H}^{+23}$. In the presence of alcohol, the same situation occurs as in water, *viz.* that the sorption of ^{137}Cs (^{86}Rb) on acid ammonium salts of HPA is lower than that on normal salts. The dependence of ^{137}Cs (^{86}Rb) sorption on the concentration of ammonium ions in 50 % alcoholic medium is shown in Fig. 9.

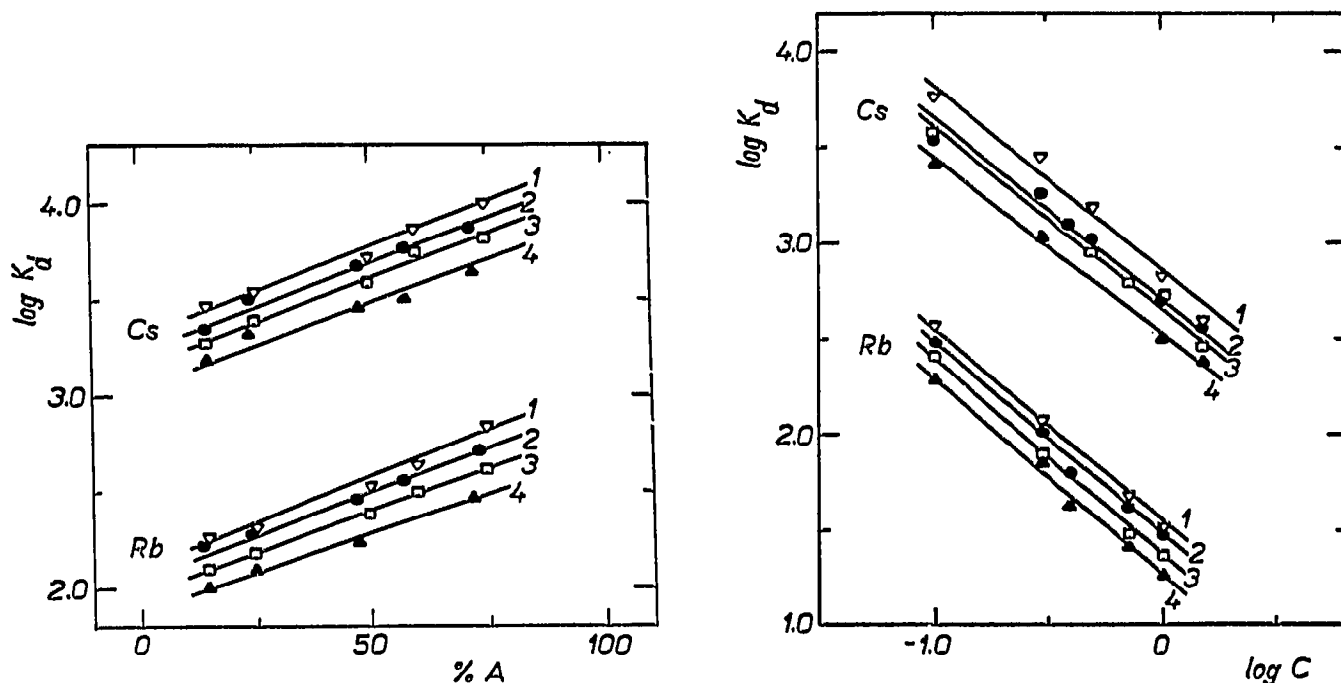


Fig. 8. Dependence of distribution coefficient K_d for Cs and Rb on alcohol content in solution. K_d = Distribution coefficient (ml/g); % A = volume percentage of methanol (ethanol) in solution. 1 = $(\text{NH}_4)_3\text{PMo}$, CH_3OH ; 2 = $(\text{NH}_4)_3\text{PMo}$, $\text{C}_2\text{H}_5\text{OH}$; 3 = $(\text{NH}_4)_2\text{HPMo}$, CH_3OH ; 4 = $(\text{NH}_4)_2\text{HPMo}$, $\text{C}_2\text{H}_5\text{OH}$; $[\text{NH}_4\text{NO}_3] = 0.1 \text{ M}$. $[\text{HNO}_3] = 0.01 \text{ M}$.

Fig. 9. Dependence of distribution coefficient K_d for Cs and Rb on ammonium nitrate concentration in 50 % alcohol. K_d = Distribution coefficient (ml/g); C = molar concentration of NH_4NO_3 . 1 = $(\text{NH}_4)_3\text{PMo}$, CH_3OH ; 2 = $(\text{NH}_4)_3\text{PMo}$, $\text{C}_2\text{H}_5\text{OH}$; 3 = $(\text{NH}_4)_2\text{HPMo}$, CH_3OH ; 4 = $(\text{NH}_4)_2\text{HPMo}$, $\text{C}_2\text{H}_5\text{OH}$; $[\text{HNO}_3] = 0.01 \text{ M}$.

The results show that $\log K_{d(\text{Cs}, \text{Rb})} = f(\log [\text{NH}_4^+])$ is linear with a slope of -1 and the K_d values are higher throughout the whole concentration range studied when compared with those obtained in an aqueous medium. As the courses of the relation plotted in Fig. 9 are coincident, all the conclusions drawn for the sorption of ^{137}Cs (^{86}Rb) in aqueous medium in the presence of NH_4^+ may be applied to these relations and the values of the selectivity coefficients $K_{\text{Cs}/\text{NH}_4}$ ($K_{\text{Rb}/\text{NH}_4}$) and the separation factors $\alpha_{\text{Cs}/\text{Rb}}$ may be calculated. The results are summarized in Table IX.

TABLE IX

VALUES OF SELECTIVITY COEFFICIENTS K_{Cs/NH_4} , K_{Rb/NH_4} AND SEPARATION FACTORS $\alpha_{Cs/Rb}$ FOR EXCHANGE IN AMMONIUM SALTS OF PHOSPHOMOLYBDIC ACID IN ALCOHOLIC-AQUEOUS MEDIUM
 $[HNO_3] = 0.01 M$.

| Ion exchanger | K_{Cs/NH_4} | | $K_{Cs/Rb}$ | | $\alpha_{Cs/Rb}$ | |
|----------------|-------------------|--------------------|------------------|--------------------|------------------|--------------------|
| | 50 % CH_3OH | 50 % C_2H_5OH | 50 % CH_3OH | 50 % C_2H_5OH | 50 % CH_3OH | 50 % C_2H_5OH |
| $(NH_4)_3PMo$ | 6.2×10^2 | 5.5×10^2 | 34.8 | 30.8 | 18.0 | 17.9 |
| $(NH_4)_2HPMo$ | 4.8×10^2 | 3.5×10^2 | 23.1 | 19.7 | 20.8 | 18.0 |

The selectivity coefficient values K_{Cs/NH_4} (K_{Rb/NH_4}) measured in alcoholic-aqueous medium are considerably higher (2-3 times) than those measured in water. Therefore, the efficiency of the separation of trace amounts of caesium as well as rubidium seems to be increased by the presence of alcohol. Nevertheless, the separation factor values are lower than those obtained in water. Hence, the alcoholic-aqueous medium appears to affect only the magnitude of ^{137}Cs (^{86}Rb) sorption, which increases in this medium, while the separation of the two elements (Cs, Rb) is not positively affected by alcoholic-aqueous medium.

SUMMARY

The sorption of ^{137}Cs and ^{86}Rb on acid and normal ammonium and thallos phosphomolybdate and phosphotungstate was studied under static conditions. The values of the distribution and selectivity coefficients, which characterize the sorption of ^{137}Cs and ^{86}Rb on the above-mentioned sorbents under different conditions (the presence of ammonium and thallos salts, organo-aqueous medium), were determined together with the values of the separation factors for both elements, and an interpretation of the mechanism of sorption of caesium and rubidium on the sorbents studied was suggested.

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