SORPTION OF POLYVALENT ELEMENTS ON SILICA GEL. II.*

SORPTION OF PROTACTINIUM ON SILICA GEL FROM MIXED AQUEOUS–ORGANIC SOLUTIONS OF HCl AND HNO₃

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The effect of methanol, ethanol, 1-propanol, 2-propanol, acetone, and dioxane on the sorption of protactinium on silica gel has been studied. It has been found that in the presence of these solvents the sorption of protactinium decreases and the sorption kinetics is slower. The values of the distribution coefficients depend not only on the composition of the solution but — in several cases — also on its age. The sorption kinetics is mainly governed by the structure of silica gel. The effect of alcohols on the sorption of protactinium increases with the increasing number of carbon atoms in the alcohol molecule. The results are explained by the formation of ionic associates. The associates in solutions with the concentrated hydrochloric acid have the probable formula $[SH(H_2O)_n.S]_{x-5}.PaCl_x$ (where S denotes the organic solvent molecule and $x = 6{-}8$). In the case of acetone and dioxane the formation of the well-sorbed associates $(SH.H_2O)_{x-5}.PaCl_x$ is assumed. The sorption of protactinium from the hydrochloric and nitric acid solutions in the presence of methanol and ethanol is compared.

Recently, a considerable attention has been paid to the development of separation procedures using the mixed aqueous–organic solutions. It turned out that the presence of an organic solvent in exchange reactions led in many cases to better separation factors[1]. The use of mixed solutions improves the separation of several elements even in the case of separation on silica gel[2-5]. However, a rather low number of papers deal with the application of mixed solutions on the sorption on inorganic sorbents. The sorption of protactinium on silica gel from the aqueous–alcoholic solutions has been studied only by Davydov and coworkers[6]. They have found that protactinium sorbed on the column of silica gel can be eluted by a mixture of ethanol and 9M-HNO₃ (1 : 1) or by octanol saturated with nitric acid. However, no detailed data on the effect of the concentration of acid and ethanol on the sorption of protactinium were published in their work.

For this reason we have investigated in detail the sorption of protactinium on silica gel from mixed solutions. We have decided to study the sorption in the presence of the hydrochloric acid and nitric acid and lower aliphatic alcohols, acetone and dioxane have been used as the organic component.

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EXPERIMENTAL

The preparation of the stock solutions of protactinium, the kinds and origin of sorbents and the method of their treatment as well as the experimental procedure have been described[7]. The organic solvents used were all of the analytical grade and they were dried and redistilled before use. The content of water never exceeded 0·5%. Dioxane was purified by heating with solid KOH and by sorption on the column of active aluminum oxide[8]. The mixed solutions of the given composition were prepared immediately before the experiment. The samples were prepared by mixing the components in this sequence: distilled water, 11M-HCl (HNO₃), the organic solvent and last the stock solution of protactinium in 11M acid. The distribution coefficient K_d is defined as

$$K_d = y(1 - y)^{-1} . V . m^{-1} ,$$

where y is the fraction of protactinium in the solid phase, m the weight of the sample of silica gel (0·05 g) and V the initial volume of the liquid phase (2 ml). The calculation of the composition of solutions and the determination of the distribution coefficients had not been corrected for volume changes caused by the mixing of organic solvents and aqueous solutions as these changes did not exceed 5 vol. %. The concentration of the acid (C_{HCl}, C_{HNO_3}) has been always recalculated for the total volume of the aqueous–organic mixture, the content of organic solvents is expressed in volume per cents.

RESULTS

The sorption of protactinium from the mixtures of hydrochloric acid with methanol, ethanol, 1-propanol, 2-propanol, acetone, and dioxane as a function of the composition of the solution is given in Figs 1 − 6. In weakly acidic solutions the values of K_d decrease for the organic solvent concentrations <50 vol. % and at higher concentrations they reach maximum. At a higher acidity the presence of an organic solvent generally decreases the value of the distribution coefficient. The nature of the dependence of K_d on the composition of the solution is of the same character for all solvents used. The effect of alcohols on the sorption of protactinium increases with the increasing number of carbon atoms in the molecule. It should be mentioned that the solutions with a high content of acetone change their colour to yellow or orange after being shaken for several hours. This is probably due to the formation of by-products (presumably condensation products). The time interval after which the colour is observable and also its intensity depend on the composition of the solution. (Fig. 11). The experiments in which this effect has been observed are indicated in the corresponding figures. Solutions containing more than 70% of dioxane consist of two immiscible phases. Figs 7 and 8 present the values of distribution coefficient of protactinium on silica gel (with narrow and wide pores, respectively) from the mixture HCl–ethanol. A comparison of these results with those of Fig. 2 reveals that the effect of the silica gel structure on the sorption is small. However, the silica gel structure affects the sorption kinetics (Fig. 9). The sorption rate decreases with the decreasing diameter of pores on silica gel. From the comparison with the results of our preceding paper[7] it follows that the rate of equilibrium establishment is a little lower in mixed solutions than in pure aqueous solutions. This rate does not depend on the number

of carbon atoms in the molecule of the alcohol used. The results for the sorption kinetics at various concentrations of the hydrochloric acid and at various contents of ethanol and acetone are given in Figs 10 and 11, respectively. The increasing fraction of the organic solvent in the mixture not only slows down the sorption process but causes also a deviation from the exponential character of the curves $y = f(t)$ at higher acid concentrations. The values of the distribution coefficients of protactinium from the mixtures HNO_3–CH_3OH and HNO_3–C_2H_5OH are presented in Figs 12 and 13, respectively. Also in these mixtures the substitution of water in the solution by an organic solvent decreases the sorption of protactinium. No substantial difference between the effect of methanol and ethanol has been observed. However, the solutions containing ethanol are less resistant against oxidation in the presence of nitric acid, if its overall concentration is higher than 4M. These results confirm the observations of Davydov and coworkers that protactinium can be desorbed from silica gel by mixtures of nitric acid and an alcohol. However, we suppose that the mixtures containing the hydrochloric acid are more convenient for this purpose.

DISCUSSION

From the studies of Zr, Hf, Nb, and Ta sorption under analogous conditions it follows that the sorption of these elements depends on the formation of complexes
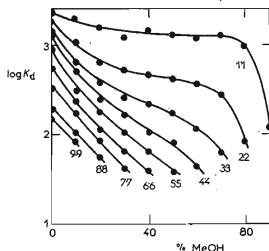

Fig. 1

Sorption of Protactinium on Silica Gel from the Mixed Solutions of the Hydrochloric Acid and Methanol (MeOH)

Numbers on curves indicate the total molar concentration of the hydrochloric acid (C_{HCl}). The ratio of the liquid and solid phase $V/m = 40$ ml/g, the sorption time t 75 h, $T = 22 \pm 2°C$. Silica gel CH, the specific surface 375 m^2/g, granularity 0·10 mm.

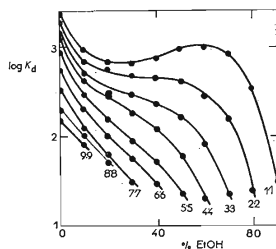Fig. 2

Sorption of Protactinium on Silica Gel from the Mixed Solutions of the Hydrochloric Acid and Ethanol (EtOH)

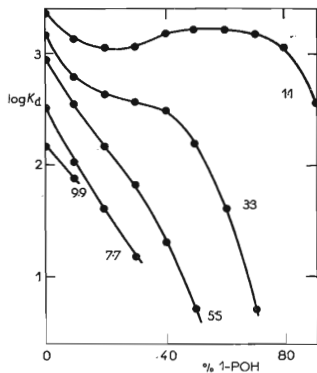Notation and sorption conditions cf. Fig. 1.

FIG. 3

Sorption of Protactinium on Silica Gel from the Mixed Solutions of the Hydrochloric Acid and 1-Propanol (1-POH)

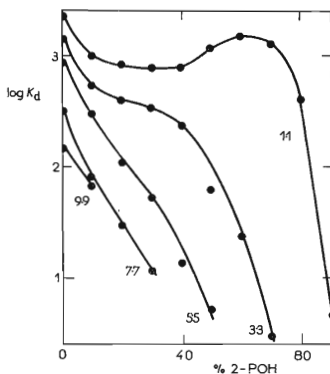   Notation and sorption conditions *cf.* Fig. 1.

FIG. 4

Sorption of Protactinium on Silica Gel from the Mixed Solutions of the Hydrochloric Acid and 2-Propanol (2-POH)
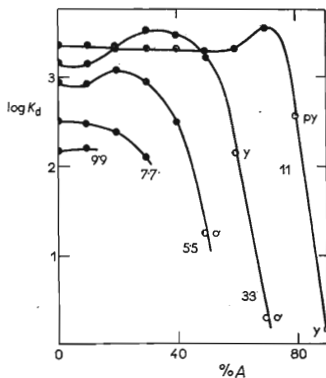
   Notation and sorption conditions *cf.* Fig. 1.

FIG. 5

Sorption of Protactinium on Silica Gel from the Mixed Solutions of the Hydrochloric Acid and Acetone (A)

   Notation and sorption conditions *cf.* Fig. 1. Solution colours: py pale yellow, y yellow, o orange.

and on their solvation, on the salting-out of metal complexes into the solid phase, and on the selective sorption of organic solvents[5]. The addition of organic solvents to the liquid phase increases usually the sorption of tetravalent elements and decreases the sorption of pentavalent elements. The comparison with results obtained in this study shows that there is an extensive analogy between the behaviour of protactinium and niobium.
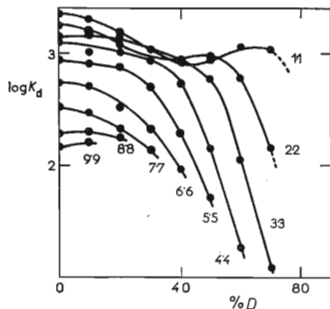

FIG. 6

Sorption of Protactinium on Silica Gel from the Mixed Solutions of the Hydrochloric Acid and Dioxane (D)

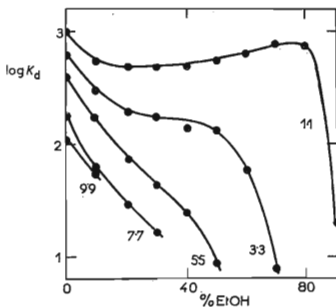Notation and sorption conditions cf. Fig. 1.

FIG. 7

Sorption of Protactinium on Silica Gel from the Mixed Solutions of the Hydrochloric Acid and Ethanol (EtOH)

Silica gel Gw, the specific surface 340 m²/g, granularity 0·10 mm. Other conditions and notation cf. Fig. 1.
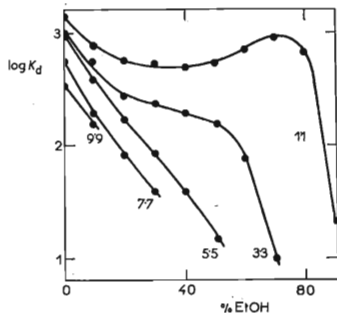

FIG. 8

Sorption of Protactinium on Silica Gel from the Mixed Solutions of the Hydrochloric Acid and Ethanol (EtOH)

Silica gel Ge, the specific surface 780 m²/g, granularity 0·10 mm. Other conditions and notation cf. Fig. 1.

Because the mixed solutions were prepared by admixing the individual components already in the presence of silica gel, the establishment of the chemical equilibrium proceeds simultaneously with the protactinium sorption. The sorption kinetics depends thus on several simultaneous processes. From the results we may conclude that a fast sorption of chloro complexes of protactinium starts immediately after the dilution of the stock solution in 11M-HCl[7]. However, a gradual hydrolysis of these complexes and their solvation by molecules of the organic solvent present proceed simultaneously. In several cases (*e.g.* in the sorption from acetone solutions) the sorption depends also on the age of the mixed solution due to the formation of by-products. Both the solvation and the formation of by-products could cause a partial desorption of the protactinium already sorbed on the solid phase. This fact follows from Figs 10 and 11 in which the curves *3* and *5* have not the regular exponential character that is typical for processes depending only on the diffusion of the sorbate into the solid phase.
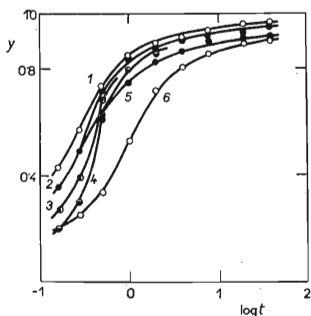

FIG. 9

Sorption Kinetics of Protactinium on Silica Gel from the Mixed Solutions of the Hydrochloric Acid and Alcohols

y Fraction of the sorbed protactinium; *t* sorption time (hours); C_{HCl} 1·1 mol l^{-1}; the content of alcohols 50 vol. %. Curve *1* methanol; *2*, *5*, *6* ethanol; *3* 1-propanol; *4* 2-propanol; *1—4* silica gel CH; *5* silica gel Gw; *6* silica gel Ge. The silica gel granularity was 0·13 mm in all experiments; $V/m = = 40$ ml g^{-1}.
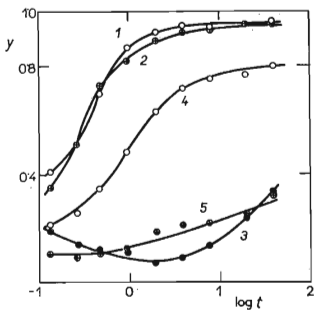
FIG. 10

Sorption Kinetics of Protactinium from the HCl–Ethanol Solutions

Curves *1*, *2*, *3* 1·1M-HCl; *4* 3·3M-HCl; *5* 5·5M-HCl; *1* 10% EtOH; *2*, *4*, *5* 50% EtOH; *3* 90% EtOH. Silica gel CH, other conditions see Fig. 9.

The effect of the organic solvent on the sorption of protactinium is supposed to be due to the formation of solvates. The obtained experimental data indicate that solvation plays an important role especially in those cases when protactinium is in the solution present predominantly in the form of anionic chloro complexes. Fig. 14 presents the values of $\log K_d$ of protactinium as a function of the molar ratio of the organic solvent concentration (C_{org}) to the hydrochloric acid concentration (C_{HCl}). The individual curves relate to the sorption from solutions prepared by mixing 11M-HCl with the solvent in various ratios so that these results constitute a complete analogy to the sorption from an isomolar series of solutions. From Fig. 14 it is evident that for all used alcohols the values of K_d reach a minimum at the ratio $C_{org} : C_{HCl} = 2$. Because the sorption depends on the changes of the sorbate states caused by the changing composition of the solution, the obtained value of the ratio of $C_{org} : C_{HCl}$ could indicate the formation of stable solvates consisting of one $\overset{\mathrm{I}}{\mathrm{HCl}}$ molecule with two molecules of the organic solvent and their reaction with protactinium. This assumption is evidently incomplete as it does not take into consideration the presence of water molecules in the mixture. The molar concentration of water in 11M-HCl corresponds to the value of $C_{H_2O} = 3 \cdot 88\, C_{HCl}$, and it can be assumed that the overwhelming part of water participates in the formation of the hydroxonium cation H_3O^+ and in its hydration. Because all the used solvents are easily polarized in the field of proton
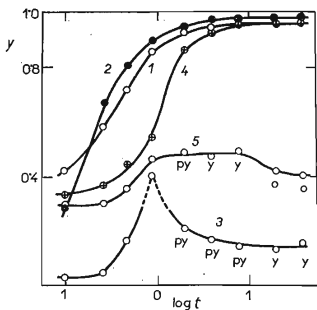

Fig. 11

Sorption Kinetics of Protactinium from the HCl–Acetone (A) Solutions

Curves 1, 2, 3 1·1M-HCl; 4 2·75M-HCl; 5 5·5M-HCl; 1 10% A; 2, 5 50% A; 4 58% A; 3 90% A. Solution colours: py pale yellow, y yellow, o orange. Silica gel CH, other conditions see Fig. 9.
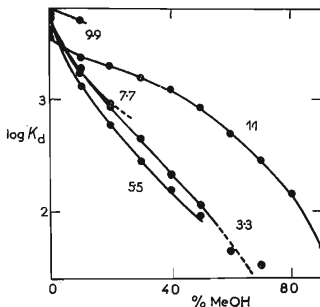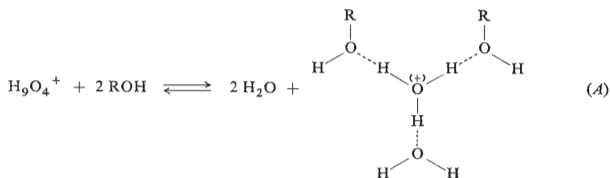

Fig. 12

Sorption of Protactinium on Silica Gel from the Mixed Solutions of the Nitric Acid and Methanol (MeOH)

Notation and sorption conditions cf. Fig. 1.

(hydroxonium), the dilution of the acid by an organic solvent leads to the gradual substitution of water molecules in the hydration shell of hydroxonium. In the case of alcohols this process can be illustrated by this scheme:

$$H_9O_4^+ + 2\ ROH \rightleftharpoons 2\ H_2O + \qquad\qquad (A)$$

or, eventually, by

$$H_9O_4^+ + 2\ ROH \rightleftharpoons 2\ H_2O + \qquad\qquad (B)$$
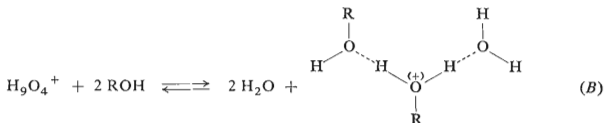
(where R means the radical CH_3-, C_2H_5-, or C_3H_7-, respectively). From preliminary considerations it turns out that the formation of stable oxonium ions $[SH(H_2O)_n \cdot S]^+$, that are capable to form ionic associates with metal ions (where S is the organic solvent molecule), is more probable. Their higher hydrophobic character can be easily explained by the differences between the effect of individual organic solvents and namely by the differences observed during the sorption from alcoholic solutions and from solutions of acetone and dioxane. This assumption is also corroborated by the lower mobility of the proton bound to the molecule of the organic solvent.

Because protactinium is present in the concentrated hydrochloric acid in the form of $PaCl_x^{5-x}$ complexes $(x = 6-8)$ cf.[7,9], the composition of associates formed in this case corresponds to the formula $[SH.(H_2O)_n.S]_{x-5}.PaCl_x$. The sorption of these associates on silica gel is substantially lower than the sorption of analogous hydrated complexes in an aqueous medium. The decrease of the sorption rate is understandable in regards to the large dimensions of the solvated associates. From the shapes of individual curves in Fig. 14 we may conclude that the most stable associates are formed in solutions with 2-propanol. However, the problem of the stability and sorption of solvates as well as the problem of their composition needs further investigations. The sorption of the organic solvent itself can play an important role in these systems.

The protactinium sorption from acetone and dioxane solutions differs from the sorption from alcoholic solutions by the convex shape of the respective curves in Fig. 14 at the low ratio $C_{org} : C_{HCl}$ and also by the fact that they have no minimum at

$C_{org} : C_{HCl} = 2$. This difference is understandable if we recall the different structures of alcohols and ketones. The solvation of hydroxonium in the acetone or dioxane medium proceeds evidently according to the scheme

$$H_9O_4^+ + (CH_3)_2CO \rightleftarrows 3 H_2O + (CH_3)_2C=O^+—H \cdots OH_2 . \qquad (C)$$
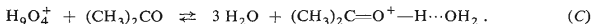
An oxonium ion $(CH_3)_2C=O^+—H \cdots O=C(CH_3)_2$ differing substantially by its structure from the structure of analogous alcoholic solvates is formed by further solvation. Higher solvation is, however, impossible in this case. The convex shape of curves can be explained by the formation of an easily sorbable solvate with one solvent molecule, *i.e.* $(SH.H_2O)_{x-5}.PaCl_x$. The shape of the right-hand-side part of the respective curves in Fig. 14 depends not only on the sorption properties of the associate $(SHS)_{x-5}PaCl_x$ but also on the formation of by-products and/or of two immiscible phases.

In the transition to less acidic solutions the minimum at $C_{org} : C_{HCl} = 2$ becomes more shallow and in the case of acetone and dioxane the convex character of the curves
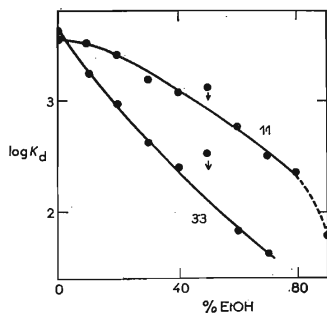

Fig. 13

Sorption of Protactinium on Silica Gel from the Mixed Solutions of the Nitric Acid and Ethanol (EtOH)
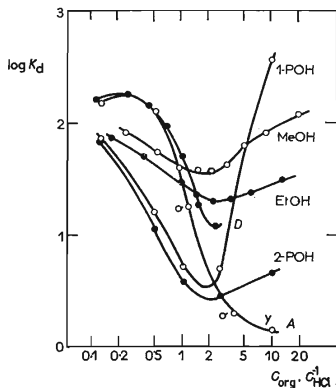
Notation and sorption conditions *cf.* Fig. 1.

Fig. 14

Sorption of Protactinium as a Function of the Ratio of the Molar Concentrations of the Organic Solvent (C_{org}) to that of the Hydrochloric Acid (C_{HCl})

The presented data are those of the sorption of protactinium from the mixture of 11M-HCl and the respective organic solvent. Notation is the same as in Figs 1—6.

becomes more and more outstanding. The respective data have been determined by the interpolation from Figs 1—8 and they are not presented in this paper. However, at lower concentrations of the hydrochloric acid the analysis of results is more complicated by the complexity of the equilibrium between the individual chloro complexes of protactinium and by their hydrolysis. It is, however, probable that associates of an analogous composition can be formed even in the case of anionic hydrochloro complexes[7,9] of the general formula $Pa(OH)_n Cl_x^{5-n-x}$ $(n + x > 5)$.

The undulate character of the sorption curves from solutions with the total concentration of the hydrochloric acid 1—3M (Figs 1—6) is also very interesting. A similar behaviour has been already found for several other elements[5]. This feature can be caused by the selective sorption of the organic solvent, *i.e.* by the inhomogeneous distribution of the organic component between the intercapillary solution and the free liquid phase. This question, however needs further investigations.

In the paper[3] it has been found that niobium in the presence of dioxane is not sorbed from solutions of 1—5M-HCl. This has been explained by the formation of dioxane complexes. In the case of zirconium, hafnium and tantalum no similar effect of dioxane on their sorption has been observed. From Fig. 6 it follows that the protactinium sorption from aqueous-dioxane solutions is comparable to the sorption from the solutions of all other solvents used. It can be therefore concluded that the formation of dioxane complexes is specific only for niobium from all the studied elements.

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