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Original Scientific Paper

Precipitation and Hydrolysis of Thorium(IV) in Aqueous Solution. II. Influence of pH and Neutral Electrolytes upon the Precipitation in the System Thorium Nitrate — Potassium Phthalate*

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The influence of the pH and other neutral electrolytes upon the precipitation and hydrolysis of thorium(IV) in aqueous solutions of thorium nitrate and potassium phthalate was investigated. A three-dimensional concentration tyndallogram in which turbidity has been plotted against the concentration of potassium phthalate and the pH, at constant concentration of Th(IV) $1.25 \times 10^{-3}M$, shows various precipitation and dissolution regions of the system. The following concentration regions were marked and discussed: the concentration region where sudden precipitation of thorium hydroxide occurs, the region of thorium hydroxide stable sols, the region of thorium phthalate sols, the region of unstable systems in which crystals appear after a few days' aging and the region of stable clear solution at rather high pH values.

The effect of neutral electrolytes upon the precipitation in the region of stable clear solution was investigated. It was determined that neutral electrolytes influence to a great extent the precipitation at the boundary of thorium phthalate precipitate (pH = 5).

INTRODUCTION

In the system thorium nitrate — potassium hydroxide, the hydrolysis of thorium occurs at pH above 3.^{1,2,3} The precipitation depends on the pH and the concentration of thorium nitrate.⁴ Thomas^{5,6} has examined the influence of various organic acid salts on dialyzed sols of thorium hydroxide. According to his results all added salts of organic acids increase the pH of the sols and change the charge of the micella. The precipitation does not occur even at rather high pH values.

Thorium phthalate was not much investigated. M. Bobtelsky and B. Gadda⁷ reported some results of heterometric titrations of thorium nitrate

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with potassium phthalate and *v.v.* Some of our earlier results on precipitation in the system thorium nitrate — potassium phthalate^{8,9} suggested the existence of optically clear systems even at high pH values.

Neutral electrolytes effected solid phase formation in some of those systems. In order to get a better explanation of the phenomena observed, systematic studies of the system thorium nitrate — potassium phthalate were undertaken. The influence of pH and neutral electrolytes on precipitation and dissolution in a great concentration range of potassium phthalate and neutral electrolytes at constant Th(IV) concentration are the subject of this paper.

RESULTS

The influence of pH upon precipitation in the system thorium nitrate—potassium phthalate was examined at a constant concentration of added thorium nitrate.

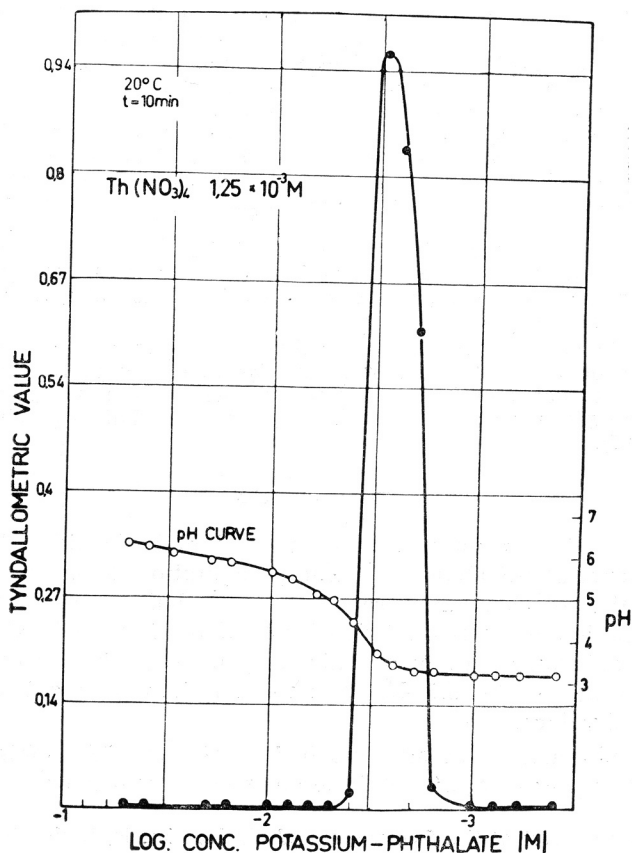


Fig. 1. 10 min. concentration tyndallogram and the corresponding pH curve of the system: $1.25 \times 10^{-3} \text{M Th(NO}_3)_4$ — potassium phthalate (var.).

In Fig. 1. a typical tyndallogram curve is presented with the corresponding pH curve of the system thorium nitrate ($1.25 \times 10^{-3}M$) — potassium phthalate (var.). The concentration tyndallogram was obtained from earlier measurements.^{8,9} The tyndallogram curve has a characteristic isoelectric maximum on both sides of which the systems are optically clear.

In Fig. 2. the UV spectra of the clear systems with potassium phthalate in excess are compared with the absorption curves of potassium phthalate of the same concentrations and at the same pH values. It is obvious that thorium nitrate has no influence on the absorption spectrum of potassium phthalate at these wave lengths.

Fig. 3. shows the influence of the change of potassium hydroxide and nitric acid concentrations, respectively, on systems of thorium nitrate ($1.25 \times 10^{-3}M$) — potassium phthalate (const.) for three different potassium phthalate concentrations. The tyndallogram and the corresponding pH

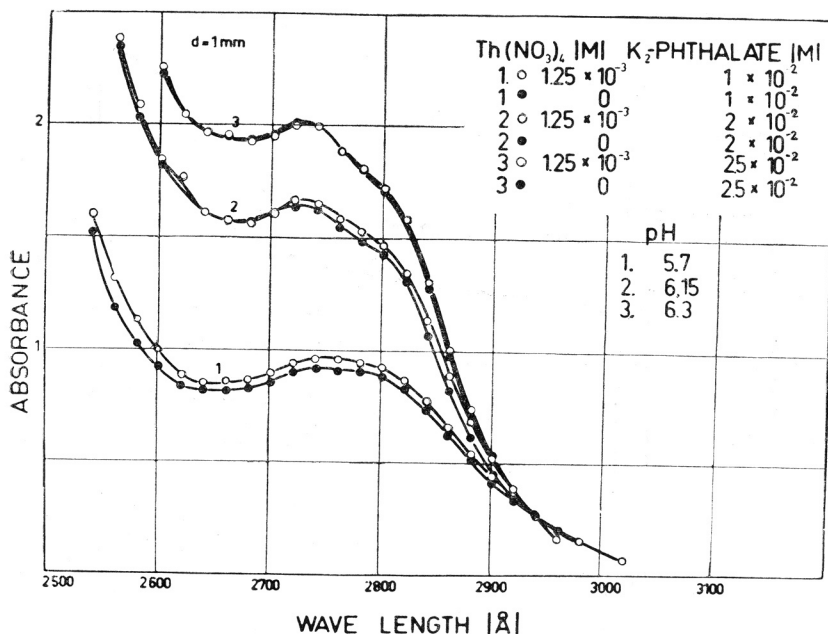


Fig. 2. The absorption curves in the UV range of spectrum of the systems: $1.25 \times 10^{-3}M$ $Th(NO_3)_4$ — potassium phthalate $1 \times 10^{-2}M$ (1), $2 \times 10^{-2}M$ (2), $25 \times 10^{-2}M$ (3) compared with absorption curves of potassium phthalate solutions at the same concentrations and pH values. The blank is bidistilled water, $d = 1$ mm.

values are plotted against the concentration of nitric acid and potassium hydroxide. It is evident that the potassium phthalate concentration greatly influences the phenomena. Two regions of sedimentation exist for the concentration ($8 \times 10^{-3}M$) of potassium phthalate (curve 2). One lies in the acid medium and corresponds to the precipitation of thorium phthalate. The other is the region of thorium hydroxide precipitation above pH 6. Between these two regions there is a region of optically clear systems.

At high concentrations of potassium phthalate (curve 1) the precipitation occurs in alkaline medium only.

At the concentration of $2 \times 10^{-3} M$ potassium phthalate (curve 3) there is a wide precipitation region with sudden sedimentation at medium pH values.

In order to get a clear idea about the influence of potassium phthalate concentration and the pH variation on the existence of precipitation and dissolution regions, a three-dimensional concentration tyndallogram was constructed. Turbidity values were plotted against the pH and against the concentration of potassium phthalate. The concentration of thorium nitrate was kept constant at $1.25 \times 10^{-3} M$.

Fig. 4. is a parallel projection of the three-dimensional diagram. It consists of many parallel sections. Each section represents a concentration of potassium phthalate which was kept constant and the pH varied by the addition of nitric acid or potassium hydroxide as shown in Fig. 3.

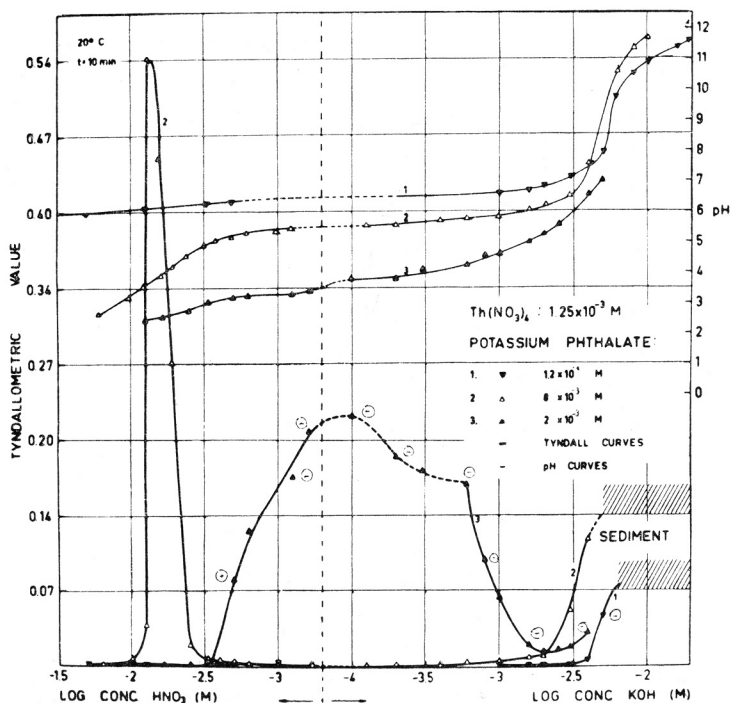


Fig. 3. 10 min. concentration tyndallogram and corresponding pH curves of the system:

1. $1.25 \times 10^{-3} M$ $\text{Th}(\text{NO}_3)_4$ — potassium phthalate $1.2 \times 10^{-1} M$ — HNO_3 , i.e. KOH var.
2. $1.25 \times 10^{-3} M$ $\text{Th}(\text{NO}_3)_4$ — potassium phthalate $8 \times 10^{-3} M$ — HNO_3 , i.e. KOH var.
3. $1.25 \times 10^{-3} M$ $\text{Th}(\text{NO}_3)_4$ — potassium phthalate $2 \times 10^{-3} M$ — HNO_3 , i.e. KOH var.

Fig. 5. is the ground plane of the diagram shown in Fig. 4., giving the isohypsas of turbidity (curves 1—9). It clearly defines the limits of the concentration regions of sedimentation, of unstable solution and of stable clear solutions.

The tyndallogram presented in Fig. 1. is the cross-section *d* in this diagram. The cross-sections *a*, *b* and *c* are constructed from the curves 1, 2 and 3 in Fig. 3.

The effect of neutral electrolytes as observed earlier^{8,9} was also investigated more completely. Concentrations of potassium phthalate were chosen so as to obtain systems in the region of stable clear solutions shown on the three-dimensional concentration tyndallogram (Fig. 4., 5.).

Fig. 6. shows the influence of the concentrations of lithium, calcium and yttrium nitrate on the formation of a precipitate in the system thorium nitrate — potassium phthalate for several concentrations of potassium phthalate.

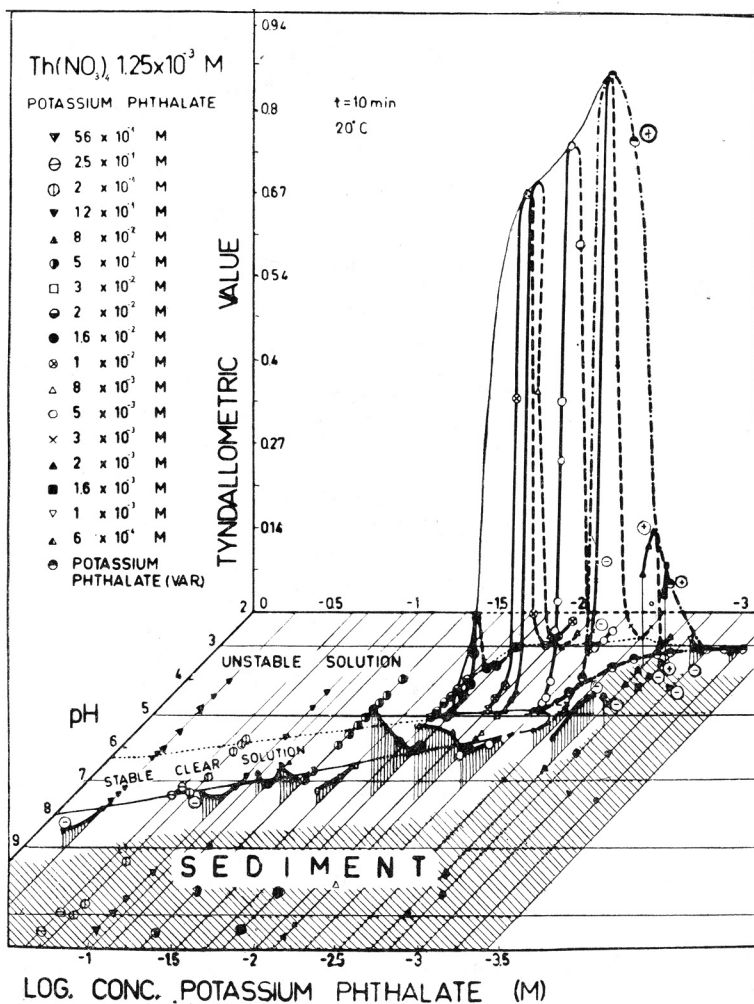


Fig. 4. Parallel projection of the three-dimensional concentration tyndallogram. The turbidity is plotted against the concentration of potassium phthalate and against the pH. The concentration of thorium nitrate is constant (1.25 × 10⁻³ M). The turbidities were measured 10 min. and the pH values 60 min. after the precipitation components had been mixed.

Tangents on the steepest part of the turbidity curve give the precipitation values of the electrolytes.

From the pH curves it is evident that the pH of systems decreases with increased electrolyte concentration. The precipitation always begins at $\text{pH} \approx 5$.

In Fig. 7. the precipitation values of various electrolytes are plotted against the concentration of potassium phthalate. Earlier results^{8,9} are compared with the new and found in good agreement.

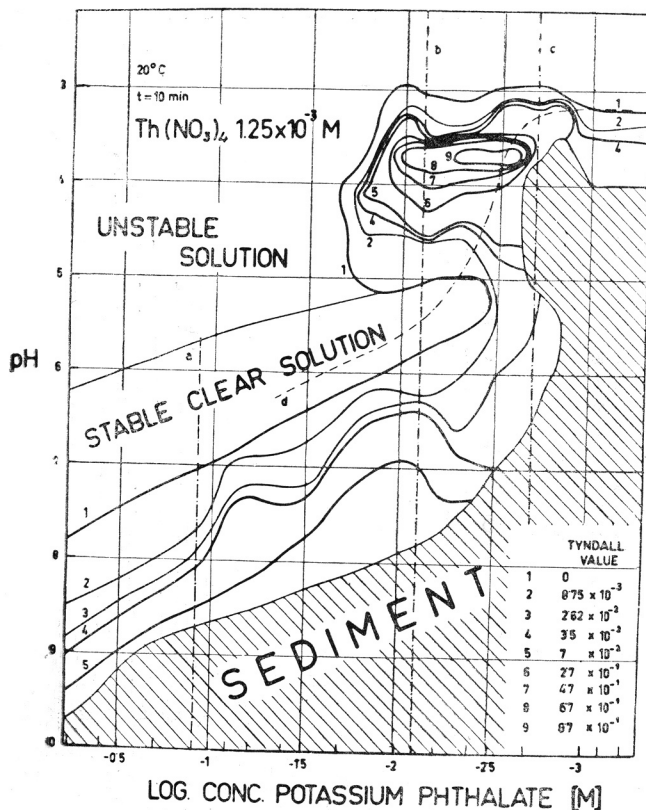


Fig. 5. The ground plan of the precipitation diagram shown in Fig. 4., constructed with the isohypsas of turbidity.

A three-dimensional diagram Fig. 8. will give a good survey of the conditions (concentration range of potassium phthalate and pH) under which the neutral electrolyte effects the precipitation.

Fig. 8. consists of two space diagrams. In the lower diagram the effect of precipitation is shown on examples of Li^+ , Ca^{2+} , and Y^{3+} ions. The turbidity is plotted against the concentration of potassium phthalate (C_1) and the concentration of neutral electrolyte (C_2).

The upper diagram shows an effect of a decreasing pH. The pH is plotted against C_1 and C_2 . In order to clarify the space form of these

diagrams the turbidity planes are cut by several planes. π_2 , π_3 and π_4 are parallel planes, while the plane standing for a given turbidity is parallel to C_1 and C_2 axes.

The plane π_1 separates the range of phthalate concentration in which precipitation occurs without the addition of an electrolyte from the range in which the solid phase can be precipitated only after the addition of an electrolyte.

At concentrations higher than $2.5 \times 10^{-2} M$ of potassium phthalate the systems remain clear even after the addition of neutral electrolytes.

The concentration range where neutral electrolytes effect precipitation is pretty narrow according to potassium phthalate concentration.

In the upper diagram the pH curves are cut by the plane π_5 where $pH = 5$. This is the critical value for the beginning of precipitation with neutral electrolytes.

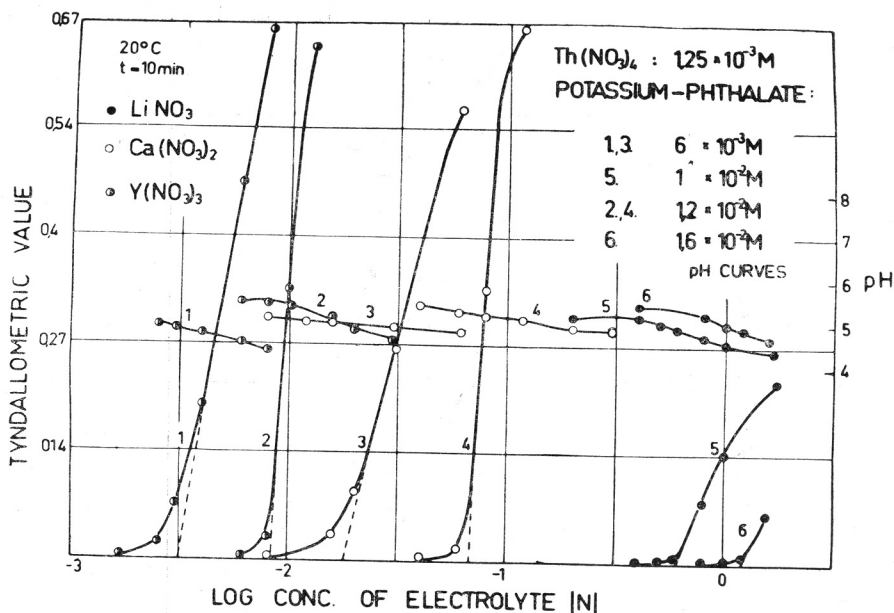


Fig. 6. 10 min. concentration tyndallograms and the corresponding pH curves of the systems:

1. $1.25 \times 10^{-3} M$ $Th(NO_3)_4$ — $6 \times 10^{-3} M$ potassium phthalate — $Y(NO_3)_3$ (var.)
2. $1.25 \times 10^{-3} M$ $Th(NO_3)_4$ — $1.2 \times 10^{-2} M$ potassium phthalate — $Y(NO_3)_3$ (var.)
3. $1.25 \times 10^{-3} M$ $Th(NO_3)_4$ — $6 \times 10^{-3} M$ potassium phthalate — $Ca(NO_3)_2$ (var.)
4. $1.25 \times 10^{-3} M$ $Th(NO_3)_4$ — $1.2 \times 10^{-2} M$ potassium phthalate — $Ca(NO_3)_2$ (var.)
5. $1.25 \times 10^{-3} M$ $Th(NO_3)_4$ — $1 \times 10^{-2} M$ potassium phthalate — $LiNO_3$ (var.)
6. $1.25 \times 10^{-3} M$ $Th(NO_3)_4$ — $1.6 \times 10^{-2} M$ potassium phthalate — $LiNO_3$ (var.)

DISCUSSION

The three-dimensional concentration tyndallogram (Fig. 4., 5.) shows two well distinguished precipitation regions. One of them at low pH values and a narrow concentration range of potassium phthalate is due to the precipitation of thorium phthalate.

From the stability constants of phthalic acid¹⁰

$$K_1 = \frac{[H^+][H-Phth.^-]}{[H_2-Phth.]} = 1.26 \times 10^{-3}$$

$$K_2 = \frac{[H^+][Phth.^{2-}]}{[H-Phth.^-]} = 3.1 \times 10^{-6}$$

the percentage of ionic species existing in the solution at different pH values was calculated and plotted in a diagram (Fig. 9).

It can be read from the plot that in the pH range, where this precipitation maximum occurs (pH 3–5), H–Phth⁻ is the predominant ionic species in the solution.

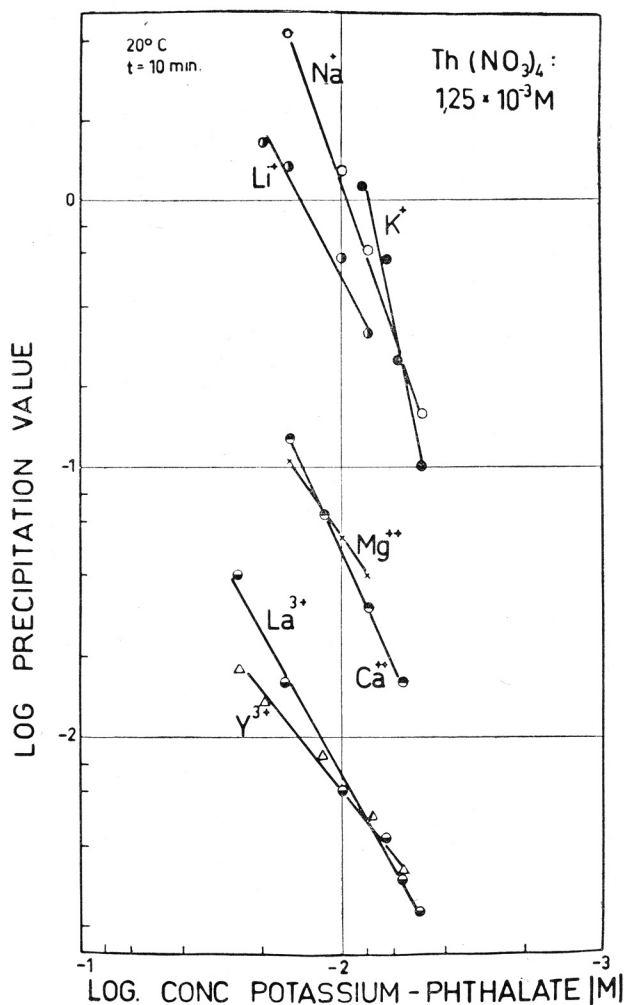


Fig. 7. Log. of precipitation values of various electrolytes plotted against the concentration of potassium phthalate in the system Th(NO₃)₄ 1.25 × 10⁻³M — potassium phthalate (var).

The molar ratio of thorium nitrate to potassium phthalate was found to be 1 : 2 at the maximum of the precipitation. It means that two $H-Phth^-$ ions are bound to one thorium ion. According to these results, in this range of concentration the most likely composition of the precipitate is $Th(H-Phth^-)_2(OH)_2$.

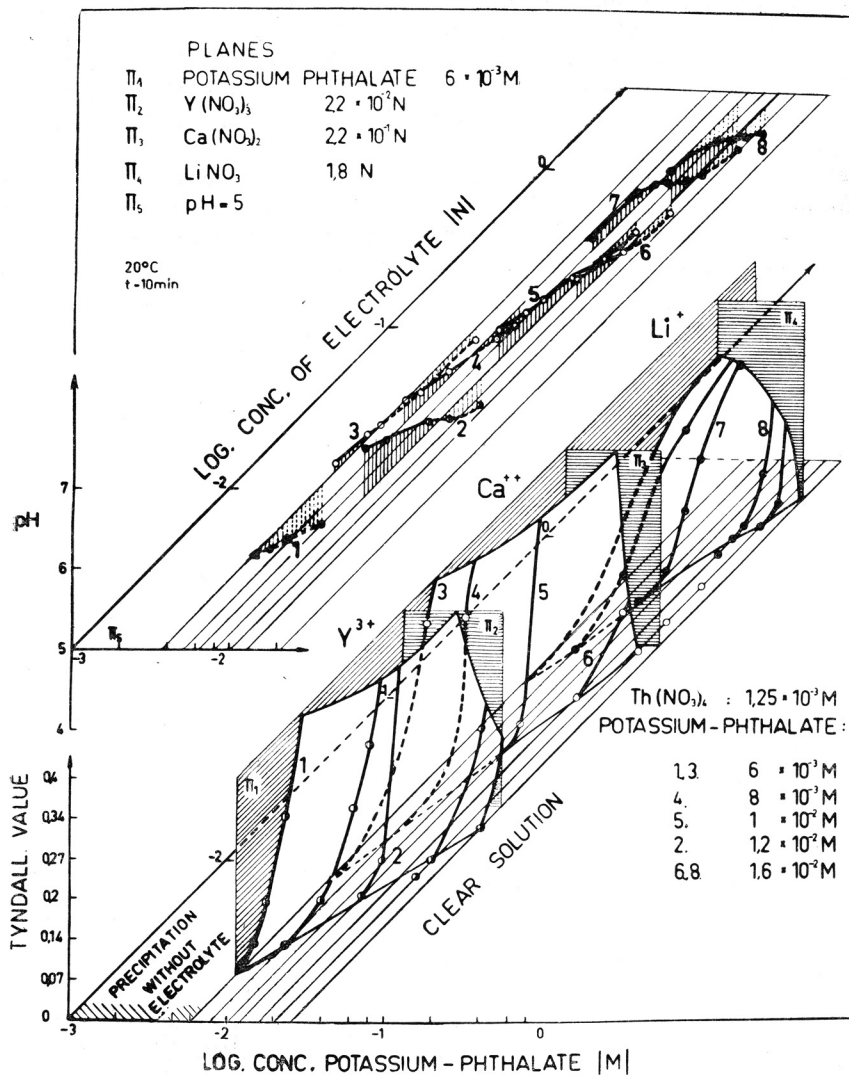


Fig. 8. Turbidity and pH values are plotted against the concentration C_1 of potassium phthalate and the concentration C_2 of yttrium, calcium and lithium nitrate. The turbidity planes are cut with planes π_1 , π_2 , π_3 , and π_4 to get a clearer view of the three-dimensional tyndallogram. The pH diagram is cut with a plane at pH = 5.

At high pH values there is a range of thorium hydroxide precipitation over the whole area of potassium phthalate concentrations.

Remarkable is the great difference between the 10 min. tyndallogram values of the two precipitation regions (Fig. 4). While in the thorium

phthalate precipitation region sols of high turbidity occur, in the range of thorium hydroxide the precipitation is rapid. In 10 min. a fluffy precipitate prevails in the whole region, the range of stable sols being narrow.

At potassium phthalate concentrations lower than $1 \times 10^{-3} M$ (excess of thorium nitrate), thorium hydroxide is precipitated in the whole pH range above pH 3.5. In the presence of potassium phthalate the charge of thorium hydroxide sols is negative. Thorium phthalate sols are charged positively when less than two moles of potassium phthalate have been added to thorium nitrate. On the opposite side of the thorium phthalate maximum sols are charged negatively (Fig. 4.).

At high concentrations of potassium phthalate the thorium phthalate maximum turns to a region of unstable solutions where crystals appear after a few days' aging. The crystals contain a thorium and a phthalate ion as determined qualitatively. The exact composition is not yet known.

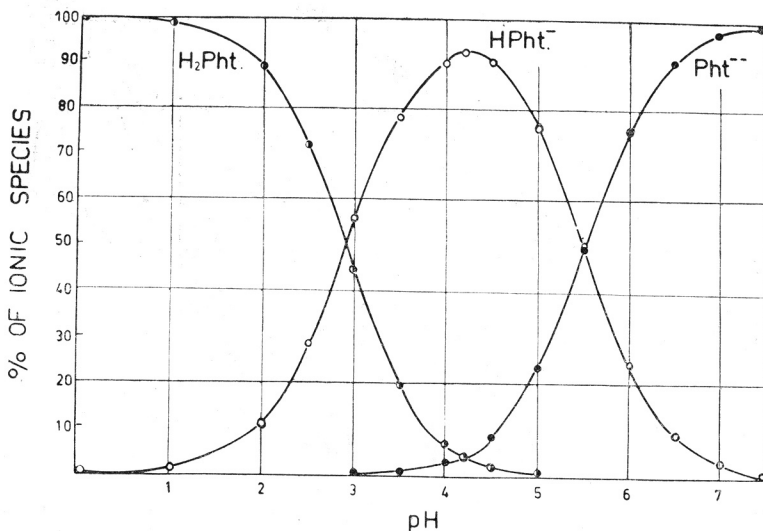


Fig. 9. The percentage of ionic species of phthalate plotted against pH. The diagram is calculated from the stability constants of phthalic acid¹⁰ $K_1 = 1.26 \times 10^{-3}$ and $K_2 = 3.1 \times 10^{-6}$ at 25°C.

The two precipitation regions and the region of unstable solutions are divided by a narrow region of stable clear solutions (Fig. 4., 5.) in the pH range, where otherwise thorium hydroxide would precipitate⁴ if potassium phthalate had not been present in the solution. The existence of thorium complexes in this region could not be confirmed by measurements of the UV spectra (Fig. 2.).

The influence of a great variety of neutral electrolytes on the formation of the solid phase in this region was examined. As a general feature it was found that the precipitation occurs at values of pH = 5 and lower, i.e. at the boundary of thorium phthalate precipitation region. In the presence of all electrolytes investigated the turbidities were greatly increased. The precipitation values are dependent linearly on the concentrations of potassium

phthalate (Fig. 7). The straight lines obtained are very steep. The lower the hydrolysis constant of the electrolyte, the higher the slope of the straight line. The Schulze-Hardy rule¹¹ is valid for our systems too, but the precipitation values are ten or more times greater than their coagulation values obtained with silver halides.¹²

It is obvious that the coagulation is not the only phenomenon to be taken into account in this case. The lowering of the pH of the systems (the critical pH for precipitation being $\text{pH} = 5$) might be in connection with the dependence of precipitation values on the hydrolysis constants of the electrolytes. The very high precipitation values, especially of the univalent electrolytes indicate that salting out effects should not be excluded.

CONCLUSION

The three-dimensional concentration tyndallogram of the system thorium nitrate (const.) — potassium phthalate (var.) — pH (var.) clearly shows the regions of the critical precipitation and dissolution. The concentration range where the precipitation occurs indicates the composition of the precipitates.

Neutral electrolytes appreciably effect the precipitation at the boundary of the thorium phthalate precipitation region.

EXPERIMENTAL

Turbidity measurements were performed with a Zeiss tyndallometer joined to a Pulfrich photometer. The method was described earlier.¹³ A green filter (wave length $530 \text{ m}\mu$) was used. The systems were prepared in glass tubes by mixing 5 ml. of thorium nitrate and 5 ml. of potassium phthalate.

The different pH values were obtained by the addition of various concentrations of potassium hydroxide and nitric acid solutions, respectively, before the precipitation components were mixed. Potassium hydroxide was added to the potassium phthalate solution while nitric acid was added to the solution of thorium nitrate.

When the effect of various neutral electrolytes was investigated the solutions of the electrolytes were added to the solution of thorium nitrate before the precipitation.

The concentration of the components is always given for the whole volume, i.e. for 10 ml. at 20°C . The thorium nitrate concentration was kept constant at $1.25 \times 10^{-3} \text{ M}$ in all experiments. The glass tubes were thermostated in a constant temperature bath at $20^\circ \pm 0.1^\circ \text{C}$.

The spectrophotometric measurements in the UV range of the spectrum were performed by the use of the Hilger — Watts spectrophotometer, model H 700 — 307.

The acidity of the systems was measured with a glass electrode 60 min. after the solutions had been mixed. The charge of sols was determined by the ultra-microscopic electrophoresis technique.

Materials

All the chemicals used were analytically pure and all the solutions prepared with bidistilled water. The standard solution of thorium nitrate was prepared by dissolving Hopkin & Williams, Analar thorium nitrate. The concentration of thorium was determined gravimetrically by precipitation with oxalic acid.¹⁴ Thorium nitrate solutions were freshly diluted before each experiment from a standard solution (0.05 M).

Potassium phthalate was determined potentiometrically by titration with potassium hydroxide.

The concentrations of the neutral electrolyte were determined by the ion exchange technique.¹⁵

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IZVOD

Taloženje i hidroliza torija(IV) u vodenoj otopini. II. Utjecaj pH i neutralnih elektrolita na taloženje u sistemu torijev nitrat—kalijev ftalat

H. Bilinski, H. Füredi i B. Težak

Ispitivan je utjecaj pH i neutralnih elektrolita na taloženje torija(IV) u vodenim otopinama torijeva nitrata, kalijeva ftalata i pH. Prikazana su i diskutirana slijedeća koncentracijska područja: područje u kojem dolazi do momentnog taloženja torijeva hidroksida, područja solova torijeva hidroksida, područje solova torijeva ftalata, područje nestabilnih sistema, u kojima stajanjem ispadaju kristali i područje stabilnih bistrih otopina, kod relativno visokih pH vrijednosti.

Ispitivan je efekt neutralnih elektrolita na taloženje u području stabilnih bistrih otopina. Utvrđeno je, da neutralni elektroliti uzrokuju stvaranje znatnih količina taloga na granici područja taloženja torijeva ftalata kod pH = 5.

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