

THE SORPTION OF UO_2^{2+} AND Th^{4+} IONS ON SILICA GEL IN THE PRESENCE OF SOME POLYAMINOPOLYCARBOXYLIC ACIDS

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Distribution coefficients of UO_2^{2+} and Th^{4+} ions were determined for the system silicagel-aqueous solutions of several polyaminopolycarboxylic acids, citric acid and tartaric acid. The corresponding separation factors were calculated for $I \leq 0.1$ and $I = 1$.

Recently silica gel has often been used for separations of trace amounts of uranium from complex solutions obtained after the decomposition of rocks and minerals¹⁻⁶. It has also been successfully used in analyses of strongly mineralized waters of deep circulation⁷. The disadvantage of so far developed methods is first of all in the partial sorption of thorium and in retaining of some other metal ions which makes the final spectrophotometric determination of uranium more complicated. Results of preliminary experiments have indicated that the application of some new compounds from the group of polyaminopolycarboxylic acids might increase the selectivity of the sorption process. The stability of chelates of these compounds with Th^{4+} ions (and also with other metals) is very high as compared with that of UO_2^{2+} chelates⁸⁻¹¹. Theoretical considerations have revealed⁸ that an effective method for the separation of uranium from thorium will also be generally applicable for chromatographic separations of uranium from other accompanying metals.

Basic conditions of a successful chromatographic separation may be characterized by values of distribution coefficients (D). In this paper, therefore, the values of D^{U} and D^{Th} were determined in the system containing silica gel, ions of UO_2^{2+} and Th^{4+} and solutions of the following chelating agents: triethylenetetramine- N,N,N',N'' , N''',N'''' -hexaacetic acid (TTHA), diethylenetriamine- N,N,N',N'' , N''',N'''' -pentaacetic acid (DTPA), 1,2-diaminocyclohexane- N,N,N',N'' -tetraacetic acid (DCTA), EDTA, nitrilotriacetic acid (NTA), iminodiacetic acid (IDA) and glycine. The obtained results have been supplemented by data about the behaviour of both metal ions in solutions of analytically important organic hydroxy-acids (citric and tartaric acids) which proved to be useful in chromatographic separations of uranium and tin^{4-6,12} from a number of accompanying metals.

EXPERIMENTAL

Apparatus and solution. Absorption spectra were recorded on a Unicam SP 800 spectrophotometer. pH was measured using a digital pH meter PHM 62 (Radiometer, Denmark).

The preparation of silica gel has already been described in the previous paper⁶. Exchange capacity of the gel (dried at 120°C to constant weight) determined by the sorption of $\text{Zn}(\text{NH}_3)_4^{2+}$ (ref.¹³) was 1.9–2.1 meq/g. Specific surface was found to be 350–400 m²/g. Solutions (0.1M) of the used chelate-forming acids were prepared in form of diammonium or disodium salts by dissolving the required amount of the acid in a solution having a known concentration of NH_4OH or NaOH . TTHA (Fluka) and DTPA (Schuchard) were used. 0.25% solution of Arsenazo III was prepared from the purified substance¹⁴ in 0.01M- NaOH . Stock solutions (0.01M) of Th^{4+} and UO_2^{2+} were prepared by dissolving the respective compounds in 0.01M- HNO_3 or HCl .

Used analytical methods. Thorium was determined spectrophotometrically using Arsenazo III (ref.¹⁴) in the medium of 4M- HCl where low concentrations (<0.01M) of the used chelating agents do not interfere. UO_2^{2+} ions were determined spectrophotometrically using the same agent in solutions of 4M- HClO_4 (ref.¹⁵). The weak interference of some chelating agents was eliminated by their addition into standard solutions. Chlorides even in the concentration 0.01M do not interfere.

Determination of distribution coefficients D^{U} and D^{Th} . The course of the sorption process on a column in the presence of EDTA (DCTA) for uranium and thorium was studied in previous papers in detail^{4–6}. The comparison of dependences of distribution coefficients and separation factors (S) for EDTA and DCTA with analogous functions for other chelating agents makes possible the unbiased evaluation of the contribution of these new chelating agents for the improvement of the chromatographic separation of UO_2^{2+} from excess of Th^{4+} . The following method was used to determine distribution coefficients: Transfer 0.02 meq of particular cation into a 50 ml beaker, add 10 ml of 0.1M solution of chelating agent and adjust pH by dilute ammonia or nitric acid. Make the solution up to 50 ml and transfer quantitatively into a 100 ml polyethylene bottle into which a weighed amount of silica gel that corresponds to 1 g of the dry gel has already been placed. Agitate the reaction mixture for 8 hours using a laboratory shaker. After the equilibrium has been reached, filter the solution through a sintered glass filter, determine pH and equilibrium concentrations of UO_2^{2+} or Th^{4+} respectively. For solutions with the ionic strength $I = 1$ a sufficient amount of 4M- NaCl was added and pH was adjusted by 2.5M- HCl .

Functions of D were studied in the pH range 4–9. To eliminate the undesirable complexing effects of anions in common buffers, natural buffer capacity of the studied polyaminopolycarboxylic acids was employed. In solutions of tartaric and citric acids pH has very much changed before reaching the equilibrium, particularly between 6–8. In solutions of glycine which forms only weak complexes with the studied metals, Th^{4+} and UO_2^{2+} started to hydrolyze at pH > 5. For the same reason the distribution coefficients D^{U} in the presence of DCTA were determined only at pH < 6.5.

RESULTS AND DISCUSSION

Fig. 1 shows that in all studied systems with the exception of IDA and glycine the values of D^{U} are greater than D^{Th} at pH 4–7.5. With the decreasing concentration of hydrogen ions in this pH range the values of both D^{U} and D^{Th} increase up to the maximum at pH 8 and then in alkaline region they both start to decrease. Exceptional is the behaviour of TTHA where distribution coefficients of Th^{4+} do not change from pH 4–6. If ionic strength is increased (from $I \leq 0.1$ to $I = 1$) the values of D^{U} and D^{Th} notably increase.

The above facts can be compared with general laws⁸ derived for ion-exchange on

cation-exchangers. For strong acid monofunctional cation-exchanger the distribution coefficient of a metal depends on its selectivity coefficient and increases with the decreasing concentration of a counter-ion. At the constant concentration of a counter-ion the value of D^{Me} decreases with the increasing stability of the complex of metal with a complexing agent. For weak acid cation-exchangers similar principles may be applied. The high affinity of H^+ ions to functional groups, however, affect the equilibria. Similarities of titration curves of weak acid cation-exchangers with those of silicagel give evidence of their relation. Silica gel nevertheless is not a monofunctional exchanger because its silanole groups are differently linked to the basic matrix and they are not mutually equivalent. Their acidity ($\text{p}K = 6-9$) is much lower¹⁶⁻¹⁹ than that of functional groups of carboxylic cation exchangers. Selectivity coefficients of the reaction (A) were determined for silicagel but the results vary in a wide range

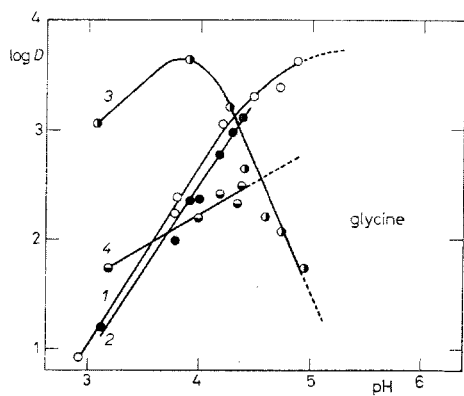
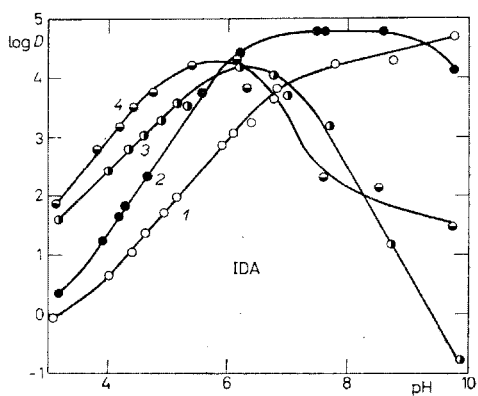
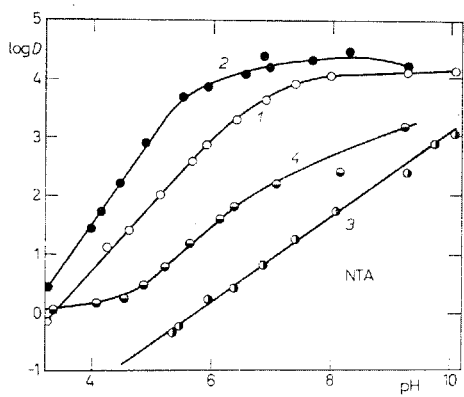
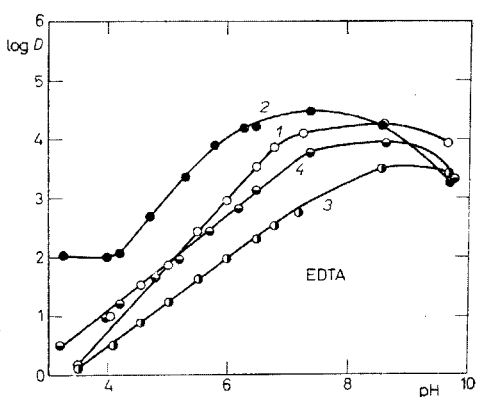
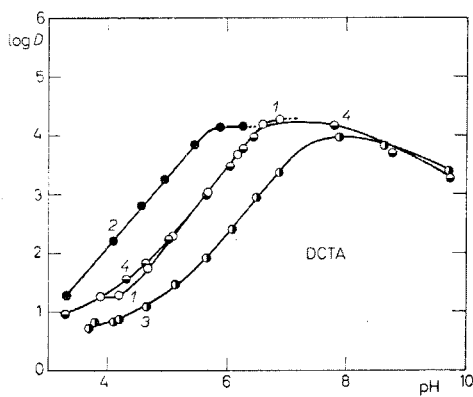
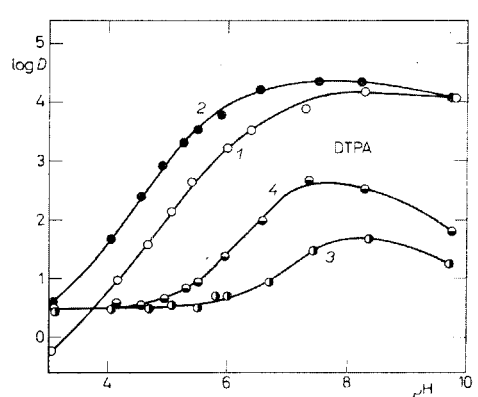


depending on the used experimental technique^{16,19-31}. Although the reaction of alkali metal ions with the gel is considered exclusively as a process of ion-exchange, the physical adsorption and ionic exclusion¹⁹ may also occur.

In acidic medium ($\text{pH } 4-6$) silica gel behaves as an exchanger in the H^+ form. The effect of increasing stability of chelates of uranium with increasing pH has not been observed for the studied systems. Even though this phenomenon takes place at least to a small extent, the mechanism of a simple sorption governed by the concentration of a counter-ion clearly predominates. This mechanism is only very little affected by the chelate-formation which results in a linear increase of $\log D^{\text{U}}$ in the acidic medium.

With decreasing concentration of H^+ ions the D^{Th} increases. This increase however is much more influenced by the competitive reaction, *viz.* the formation of Th^{4+} chelates whose formation constants are much higher than those of uranyl ions. The difference in stability of both chelates is well manifested by the course of dependence of D^{Th} on the H^+ ion concentration. As the number of coordinated groups in studied polyaminopolycarboxylic acids increase, the values of thermodynamic stability constants of Th^{4+} chelates increase in the series $\text{NTA} < \text{EDTA} < \text{DCTA} < \text{DTPA} < \text{TTHA}$ (refs⁹⁻¹¹). In solutions of the mentioned chelating agents, the values of D^{Th} decrease in the same series. For TTHA however, where the value of the constant ($\log K_{\text{Th}}^{\text{T}} = 31.9$) is the highest from all studied chelons, the increase of D^{Th} as a function of increasing pH is completely suppressed. For IDA the sorption of Th^{4+} in weakly acidic solutions is affected only very little and due to the higher affinity the values of D^{Th} are higher than those of D^{U} which is shown by experimental results for both metals presented in Fig. 1.

In solutions of higher pH the functional silanole groups start to change from the H^+ into Na^+ form. Due to the different acidity of individual groups this change

*a**b**c**d**e**f*

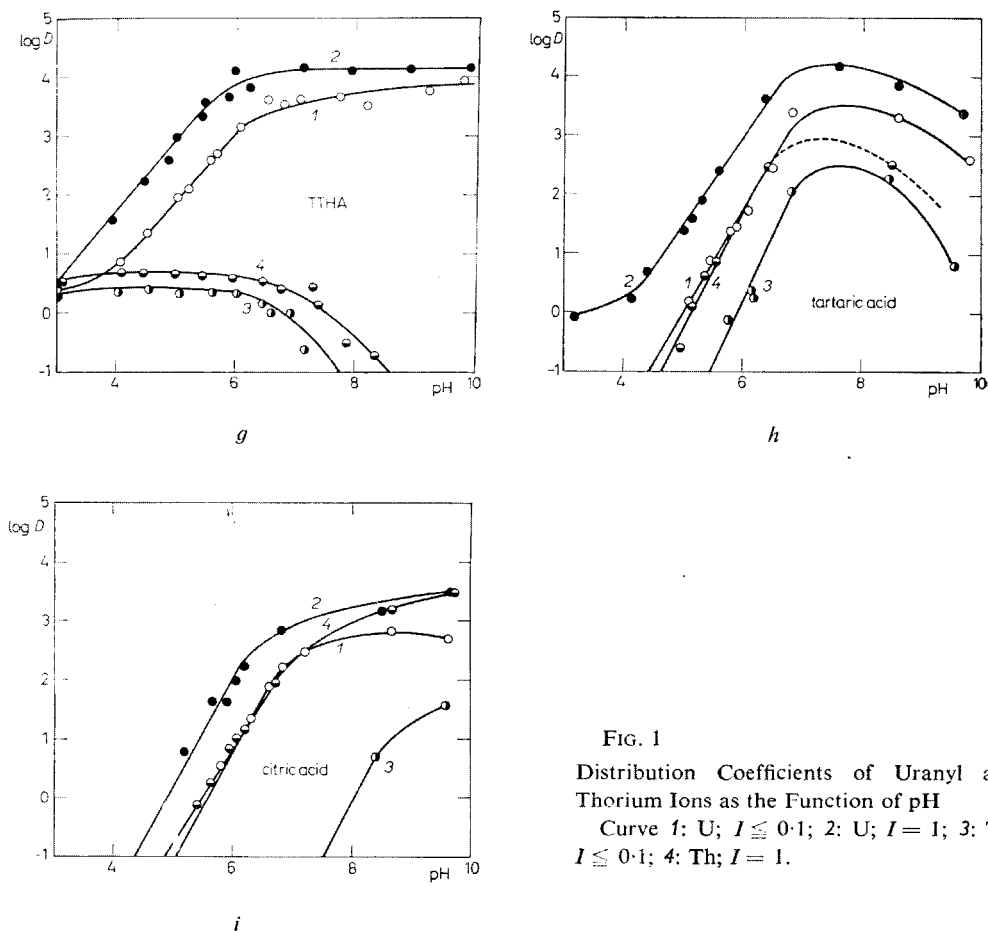


FIG. 1

Distribution Coefficients of Uranyl and Thorium Ions as the Function of pH

Curve 1: U; $I \leq 0.1$; 2: U; $I = 1$; 3: Th; $I \leq 0.1$; 4: Th; $I = 1$.

is gradual and in neutral and weakly acidic solutions both forms are likely to be present ($\equiv\text{SiOH}$, $\equiv\text{SiONa}$). Simultaneously the conditional stability constants are further increasing. The result is that the increase of distribution coefficients D^{U} and D^{Th} comes to a stop and that their values may even start decreasing.

The increase of distribution coefficients with increasing ionic strength is the main difference between silicagel and a weak acid carboxylic cation-exchanger (*e.g.* Amberlite IRC 50) for which the values of distribution coefficients decrease with increasing I (ref.³²). In case of silicagel the high ionic strength causes obviously a drop of activity of hydrogen ions and subsequently the increase of dissociation of functional groups which makes the sorption of the studied metal ions easier. This phenomenon can be employed for chromatographic separation of uranium from strongly minera-

lized waters and/or solutions obtained after the decomposition of rocks and low-grade ores by fusion with salts of alkali metals.

From the obtained values of distribution coefficients the separation factors $S = D^U/D^{Th}$ have been calculated for all studied agents at various pH. Fig. 2 shows how the values of $\log S$ increase with decreasing concentration of hydrogen ions, reach maximum at pH 6–7 and then start to decrease. When ionic strength is increased this maximum is shifted toward higher concentrations of hydrogen ions (by approximately one pH unit). For TTHA and IDA however, the maximum is not reached within the studied pH interval. The plots show a steady and steep increase of $\log S$ toward the alkaline medium.

Based on the values of S the following conclusions for the chromatographic separation of studied metals can be made:

Glycine can hardly be used in actual separations since the low stability of its chelates causes hydrolysis of both metals at pH > 5 and the values of separation factors are too low.

IDA is the only chelating agent for which $D^U < D^{Th}$ in the pH range 4–6. This gives a theoretical possibility for the separation of excess uranium from thorium.

NTA. Separation factors at pH 4.5–8 are high enough to enable the separation of both studied ions with higher efficiency than that of generally used EDTA.

EDTA does not allow the complete separation of uranium from excess thorium. This is in agreement with results of separations on a column⁶.

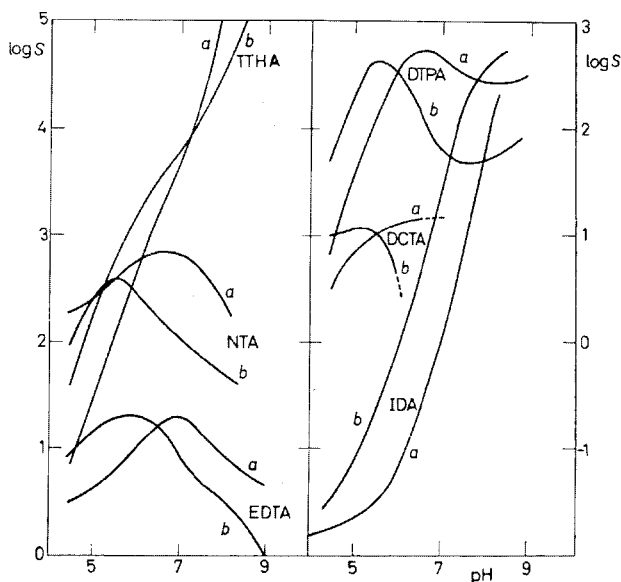


FIG. 2
Separation Factors as a
Function of pH
a) $I \leq 0.1$; b) $I = 1$.

DCTA. Although the difference in stability constants of UO_2^{2+} and Th^{4+} complexes is higher than for EDTA, the values of separation factors and hence conditions of a successful separation are for this acid the lowest.

DTPA. High values of separation factors give basic conditions for the separation of uranium from excess of thorium in the pH interval 5–9.

TTHA. The values of S are the highest of all studied systems. They increase toward the alkaline region where the separation factor reaches the value 10^5 . TTHA therefore appears to be the most promising agent for the separation of both elements.

Citric and tartaric acids. The difference in values of D^{U} and D^{Th} is quite high in the medium of low ionic strength. The absolute values of D^{U} , nevertheless, are too low.

The obtained dependences have been used for analytical separations of UO_2^{2+} and Th^{4+} ions on a column of silica gel³³.

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