

**SORPTION OF METAL IONS ON A STRONG ACID
CATION-EXCHANGER IN THE PRESENCE
OF TRIETHYLENETETRAMINE - N, N, N', N'', N''', N'''' -
HEXAACETIC ACID**

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The effect of triethylenetetramine hexaacetic acid (TTHA) on the sorption of 20 metal ions on a strong acid cation-exchanger was studied. Distribution coefficients of Cu^{2+} , Mg^{2+} , Ca^{2+} , Sr^{2+} , Ba^{2+} , Be^{2+} , Zn^{2+} , Cd^{2+} , Al^{3+} , In^{3+} , Tl^+ , Th^{4+} , Pb^{2+} , Bi^{3+} , Cr^{3+} , UO_2^{2+} , Mn^{2+} , Fe^{3+} , Co^{2+} and Ni^{2+} were determined by the batch method in the system Dowex 50W X8 resin-buffered solution of the studied ion containing TTHA at varying concentration of hydrogen ions. The obtained dependences are presented in diagrams.

The introduction of chelate-forming substances into inorganic analysis^{1,2} has been a great contribution for improvement of the selectivity of an ion-exchange. The compounds from the group of polyaminopolycarboxylic acids³⁻⁵ are highly effective.

Triethylenetetramine-N,N,N',N'',N''',N''''-hexaacetic acid (TTHA) possesses in the series of presently used polyaminopolycarboxylic acids the highest number of functional chelating groups⁶. TTHA is also noted for its chelates of high stability, especially those with metal ions of higher charge which, depending on pH, form series of hydrogen and hydroxy complexes. The polynuclear complexes are formed^{7-18,29} in most cases. The reactions of TTHA with metal ions have so far been studied from the point of view of volumetric analysis¹⁹⁻²¹. The application of TTHA in polarography has also been described²². The introduction of TTHA into an ion-exchange chromatography is likely to be prospective mainly due to the important chelating properties of the acid.

In this paper the effect of TTHA on the behaviour of a number of metal ions, *i.e.* Cu^{2+} , Mg^{2+} , Ca^{2+} , Sr^{2+} , Ba^{2+} , Be^{2+} , Zn^{2+} , Cd^{2+} , Al^{3+} , In^{3+} , Tl^+ , Th^{4+} , Pb^{2+} , Bi^{3+} , Cr^{3+} , UO_2^{2+} , Mn^{2+} , Fe^{3+} , Co^{2+} and Ni^{2+} has been studied during their sorption on a strong acid cation-exchanger Dowex 50 X8.

EXPERIMENTAL

Apparatus and Solutions

PHM 4 (Radiometer) pH-meter was used to measure pH of solutions. Analytical determinations by atomic absorption spectrometry were carried out on a Perkin-Elmer 306, spectrophotometric

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determinations on a Unicam SP 800 and the fluorometric determination of Be using an H 960 (Hilger and Watts) instruments.

0.1M solutions of perchlorates of studied metals were prepared as follows: Cu^{2+} , Zn^{2+} , Cd^{2+} , In^{3+} , Pb^{2+} and Bi^{3+} -pure metals Research Institute for Metals, (Panenské Břežany) were dissolved in HNO_3 , the obtained solutions evaporated several times with HClO_4 and finally diluted up to the required volume. Mg^{2+} , Ca^{2+} , Sr^{2+} , Ba^{2+} , Be^{2+} and Mn^{2+} -pure carbonates (Johnson and Matthey, Merck, Lachema) were dissolved in HClO_4 and made up to the final volume. Fe^{3+} — Fe_2O_3 (Johnson and Matthey) was dissolved in HCl and evaporated with HClO_4 . Al^{3+} , Th^{4+} and UO_2^{2+} -aluminium chloride (C. Erba), thorium and uranyl nitrates (Merck) were dissolved in water, the respective metal hydroxides were precipitated by ammonia, then washed and dissolved in the known amount of HClO_4 . Cr^{3+} , Co^{2+} and Ni^{2+} -sulphates of these metals (Lachema) were dissolved in water, solutions adjusted to pH 2.5 and passed through the column of a cation-exchanger in the H^+ -form. The sorbed ions were stripped by dilute HClO_4 , eluates evaporated almost to dryness and the residue dissolved in the known amount of water. Tl^+ -solution of thalous sulphate (Lachema) was passed through the column of an anion exchanger in the OH^- -form. The obtained solution of thalous hydroxide was neutralized by HClO_4 , the exact concentration of Tl was determined gravimetrically and the 0.1M solution was then prepared by appropriate dilution. The concentrations of all solutions were checked gravimetrically or by EDTA titrations.

$5 \cdot 10^{-3}\text{M}$ -TTHA was prepared by weighing 2.473 g of the acid (Fluka) and dissolving it in 1000 ml of 0.01M-NaOH.

Strong acid cation exchanger Dowex 50W X8 (50—100 mesh, Fluka) was decanted, several times recycled, transferred to the Na^+ -form by 5% NaCl and air-dried. The moisture content and exchange capacity were determined by common methods. The capacity of the air-dried exchanger was 4.78 meq. g^{-1} . All other used reagents were of the highest available purity grade.

Analytical Methods

Common atomic absorption spectrometric methods²³ were used to determine most metal ions, *i.e.* Cu^{2+} , Mg^{2+} , Ca^{2+} , Sr^{2+} , Ba^{2+} , Zn^{2+} , Cd^{2+} , In^{3+} , Tl^+ , Pb^{2+} , Cr^{3+} , Mn^{2+} , Fe^{3+} , Co^{2+} and Ni^{2+} . The acetylene-air mixture was used to feed the flame. The concentrations of metals were determined by means of calibration curves plotted as absorbances of standard solutions of the same composition as the analyzed solution.

Spectrophotometric methods were used to determine Al^{3+} , Bi^{3+} , UO_2^{2+} and Th^{4+} . For bismuth, the absorption of its chloride complex²⁴ in 4M-HCl was measured at 327 nm. Aluminium was determined after the mineralization of organic matter by the reaction of Al with Chromazurol S (ref.²⁵) in the solution buffered to pH 6.1 at 553 nm. For the determination of uranyl ions the colour of their complex with Arsenazo III in 4M- HClO_4 was employed and the maximum absorption²⁶ measured at 656 nm. Arsenazo was also used to determine thorium²⁶ in the 4M-HCl medium at the wavelength of 670 nm.

The method of the determination of beryllium was based on the fluorescence of its complex with morine in the alkaline medium²⁷. 10^{-5}M quinine sulphate was used as the standard solution. It has been found that TTHA does not interfere in the determination of beryllium.

Determination of Distribution Coefficients

The behaviour of metal ions in their sorption on an ion exchanger as well as the effect of the chelating agent is best followed by the determination of distribution coefficients D , that determine

the concentration ratio of the studied metal in both the exchanger and liquid phase. The value of the distribution coefficient is determined by the selectivity coefficient of the studied element in relation to a counter ion, and the stability of the complex. Using the given exchanger in its particular form, the most important variable is the concentration of hydrogen ions. The dependence of distribution coefficients on pH was studied at constant ionic strength and temperature.

Procedure: 5 ml of 0.01M solution of the studied ion was measured into a 50 ml beaker and 20 ml 0.005M-TTHA and 5 ml of 0.5M acetic or chloroacetic acid was added. Chloroacetic acid was used to buffer solutions in the pH range 2.0–4.0, acetic acid was used for pH 3.5–5.0 while for solutions of pH > 5 the buffer capacity of TTHA was employed. pH of the solution was then adjusted by the addition of 1M-NaOH (A ml) and the calculated volume (10–2A–X ml) of 0.5M-NaClO₄ was added to maintain the constant ionic strength $I = 0.1$ (X being the amount of NaClO₄ equivalent to NaOH present in the measured solution of TTHA). The solution was then transferred into a 50 ml volumetric flask, made up to the mark and transferred into a 100 ml polythene bottle containing a weighed amount of the exchanger which corresponded to 1 g of the dry resin. The bottles were carefully closed and their contents agitated for 12 hours. The equilibrium mixture was filtered through a sintered glass filter, and the final pH of the solution

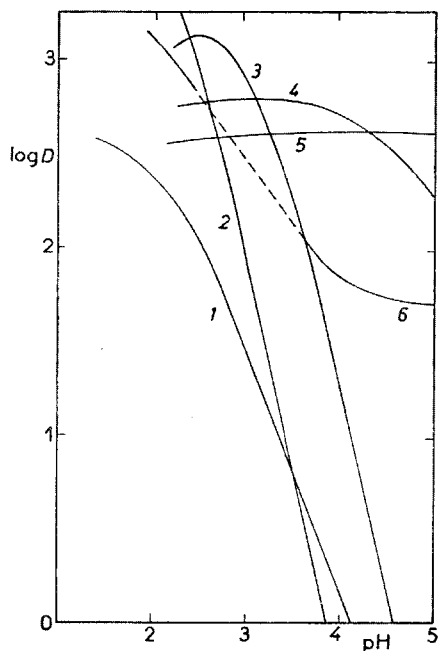


FIG. 1

Dependence of Distribution Coefficients on pH

Curve 1 Cr³⁺, 2 Al³⁺, 3 Mn²⁺, 4 Be²⁺,
5 Ti⁴⁺, 6 UO₂²⁺.

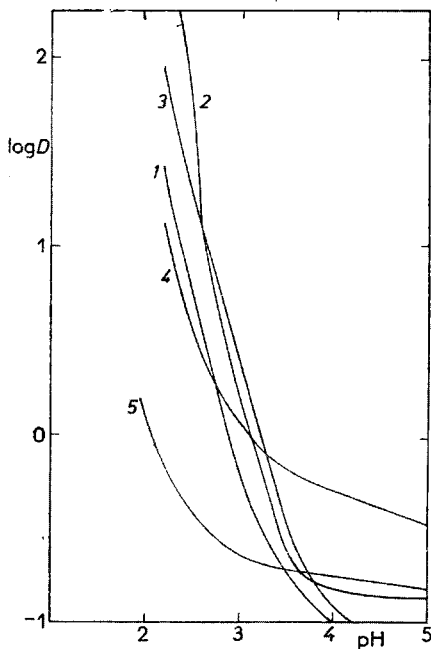


FIG. 2

Dependence of Distribution Coefficients on pH

Curve 1 Co²⁺, 2 Cd²⁺, 3 Pb²⁺, 4 Zn²⁺,
5 Cu²⁺.

was determined. The resin on the sintered glass filter was eluted by 2—4M-HCl. This procedure was used to determine the metal concentration in both the filtrate and the eluate (values were corrected for amount of the solution retained by the resin particles), and the distribution coefficients were calculated.

RESULTS

All obtained distribution coefficients are presented in Figs 1—4 as their function of equilibrium pH of the solution. The values obtained in the pH range 3·5—4 simultaneously in the medium of the chloroacetate and acetate buffer are in all cases in a good agreement. The formation of the precipitate prevented the determination of distribution coefficients of uranyl ions in the pH region of 2·4—3·8. Similar phenomenon was observed by other authors also for EDTA (ref.²⁸) and DTPA (ref.⁵). For thorium the value of D is less than 0·1 for the entire pH range.

General relations between the distribution coefficient and the complex stability (and hence pH of the solution) are reflected in all experimentally found dependences. With the decreasing concentration of hydrogen ions, the dissociation of the ligand functional groups increases and the concentration of the chelate forming anion also increases. This results in the increase of stability of chelates and decrease of values of distribution coefficients.

The values of stability constants of metal complexes with TTHA published so far^{7-18,29} vary with quite high dispersion (even by several orders of magnitude), are not consistent and are far from being complete. No data whatsoever have been published for ions such as Tl^+ , Be^{2+} , Cr^{3+} , In^{3+} and UO_2^{2+} as yet. TTHA is also noted for its great tendency to form very stable polynuclear complexes.

Critically selected data were compared with the values of stability constants of the same ions with lower homologues of the series of polyamino polycarboxylic acids³⁰. This comparison showed that in the series EDTA—DTPA—TTHA the stability

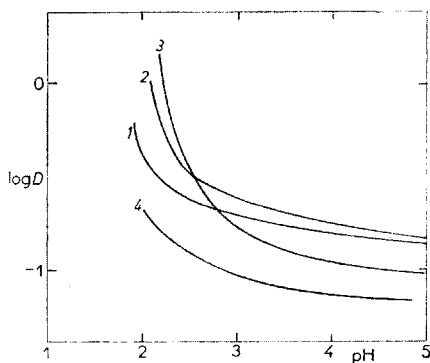


FIG. 3
Dependence of Distribution Coefficients
on pH

Curve 1 Fe^{3+} , 2 Ni^{2+} , 3 Bi^{3+} , 4 In^{3+} .

of chelates of multivalent ions increased while the stability constants of monovalent and some divalent ions (*e.g.* alkaline earth metals) are approximately equal or even slightly decrease. Divalent ions of transition metals show, on the other hand, a slight increase. The effect of the chelating agents on the sorption of metal ions on an ion exchanger changes in relation to variations in stability constants^{4,5}. Very low values of distribution coefficients of multivalent ions in the TTHA medium within the entire pH range (Fig. 3) indicate the high stability of the chelates of not only Th^{4+} and Fe^{3+} but also Bi^{3+} and In^{3+} . The comparison with the analogous behaviour of Bi^{3+} in the EDTA medium^{4,31,32} shows that the only published value of the stability of the Bi^{3+} -TTHA complex ($K_{\text{BiZ}} = 10^{17.7}$ ref.⁷) is too low. From the analogous sorption behaviour of In^{3+} and Fe^{3+} ions in the medium of all studied chelating agents^{5,32}, the similarity of the stability constants of the In -TTHA and Fe -TTHA complexes within one order of magnitude can be concluded.

The stability of aluminium complexes increases in the series EDTA – DTPA – TTHA. The values of stability constants are however too low when compared with

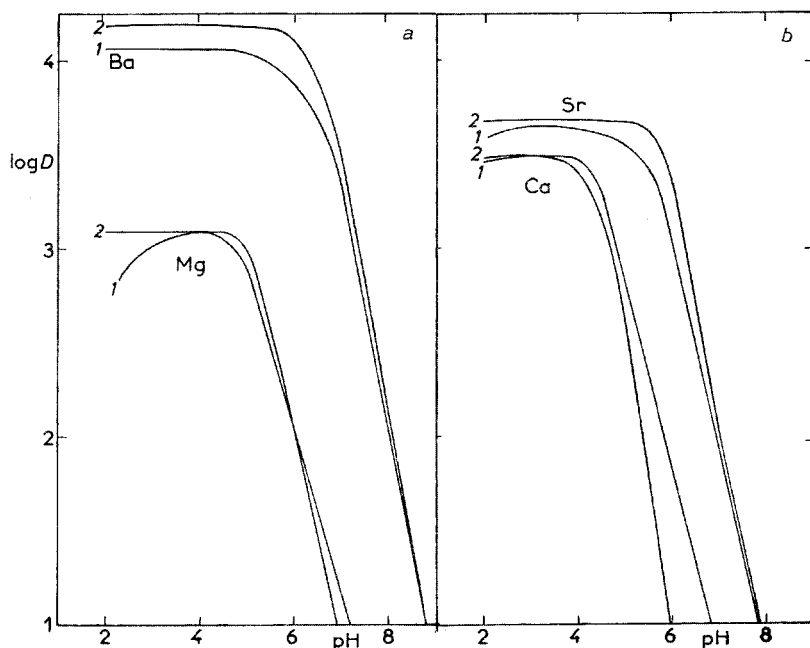


FIG. 4

Dependence of Distribution Coefficients of on pH

Curve 1 determined values; 2 calculated values. a Mg^{2+} and Ba^{2+} , b Ca^{2+} and Sr^{2+} .

other multivalent ions. The great tendency of Al^{3+} to form hydroxycomplexes has a negative influence³⁰ on the rate of its reaction with EDTA. At $\text{pH} > 3.5$, Al^{3+} is complexed only at elevated temperature. Similar phenomenon was observed also for the reaction with TTHA and the solutions had been, therefore, heated almost to the boiling point before the distribution coefficients were determined. The behaviour of Cr^{3+} ions is similar.

Distribution coefficients of ions which form low stability chelates with TTHA, such as Be^{2+} and UO_2^{2+} are affected in the studied pH range much less and the distribution coefficient of Tl^+ does not even show almost any change (Fig. 1).

The stability of chelates of ions of alkaline earth metals is also relatively low (stability constants $10^8 - 10^{10}$). This is the reason why the pH function of distribution coefficients of these ions was studied also in the region of $\text{pH} > 5$, where the effect of the presence of TTHA starts to take place. For other elements, however, a sharp drop of the values of distribution coefficients occurs in the region of $\text{pH} 2 - 5$.

The mathematical solution of the sorption equilibria for the system liquid phase-resin based on the exact thermodynamic calculations has not yet been worked out. For common calculations and the description of basic processes as well as side reactions which affect the sorption mechanism, however, the simplified calculation method³⁰ may be used with a good accuracy. The condition under which such calculations can be employed is the formation of only mononuclear complexes, which particularly for TTHA is not met for most studied metals^{7-18,29}. The simplified theoretical calculations of the functions "distribution coefficients - pH " can therefore be used only for the alkaline earth metals for which the formation of polynuclear complexes with TTHA may be, in the pH range 2 - 10, neglected. The published values of stability and complex protonization constants^{8,19,29}, TTHA protonization constants⁷ and of selectivity coefficients³⁰ were used in the calculations. The comparison of experimental and theoretical values for Mg^{2+} , Ca^{2+} , Sr^{2+} and Ba^{2+} is presented in Fig 4. A good agreement of both curves confirms that the formation of mononuclear, partially protonized complexes of these elements with TTHA has the decisive effect on their sorption.

CONCLUSION

The chelate forming effect of TTHA causes the substantial reduction of the values of distribution coefficients of most of the studied ions in their sorption on a strong acid cation exchanger. This effect is in accordance with the theoretical conditions and it depends on the stability of a particular chelate. Since the TTHA chelates, especially those of multivalent ions, are more stable than the similar chelates of lower homologues of the series of polyaminopolycarboxylic acids, the pH dependences of distribution coefficients are shifted towards the lower values when compared

with the analogous dependences found for EDTA (ref.⁴) and DTPA (ref.⁵). Significant differences in the values of distribution coefficients for several elements at appropriate pH facilitate the successful application of the chelating properties of TTHA in the course of chromatographic separations on an ion exchanger column.

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