

The general properties of water – nitrobenzene – crown – bis-1,2-dicarbollylcobaltate extraction systems

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Abstract

The extraction and stability constants in the system water – nitrobenzene have been collected and general rules valid for water – nitrobenzene – crown – bis-1,2-dicarbollylcobaltate extraction system have been found. The main principles are size compatibility of ion diameter and crown cavity diameters, the flexibility of crown, the basicity of crown and the steric factor of both the ligand and the extracted ion.

Introduction

The extraction in water – nitrobenzene system is a special case in liquid – liquid extraction field. Because nitrobenzene has high permittivity ($\epsilon = 34.8$) full dissociation of acids or salts of voluminous hydrophobic anions proceeds in nitrobenzene saturated with water. The unique orders of selectivity of water – nitrobenzene – bulky anion combination differ from any other extraction systems. The distribution ratios of alkali metal increase in the order of $\text{Li}^+ < \text{Na}^+ < \text{K}^+ < \text{Rb}^+ < \text{Cs}^+$.

Hydrogen form of bis-1,2-dicarbollylcobaltate was introduced by Rais et al. [1] for the extraction of Cs^+ cation from mineral acid into nitrobenzene. The main advantage of bis-1,2-dicarbollylcobaltate anion in comparison with other hydrophobic anion (e.g. dipicrylaminato, or tetraphenylborate) is its stability in acid medium so the extraction from mineral acid is possible. The addition of polyoxyethylene compound increases the extraction of alkali earth cations and mutual selectivity of its extraction [2]. The distribution ratio increases in the order of $\text{Ca}^{2+} < \text{Sr}^{2+} < \text{Ba}^{2+}$ [3] while for the other extractants the order of selectivity is usually quite different.

These properties caused that the bis-1,2-dicarbollylcobaltate crown extraction system can be used in radiochemistry and its modification was applied in industrial scale for the separation of $^{134,137}\text{Cs}$ and ^{90}Sr from high radioactive wastes from reprocessing [4, 5].

The aim of present review is a critical survey of published equilibrium data which deals with extraction in water - bis-1,2-dicarbollylcobaltate – nitrobenzene – polyoxyethylene compound extraction systems. Equilibrium constant values are useful especially for the mathematical modeling of extraction processes.

Theoretical part

The distribution of H^+ - bis-1,2-dicarbollylcobaltate (abbr. H^+, B^-) in water – nitrobenzene extraction system can be described by the equation



the equilibrium constant of which can be written as

$$K_{ex}(H^+, B^-) = \frac{\{H_{org}^+\}\{B_{org}^-\}}{\{H_{aq}^+\}\{B_{aq}^-\}} \approx \frac{[H_{org}^+][B_{org}^-]}{[H_{aq}^+][B_{aq}^-]} \quad (2)$$

where in braces are activities and in brackets are concentrations.

When the equilibrium constant (2) value is sufficiently high, $\log K_{ex}(H^+, B^-) = 3.2$ [2, 6], all bis-1,2-dicarbollylcobaltate is usually present in nitrobenzene phase, especially if mineral acid is present in the aqueous phase.

The extraction of metal ion M^{z+} in aqueous solution of acid – nitrobenzene solution of H^+ bis-1,2-dicarbollylcobaltate system proceeds as liquid cation exchange that can be written as



$$K_{zH}^M = K_{ex}(M^{z+}) = \frac{[M_{org}^{z+}][H_{aq}^+]^{z+}}{[M_{aq}^{z+}][H_{org}^+]^{z+}} \quad (4)$$

The extraction constants in the system with dissociation in the organic phase can be divided to two individual extraction constants, which characterizes the extraction of individual ion [7]

$$\log K_{ex}(H^+, B^-) = \log K_i(H^+) + \log K_i(B^-) \quad (5)$$

$$\log K_i(M^{z+}) = \log K_{zH}^M - z \log K_i(H^+) \quad (6)$$

It must be pointed out that the overall extraction constant cannot be thermodynamically divided to individual extraction constants, so nonthermodynamical assumption known as tetraphenylarsonium tetraphanenylborate hypothesis is usually used. The individual extraction constant of H^+ ion calculated on the basis of this hypotheses is $\log K_i(H^+) = -5.7$ [7].

The individual extraction constants cannot be defined as the ratio of concentration of ions in the organic and aqueous phases and has the practical meaning only in connection with other individual extraction constant (e.g. Eq. (5) or Eq. (6)).

Only heavy alkali metal cations (K^+ , Rb^+ , and Cs^+) are hydrophobic enough so it can be extracted directly by the nitrobenzene solution of bis-1,2-dicarbollylcobaltate. Light alkali metal, alkali earth and rare earth cations must be extracted in the form of more hydrophobic complexes.

The suitable hydrophobic ligands are usually linear or cyclic polyoxyethylene compounds - polyethylene glycols, glymes, crown ethers or calixarenes [3].

The following equilibrium constants take place during the metal extraction in the system under study:

- 1) The individual extraction constants of free ions between water and nitrobenzene (Eq. 5).
- 2) The stability and protonization constants of all complexes in the organic phase (Eq. 7 and Eq. 8).
- 3) The distribution constant K_D of polyoxyethylene compound between water and nitrobenzene (Eq. 9).
- 4) The stability and protonization constants of all complexes in the aqueous phase (Eq. 10, Eq. 11).

$$K(\text{ML}_n^{z+})_{\text{org}} = \frac{[\text{ML}_{n,\text{org}}^{z+}]}{[\text{M}_{\text{org}}^{z+}][\text{L}_{\text{org}}]^n} \quad (7)$$

$$K(\text{HL}_n^+)_{\text{org}} = \frac{[\text{HL}_{n,\text{org}}^+]}{[\text{H}_{\text{org}}^+][\text{L}_{\text{org}}]^n} \quad (8)$$

$$K_D = \frac{[\text{L}_{\text{org}}]}{[\text{L}_{\text{aq}}]} \quad (9)$$

$$K(\text{ML}_n^{z+})_{\text{aq}} = \frac{[\text{ML}_{n,\text{aq}}^{z+}]}{[\text{M}_{\text{aq}}^{z+}][\text{L}_{\text{aq}}]^n} \quad (10)$$

$$K(\text{HL}_n^+)_{\text{aq}} = \frac{[\text{HL}_{n,\text{aq}}^+]}{[\text{H}_{\text{aq}}^+][\text{L}_{\text{aq}}]^n} \quad (11)$$

The equilibrium constants between H^+ ion or metal cations and polyoxyethylene compounds in water are usually low so the protonation and complex formation in aqueous phase do not take place when the K_D value is sufficiently high.

If all equilibrium constants given above are known the individual extraction constant of complex ion ML^{z+} can be calculated using the equation

$$\log K_i(\text{ML}^{z+}) = \log K(\text{ML}_{\text{org}}^{z+}) - \log K(\text{ML}_{\text{aq}}^{z+}) + \log K_D + \log K_i(\text{M}^{z+}) \quad (12)$$

The limiting factor for the determination of individual extraction constants of crown complexes is usually the knowledge of stability constants in water.

The extraction of the ion M^{z+} by the H^+ form of bis-1,2-dicarbollylcobaltate can be in the general form described by the reaction



and the equilibrium extraction constant of Eq. (11) can be written as

$$K_{\text{ex}}(\text{ML}_n\text{H}_m^{(z+m)+}) = \frac{[\text{ML}_n\text{H}_{m,\text{org}}^{(z+m)+}][\text{H}_{\text{aq}}^+]^{z+}}{[\text{M}_{\text{aq}}^{z+}][\text{L}_{\text{aq}}]^{n+}[\text{H}_{\text{org}}^+]^{(m+z)+}} \quad (14)$$

where z is the charge of extracted cation M^{z+} and n ($= 0, 1$ or 2) is the number of ligand molecules in the extracted complex in the nitrobenzene phase. Value of m is usually $m = 0$, so only the ML_n^{z+} complexes are present in the organic phase.

The extraction of deprotonated complexes EuLH_1^{2+} and CeLH_1^{2+} have been found for PEG 200, PEG 300 and PEG 400 ligands ($m = -1$) while the extraction of protonized complexes MHL^{3+} and MHL_2^{3+} have been found for Sr^{2+} and Ba^{2+} complexation with DB18C6.

The distribution ratio of metal ion M^{z+} is given by the equation (13)

$$D(\text{M}^{z+}) = \frac{\sum_{n=0, m=-1}^{n=2, m=1} [\text{ML}_n\text{H}_{m,\text{org}}^{(z+m)+}]}{\sum_{n=0}^1 [\text{ML}_{n,\text{aq}}^{z+}]} \quad (15)$$

Some typical dependences of distribution ratio of radionuclides ^{85}Sr and ^{137}Cs on the concentrations of crowns are depicted on Fig.1 and Fig 2.

The extraction system aqueous solution of mineral acid – polyoxyethylene compound - bis-1,2-dicarbollylcobaltate – nitrobenzene can be described by equilibrium constants (2), (8-11) and (14) and the mass balance of all components,

$$c(\text{B}^-) = [\text{H}^+]_{\text{org}} + z[\text{M}^{z+}]_{\text{org}} + \sum(j+z)[\text{MH}_j\text{L}_i^{(j+z)+}]_{\text{org}} + \sum j[\text{H}_j\text{L}_i^{(j+z)+}]_{\text{org}} \quad (16)$$

$$c(\text{L}) = [\text{L}]_{\text{aq}} + [\text{L}]_{\text{org}} + \sum i[\text{HL}_i^+]_{\text{aq}} + \sum i[\text{ML}_i^{z+}]_{\text{aq}} + \sum i[\text{H}_j\text{L}_i^{j+}]_{\text{org}} + \sum i[\text{MH}_j\text{L}_i^{(j+z)+}]_{\text{org}} \quad (17)$$

$$c(\text{M}^{z+}) = [\text{M}^{z+}]_{\text{aq}} + [\text{M}^{z+}]_{\text{org}} + \sum \text{ML}_i^{z+}]_{\text{aq}} + \sum [\text{MH}_j\text{L}_i^{(j+z)+}]_{\text{org}} \quad (18)$$

$$c(\text{H}^+)_{\text{aq}} = [\text{H}^+]_{\text{aq}} + \sum \text{HL}_i^+]_{\text{aq}} \quad (19).$$

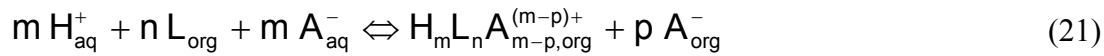
The extraction constants $K_{\text{ex}}(\text{ML}_n\text{H}_m^{(z+m)+})$ and protonization constant of ligand in nitrobenzene given by equations (14) and (8) can be calculated from the dependences of distribution ratio $D(\text{M}^{z+})$ on the total analytical concentration of ligand $c(\text{L})$. Data series with a few constant values of concentrations of bis-1,2-dicarbollylcobaltate $c(\text{B})$ and a few concentrations of acid in the aqueous phase $c(\text{H}^+)_{\text{aq}}$ have been measured (Fig. 1). General least squares minimizing program LTGW DC DISTR [8], derived from LETAGROP [9] was developed for the calculations of the equilibrium constants. Equations (2), (8-11) and (16-19) were used for this calculation.

Knowing the exchange extraction constant (Eq. 4) and the distribution constant of ligand in the system water – nitrobenzene the stability constant of extracted complex in nitrobenzene can be calculated as

$$K(\text{ML}_n^{z+})_{\text{org}} = \frac{K_{\text{ex}}(\text{ML}_n^{z+})}{K_{\text{zH}}^M K_{\text{D}}^n} \quad (20)$$

If the protonization constant of polyoxyethylene compound is too high it cannot be calculated from extraction data of metal as described previously. In that case the extraction of perchloric acid by the nitrobenzene solution of polyoxyethylene compound can be used.

This extraction can be described by common equation



where A_{org}^- is anion of perchloric acid.

The equilibrium constant of reaction (21) is defined as

$$K_{\text{ex}}(\text{H}_m \text{L}_n \text{A}_{m-p}^{(m-p)+}) = \frac{[\text{H}_m \text{L}_n \text{A}_{m-p,\text{org}}^{(m-p)+}][\text{A}_{\text{org}}^-]^p}{\{\text{H}_{\text{aq}}^+\}^m [\text{L}_{\text{org}}]^n \{\text{A}_{\text{org}}^-\}^m} \quad (22)$$

The activities of perchloric acid in the aqueous phase cannot be replaced by concentration because of high concentration ratio (0.01M – 7M HClO_4).

The electroneutrality condition in the organic phase means that

$$\sum_0^N (m-p)[\text{H}_m \text{L}_n \text{A}_{m-p,\text{org}}^{(m-p)+}] = [\text{A}_{\text{org}}^-] \quad (23)$$

and material balance of ligand can be written as

$$c_{\text{L}} = [\text{L}_{\text{aq}}] + [\text{L}_{\text{org}}] + [\text{HL}_{\text{aq}}^+] + \sum_0^N n [\text{H}_m \text{L}_n \text{A}_{m-p,\text{org}}^{(m-p)+}] \quad (24).$$

The values of equilibrium constants (22) can be calculated from perchloric data extraction by the program LTGW ACID DISTR [10], based on Eq. (22)-(24).

The protonation constant in nitrobenzene can be calculated by the equation

$$K(\text{H}_m \text{L}_n^+)_{\text{org}} = \frac{K_{\text{ex}}(\text{H}_m \text{L}_n^{m+})}{K_{\text{ex}}(\text{H}^+)^m} \quad (25)$$

The exchange in the system with comparable concentration of all components can be used for the determination of stability constant of one metal complex knowing the stability constant of the another one. The measurement of distribution constant of ^{137}Cs in the system water – MCl – CsB – crown – nitrobenzene and ^{22}Na in the system water – MCl – NaB – crown – nitrobenzene was used for the determination of stability constants.

If only CsL^+ and ML^+ exist in the organic phase Eq. (26) can write the reaction.



For $c_{\text{CsB}}^{\text{in,org}} = c_{\text{MCl}}^{\text{in,org}} = c(\text{L})$ the equation (27) is valid

$$K_{\text{ex}}(\text{M}^+, \text{CsL}^+) = \frac{1}{D_{\text{Cs}}} \frac{c_{\text{CsDCC}}^{\text{in,nb}}}{(1 + D_{\text{Cs}}) c_{\text{M}_{\text{aq}}^+}^{\text{in,org}} - c_{\text{CsDCC}}^{\text{in,nb}}} \quad (27)$$

$$\log K(\text{ML}^+)_{\text{org}} = \log K(\text{CsL}^+)_{\text{org}} + \log K_{\text{ex}}(\text{M}^+, \text{CsL}^+) - \log K \quad (28)$$

The analogical equation is valid for the exchange of ^{22}Na .

Because the extraction in water – nitrobenzene – crown – bis-1,2-dicarbollylcobaltate extraction system is always cation exchange the distribution ratio of metal depends on the difference between the affinity of the extracted complex ion and that of exchanged hole or complex ion into the organic phase.

If the formation of complexes $\text{ML}_{\text{n, aq}}^{z+}$ and $\text{HL}_{\text{n, aq}}^+$ in the aqueous phase is negligible the product $\log K(\text{ML}_{\text{org}}^{z+}) + \log K_{\text{i}}(\text{M}^{z+})$ can be used for the characterization of the extraction efficiency of ion M^{z+} and the product $\log K(\text{HL}_{\text{org}}^+) + \log K_{\text{i}}(\text{H}^+)$ characterizes the competition of cation H^+ that is present in macroconcentration. The analogical equations are valid if bis-1,2-dicarbollylcobaltate is present in another ionic form (e.g. Na^+ , Li^+ , NH_4^+ or Cs^+ salt of bis-1,2-dicarbollylcobaltate).

Because the individual extraction constants of alkali metal cations differ by four orders of magnitude the highest distribution ratios are usually found for potassium or cesium.

Knowing the value of individual extraction constant partial free enthalpy for the transport of that complex across the water - nitrobenzene interface, $\Delta G_{\text{tr}}^0(\text{ML}^{z+})$, can be calculated using the equation

$$\Delta G_{\text{tr}}^0(\text{ML}^{z+}) = -2.303 RT \log K_{\text{i}}(\text{ML}^{z+}), \quad (29)$$

The equation (29) can be used for the mutual comparison of extraction and electrochemical data.

Discussion of extraction data

There are several factors, which influence the stability constants of H^+ ion and metal ions with crown ethers and linear polyoxyethylene ligands in nitrobenzene saturated with water. The first is ion diameter – hole size compatibility principle. The other factors are basicity and deformability of ligand, steric factors and the possibility of the formation of ML_2^{z+} complexes.

The main secondary factor in water-nitrobenzene system is the number of water molecules coextracted into organic phase.

Our extraction data obtained in aqueous acid or salt solution – crown – nitrobenzene bis-1,2-dicarbollylcobaltate [11 - 16] and voltametric data of Kudo et al. [17 - 20] and Koryta et al. [21] are used for the comparison of extraction of various metal ion in the present study. It must be pointed out that the good agreement has been found between most of our extraction data and published ion-transfer polarographic measurements.

The stability constants of univalent ions with crowns and linear polyoxyethylene compounds and protonation constants of these ligands are summarized in Table 1-3.

The following rules can be found from the data in Table 1 and Fig. 3-9.

- 1) The “classic” ion diameter – hole size compatibility principle for six-membered crowns is fully valid only for unsubstituted 18C6 and flexible DCH18C6. The influence of rigid aromatic substituent is important for the complex formation of H^+ and Li^+ ions with B18C6 and DB18C6. The influence of two benzo groups is higher than the influence of one group. The differences of stability constants of H^+ and Li^+ ions between 18C6 and DB18C6 are three orders of magnitude. For that reason the distribution ratio of Na^+ ion in the system mineral acid solution – DB18C6 - bis-1,2-dicarbollylcobaltate – nitrobenzene is 100 times higher than one in the systems with 18C6 or DCH18C6.

It must be pointed out that DB18C6 forms polynuclear “sandwich” complexes with H^+ ions and Sr^{2+} or Ba^{2+} ions. This fact can be explained by rigid planar configuration of this ligand.

- 2) The addition of polyoxyethylene compound usually causes the decrease of distribution ratio of Cs^+ in water - bis-1,2-dicarbollylcobaltate – nitrobenzene extraction systems. The exception has been found for 15C5, DB15C5, DB18C6 and DB21C7 (but not for DB24C8). The formation of CsL_2^+ complexes and relatively low values of protonation constants of 15C5 and dibenzosubstituted crown (Table 1 - Table 3) cause these synergistic effects.
- 3) The stability constants of alkali metal cations have maximum value for K^+ (18C6, DCH18C6) or Na^+ ions (DB18C6, DB24C8 and linear polyoxyethylene compounds). This fact can be described by hole size – ion diameter compatibility principle for 18C6 and DCH18C6. The rigid structure of DB18C6 may change the affinity maximum in alkali metal series to Na^+ for DB18C6.
- 4) The stability constants series $Na^+ < NH_4^+ < K^+$ were found for 18-crown-6, DCH18C6 and valinomycin. On the other hand the series $NH_4^+ < K^+ < Na^+$ were found for dibenzo substituted crowns DB18C6 and DB24C8 and $NH_4^+ < Li^+ < Na^+ < K^+$ series was found for 15C5. The anomaly behavior of NH_4^+ ion is probably caused by its structure that is different that the spherical shape of metal ions.

5) It must be pointed out that the behavior of H^+ ion is specific. The ionic diameter of H_3O^+ ion is 0.13 – 0.14 nm, which is near the ion diameter of K^+ ion.

The extraction of Ca^{2+} , Sr^{2+} and Ba^{2+} in the studied systems is summarized in Table 4 – 7. The typical maxima [8] on the dependences of $\log D$ on $\log c(L)$ have been found for all almost systems under study (see Fig. 1)

The following rules can be derived from the data in Table 4-7.

- 1) The addition of polyoxyethylene compound increases the distribution ratio of Ca^{2+} , Sr^{2+} and Ba^{2+} cations.
- 2) The extraction of Ca^{2+} (i.e. distribution ratio $D(Ca)$) increases in the sequence 18-crown-6 < PEG 400 < 2-hydroxymethyl-12-crown-4 < 15-crown-5 < 2-hydroxymethyl-18-crown-6 < 12C4 < 2-hydroxymethyl-15-crown-5 < (5,11,17,23-tetra-tert-butyl-25,26,27,28-tetrakis-(N,N-diethylkarboxamidomethyleneoxy)-calix{4}aren (abbr. MR 184),
- 3) The extraction of strontium increases in sequence nitrobenzo-15-crown-5 < DB24C8 < DB21C7 < DCH24C8 < DB18C6 < DCH18C6 < DB15C5 < 12C4 < 18C6 < decyl-18C6 < CH15C5 < PEG 400 < 2HM15C5 < 2HM18C6 < B15C5 < 15C5.
- 4) The order of DCH24C8 < DB18C6 < DB24C8 < DB21C7 < 18C6 < 2-hydroxymethyl-18-crown-6 < MR 184 < 2-hydroxymethyl-15-crown-5 < PEG 400 < 15C5 was found for Ba^{2+} .
- 5) Substitution of 15-crown-5 by any group decreases the value of separation factor $\alpha(Sr/Ca)$.
- 6) The extraction of alkali earth ions in the systems with crowns increases in the sequence $Ca^{2+} < Sr^{2+} < Ba^{2+}$. The exceptions are 12C4 where $D(Ca) > D(Sr)$
- 7) The extraction decrease in the order $D(Ca) \gg D(Sr) \approx D(Ba)$ for calixarene MR 184.
- 8) The addition of polyoxyethylene compound (except 12C4 and MR-184) increase the value of separation factors $\alpha(Sr/Ca)$ and $\alpha(Ba/Sr)$.

It must be pointed out that the individual extraction constants for alkali earth, rare earth and some transition metal cations are low and mutual separation factors of that metal ions in the absence of crown are low as well (Table 8 – Table 9).

The highest values of synergistic factor for the extraction of Sr^{2+} and Ba^{2+} have been found for 15-crown-5 where just complexes ML_2^{2+} are formed in the organic phase. These complexes are only slightly hydrated because 2 x 5 oxygen atoms replace almost all water molecules hydrating the extracted ion [22]. The hydroxyl group of 2HM15C5 is not probably bonded to Sr^{2+} ion. On the other hand Ca^{2+} ion forms with 15-crown-5 both CaL^{2+} and CaL_2^{2+} complexes so a few water molecules are coextracted into nitrobenzene [22]. For that reason the separation factor $\alpha(Sr^{2+}/Ca) \approx 10^3$ found in the system with 15-crown-5 is highest among all tested polyoxyethylene compounds. The hydroxyl group of 2HM15C5 can be bonded to Ca^{2+} ion so the selectivity $\alpha(Sr^{2+}/Ca^{2+}) = 30$ is low.

The extraction of Pb^{2+} in the system with 15-crown-5 is even higher than the extraction of barium in the same system [23].

The slightly different behavior has been found for six-membered crowns, where the highest synergistic factor has been found for 2HM18C6. The maximum distribution ratio has been found in concentration region where the 1:1 complexes prevails so the hydroxyl group can be directly bound to metal ion. The synergistic factor in mineral acid solution - bis-1,2-dicarbollylcobaltate – 18C6 – nitrobenzene system is low because of high value of protonation constant of 18C6 in nitrobenzene.

While the protonation constant value of PEG 400 and p-nonylphenylnonaethylene glycol in nitrobenzene are almost identical (see Table 3) the stability constant of PEG 400 complex with Sr^{2+} in nitrobenzene is higher than that of p-nonylphenylnonaethylene glycol. It can be explained by the fact that PEG 400 has two hydroxyl groups attached at the ends of oxyethylene chain while p-nonylphenylnonaethylene glycol has only one. The number of oxyethylene units, which can be bond to H^+ ion, is lower than in the case of Sr^{2+} ion. It means that the influence of second OH group takes place only for Sr^{2+} ion.

The separation $\text{Ba}^{2+}/\text{Sr}^{2+}$ is the best in the systems with DB21C7 and DB24C8. This behavior can be explained by the ion diameter – hole size compatibility principle.

The synergistic enhancement of rare earth extraction in water – nitrobenzene - bis-1,2-dicarbolylcobaltate – crown extraction system is much lower than in analogous systems with PEGs (Table 10). The systems with crown can be used for the separation of alkali earth metals from rare earth metals.

The extraction of Eu^{3+} and Ce^{3+} in the presence of PEG 200, PEG 300 and PEG 400 proceeds by complicated mechanism. Complexes ML, ML₂ and MH-1L have been found in the organic phase [24].

Knowing the equilibrium constants in water – polyoxyethylene ligand – bis-1,2-dicarbolylcobaltate – nitrobenzene extraction systems the optimum conditions for various separations can be calculated.

These calculations have been done for the separation $\text{Sr}^{2+}/\text{Ca}^{2+}$ in the system aqueous solution of Na salt of EDTA – 15C5 - bis-1,2-dicarbolylcobaltate – nitrobenzene extraction system [25] and for the separation of $\text{Sr}^{2+}/\text{Y}^{3+}$ in the systems water – HCl – 15C5 – heptachlorodicarbolylcobaltate – nitrobenzene and water – HCl – B15C5 – heptachlorodicarbolylcobaltate – nitrobenzene [26].

In all cases it has been proved that the mathematical modeling using our equilibrium constants is useful tool for solving the separation problems.

Conclusion

The extraction in the system water – mineral acid or salt – polyoxyethylene compound – bis-1,2-dicarbolylcobaltate – nitrobenzene is more complicated than can be expected from usually used ion diameter – crown cavity diameter compatibility principle. The other important factors are the basicity and the deformability of crown, steric aspect and the angles of bonds of extracted ion. The binuclear “sandwich” complexes with H^+ ion and Sr^{2+} or Ba^{2+} ions have been proved for DB18C6. On the other hand, only SrL_2 and BaL_2 ($\text{L} = 15\text{C}5$) complexes are formed in nitrobenzene saturated with water. The addition of polyoxyethylene compound usually increases the distribution ratio of alkali earth metal ions and the selectivity of its mutual separation.

Acknowledgement

The present work has been supported by the Czech Ministry of Education, Youth and Sports of the Czech Republic, Project No. MSM 223400008 and the Grant Agency of Czech Republic grant No. 104/03/0499

Table 1.

The individual extraction and stability constants of univalent ions with polyoxyethylene compounds in nitrobenzene saturated with water

Ligand	H ⁺	Li ⁺	Na ⁺	NH ₄ ⁺	K ⁺	Rb ⁺	Cs ⁺	Tl ⁺	Ref.
log K _i ^a	-5.7	-6.7	-6.0	-4.7	-4.1	-3.4	-2.7	-3.4	[7] [27]
15C5	4.27 ^b	7.03 ^c	7.33 ^d	5.56 ^e	6.18 ^f		4.24 ^g		
B15C5	4.34 ^h	6.39 ^f	6.92 ^f		5.48 ^f	4.1 ⁱ	2.8 ⁱ		
18C6	7.56 ^j	7.9	8.0	8.6 ^k	9.53	8.14	7.0	8.39 ^l	[12] [13]
DCH18C6	7.35 ^t	8.07	7.80 ^m	8.0 ^k	8.21	7.49	6.32	8.21	[28]
B18C6	5.8 ⁱ	5.87 ⁿ	7.91 ⁿ		7.72 ⁿ	6.1 ⁱ	4.0 ⁱ		
DB18C6	4.00 ^o	4.45	7.17	6.9 ^k	6.89	5.78	4.79	6.00	[29]
DB24C8	5.75 ^p	6.20	7.20	6.24 ^k	6.33	5.97	5.90	6.55	[15]
Valinomycin			6.7	8.5	10.4 ^q	11.7	10.1	10.1	[16]
4-glym	2.67 ^r	4.31	5.12	4.26	4.36	3.68	3.06		[29]
PEG 400	5.69 ^s	6.59	7.37	6.67	6.79	6.13	5.49		[29]

^a [7], ^b [8], ^c [30], ^d [11], ^e [31], ^f [17], ^g [32], ^h [33], ⁱ [20], ^j [10], ^k [34], ^l [35], ^m [36], ⁿ [19],
^o [37], ^p [18], ^q [21], ^r [38], ^s [39]

^t Vaňura P.: unpublished results.

Table 2

Stability constants of 1:1 and 1:2 crown complexes of cesium in nitrobenzene, saturated with water.

Ligand	log K ₁	log β ₂	Ref.
15-crown-5	4.24	6.72	[32]
18-crown-6	6.54	8.64	[40]
DCH18C6	5.24	6.52	[41]
DB18C6	4.30	6.35	[42]
DB24C8	5.44	≈6.10	[43]

Table 3

Protonization constants of polyoxyethylene compounds in nitrobenzene saturated with water

Ligand	$\log K_{\text{org}}(\text{HL}^+)$	$\log K_{\text{org}}(\text{HL}_2^+)$	$\log \beta_{\text{org}}(\text{H}_2\text{L}_2^{2+})$	Ref.
12-crown-4	2.11	3.82		[44]
15-crown-5	4.27	2.05		[8]
18-crown-6	7.56	-	-	[10]
B15C5	4.34	1.76		[33]
DB18C6	4.00		10.4	[37]
4-glym	2.67	2.92		[38]
PEG 400	5.69			[39]
Slovafof 909 ^a	5.64	2.63		[45]

^a p-nonylphenylnonaethylene glycol

Table 4

Stability constants of complexes of alkali earth ions in nitrobenzene saturated with water

Ligand	$\log \beta_{\text{org}}$						Ref.
	CaL_2^{2+}	CaL_2^{2+}	SrL_2^{2+}	SrL_2^{2+}	BaL_2^{2+}	BaL_2^{2+}	
1-glym					2.35		[38]
2-glym			3.06		3.37		[38]
3-glym			4.34	6.77	5.18	8.03	[38]
4-glym			4.90	7.52	6.23	7.35	[38]
PEG 200			9.06		10.93		[46]
PEG 300			10.41		12.17		[46]
PEG 400	9.57 ^c		11.03		12.80		[46]
Slovafof 909	8.9 ^d		10.25	15.15			[47]
12C4	5.63	10.44	4.96	9.36			[44], [48]
15C5	7.46	11.6	- b	14.9	- b	16.1	[49], [8],[50]
B15C5				13.2		14.6	[33]
DB18C6 ^a			$\cong 6.1$	9.8	6.86	10.9	[51],[52]
18C6	10.1		11.50	16.24	12.47	17.78	[53], [54]
DB24C8			8.64		11.1		[19]

^a „sandwich“ complexes MHL^{3+} and MHL_2^{3+} have been found for Sr^{2+} and Ba^{2+} complexation with DB18C6. The stability constants of these complexes are $\log K(\text{SrHL}^{3+}) = 8.6$, $\log K(\text{SrHL}_2^{3+}) = 14.5$, $\log K(\text{BaHL}^{3+}) = 10.2$ and $\log K(\text{BaHL}_2^{3+}) = 15.8$.

^b only ML_2^{2+} complexes are formed for Sr^{2+} with 15C5 or B15C5 and Ba^{2+} with 15C5.

^c calculated for $\alpha(\text{Sr}^{2+}/\text{Ca}^{2+}) = 100$, Ref. [2]

^d calculated for $\alpha\text{Sr}^{2+}/\text{Ca}^{2+} = 80$, Ref. [55]

Table 5

Synergistic factors S reached during the extraction of Sr^{2+} by the nitrobenzene solution of bis-1,2-dicarbollylcobaltate and separation factors $\alpha(\text{Sr}/\text{Ca})$. S and $\alpha(\text{Sr}/\text{Ca})$ values are tabulated for the maxima on the dependences of $D(\text{Sr})$ vs. $c(\text{L})$ [56] [57] [58].

System	Concentrations	S	$\alpha(\text{Sr}/\text{Ca})$
Sr		1	2
Sr - NB15C5	0.1M HNO_3 , 0.001M H^+, B^-	13	
Sr - tetraglym	0.1M HNO_3 , 0.02M H^+, B^-	23	
Sr - DB24C8	0.1M HNO_3 , 0.010 M H^+, B^-	24	
Sr - DB21C7	0.1M HNO_3 , 0.01M H^+, B^-	57	
Sr - DCH24C8	0.1M HNO_3 , 0.01M H^+, B^-	65	
Sr - K6	0.1M HNO_3 , 0.01M H^+, B^-	90	40
Sr - 12C4	0.1M HNO_3 , 0.001M H^+, B^-	313	0.24
Sr - DB18C6	0.1M HNO_3 , 0.010 M H^+, B^-	350	45
Sr - DCH18C6	0.1M HNO_3 , 0.010 M H^+, B^-	460	95
Sr - DB15C5	0.1M HNO_3 , 0.01M H^+, B^-	1 500	160
Sr - 18C6	0.1M HClO_4 , 0.005M H^+, B^-	3 000	120
Sr - decyl-18C6	0.1M HNO_3 , 0.01 M H^+, B^-	4 000	
Sr - CH15C5	0.1M HNO_3 , 0.003M H^+, B^-	9 000	18
Sr - PEG 400	0.5M HNO_3 , 0.005M H^+, B^-	28 000	100
Sr - 2HM15C5	0.1M HNO_3 , 0.003M H^+, B^-	60 000	35
Sr - 2HM18C6	0.1M HNO_3 , 0.01 M H^+, B^-	100 000	
Sr - MR 184	0.1M HNO_3 , 0.01M H^+, B^-	150 000	0.1
Sr - B15C5	0.1M HNO_3 , 0.003M H^+, B^-	160 000	1000
Sr - 15C5	0.1M HNO_3 , 0.001M H^+, B^-	700 000	1000

Table 6

Synergistic factors S reached during the extraction of Ba^{2+} by the nitrobenzene solution of bis-1,2-dicarbollylcobaltate in the presence of polyoxyethylene ligands [46], [50 - 52], [54], [56 - 58]

Ligand	c(B)	c(HNO ₃)	log c(L)	log D(Ba)	log S(Ba)	log S(Ba)	log α (Ba/Sr)
DCH24C8	0.010	0.1	-2.3	2.00	3.17	3.17	1.7
DB18C6	0.005	0.1*	-2.6	1.65	3.40	3.40	1.3
DB24C8	0.010	0.1	-2.3	2.31	3.48	3.48	2.4
DB21C7	0.010	0.1	-2.3	3.09	4.26	4.26	2.8
18C6	0.005	0.1*	-2.8	2.74	4.49	4.49	1.1
2HM18C6	0.003	2	-2.8	0.019	4.82	4.82	
MR 184	0.001	0.1	-3.0	2.26	5.43	5.43	
2HM15C5	0.003	2	-2.8	0.86	5.66	5.66	
PEG 400	0.001	0.5*	-2.7	2.03	6.58	6.58	2.0
15C5	0.001	2.06	-2.5	1.71	7.44	7.44	1.7

* aqueous phase was the solution of HClO₄ in water

Table 7

Synergistic factors S reached during the extraction of Ca^{2+} by the nitrobenzene solution of bis-1,2-dicarbollylcobaltate in the presence of polyoxyethylene ligands [56 - 58]

Compound	c(B)	c(HNO ₃)	c(L)	log D(Ca)	log S(Ca)
18-crown-6	0.01	0.1	0.005	0.27	2.1
PEG 400 ^a					2.5
2-hydroxymethyl-12-crown-4	0.003	0.1	0.003	1.58	3.0
15-crown-5	0.02	0.1	0.018	2.17	3.4
2-hydroxymethyl-18-crown-6	0.003	0.1	0.0015	0.63	3.5
12-crown-4 ^b	0.003	0.1	0.03	1.18	4.1
2-hydroxymethyl-15-crown-5	0.003	0.1	0.0015	1.47	4.4
MR 184	0.001	1.0	0.0010	0.85	6.7

^a Ref. [2]

^b No maximum in the dependence of log D(Ca) on log c(12C4) was found till 0.1M 12C4.

Table 8

Exchange extraction and individual extraction constants of bivalent cations in the system water – nitrobenzene

Ion	K_{2H}^M	$\log K_{2H}^M$	$\log K_i(M^{2+})$	Ref.
Mg ²⁺	1.02	0.01	-11.4	[56]
Ca ²⁺	1.44	0.16	-11.2	[56]
Sr ²⁺	3.69	0.57	-10.8	[56]
Ba ²⁺	6.97	0.84	-10.6	[56]
Pb ²⁺	7.36	0.87	-10.5	a
Fe ²⁺	1.94	0.29	-11.1	a
Co ²⁺	0.90	-0.04	-11.4	a
Ni ²⁺	0.69	-0.16	-11.6	a
Cu ²⁺	0.86	-0.06	-11.5	a
Zn ²⁺	0.69	-0.16	-11.6	a
Cd ²⁺	0.78	-0.11	-11.5	a

^a Vaňura P.: Unpublished results

Table 9

Exchange extraction and individual extraction constants of trivalent cations in the system water - nitrobenzene [59]

Ion	K_{3H}^M	$\log K_i$	ΔG_0^{tr} (kJ/mol)
La ³⁺	26.5	-15.68	89.47
Ce ³⁺	26.3	-15.68	89.48
Pr ³⁺	25.3	-15.70	89.58
Nd ³⁺	23.7	-15.73	89.74
Sm ³⁺	18.7	-15.83	90.33
Eu ³⁺	16.6	-15.88	90.62
Gd ³⁺	16.1	-15.89	90.70
Tb ³⁺	14.2	-15.95	91.01
Dy ³⁺	13.5	-15.97	91.14
Ho ³⁺	12.3	-16.01	91.37
Er ³⁺	12.5	-16.00	91.33
Tm ³⁺	13.1	-15.98	91.21
Yb ³⁺	11.8	-16.03	91.47
Lu ³⁺	13.3	-15.98	91.17
Y ³⁺	13.4	-15.97	91.16
Sc ³⁺	5.71	-16.34	93.27
Fe ³⁺	7.73	-16.47	93.97

Table 10

Synergistic factors S reached during the extraction of Eu^{3+} and Y^{3+} by the nitrobenzene solution of bis-1,2-dicarbollylcobaltate in the presence of polyoxyethylene ligands

System	S	Ref.
Eu – 15-crown-5	10	[59]
Y – 15-crown-5	10	[33]
Y – benzo-15-crown-5	< 1	[33]
La – 18-crown-6 ^a	2.7	[60]
Eu – 18-crown-6 ^a	0.5	[60]
Y ^b – 18-crown-6 ^a	0.3	[60]
Eu – dibenzo-18-crown-6	0,5	[59]
Eu - PEG 200	18	[24]
Eu - PEG 300	28	[24]
Eu - PEG 400	62	[24]
Eu - PEG 1000	1000	[61]

^a Synergic effect has been found for light lanthanides while antagonistic effect has been found for heavy one

^b Almost same values S have been found for Ho-Yb

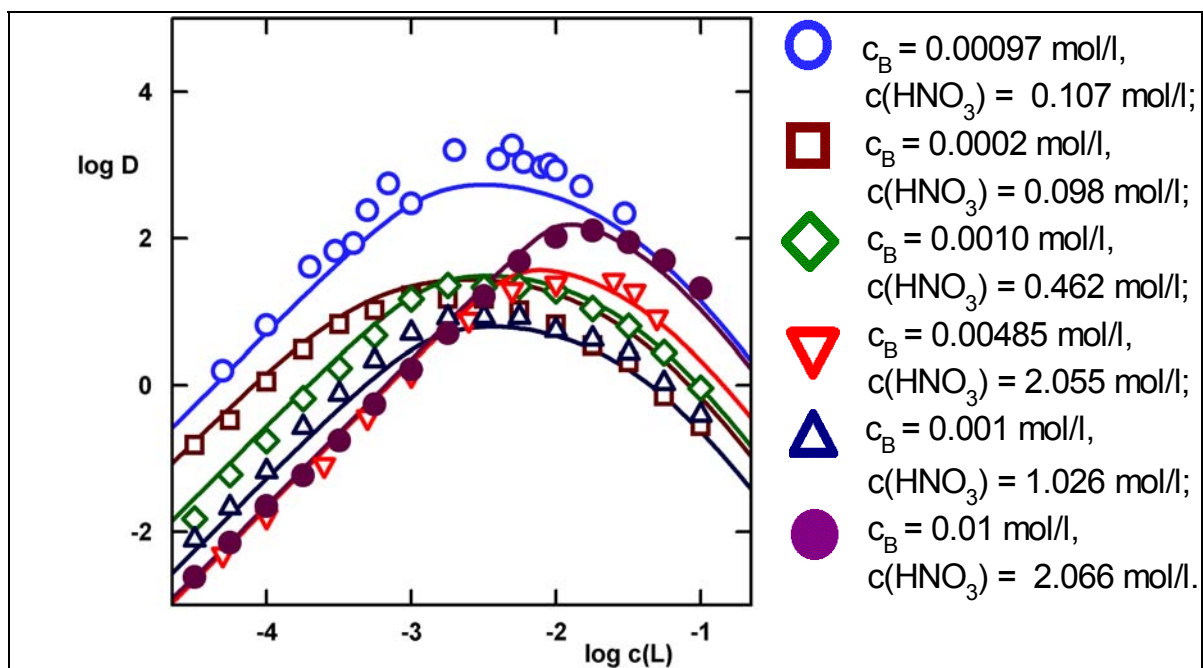


Fig. 1

The dependence of log D of log c(L) for the system water - HNO_3 - Sr^{2+} - 15C5 - nitrobenzene - bis-1,2-dicarbollylcobaltate

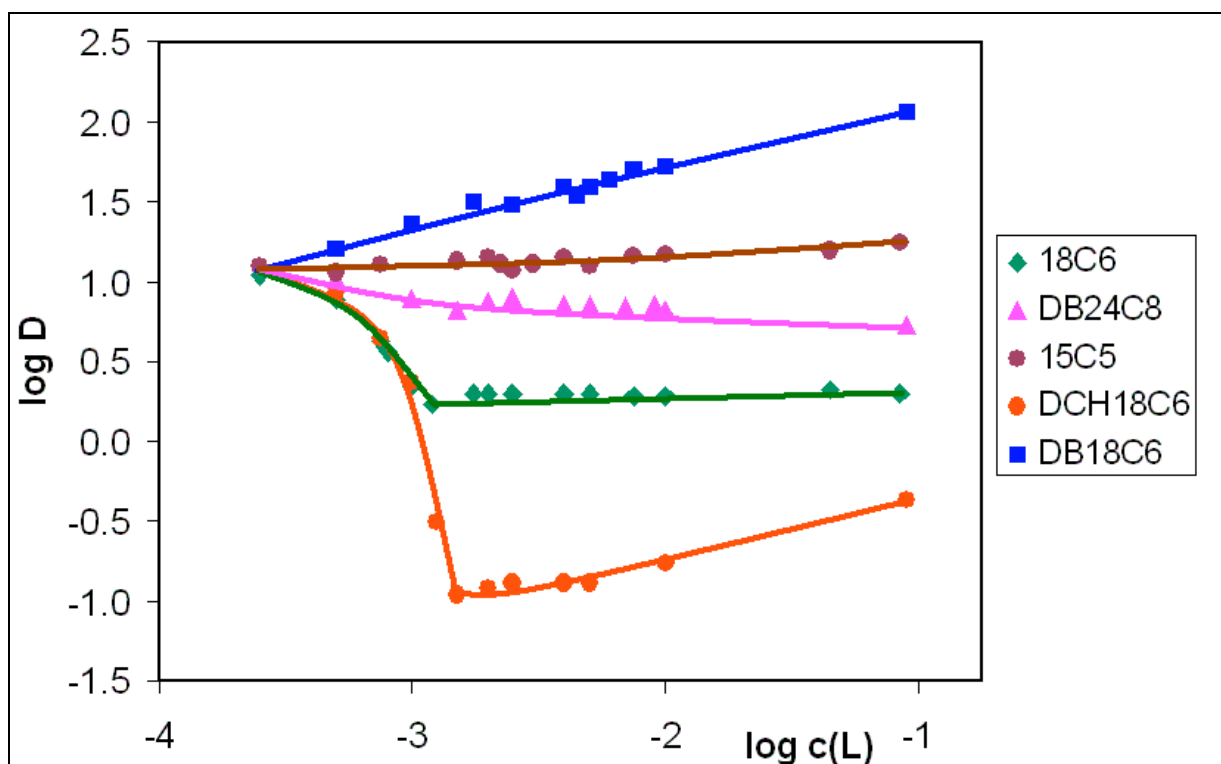


Fig. 2.

The extraction of strontium in the presence of crowns [62].
 $c(\text{HNO}_3) = 0.1 \text{ mol/L}$, $c(\text{HB}) = 0.001 \text{ mol/L}$.

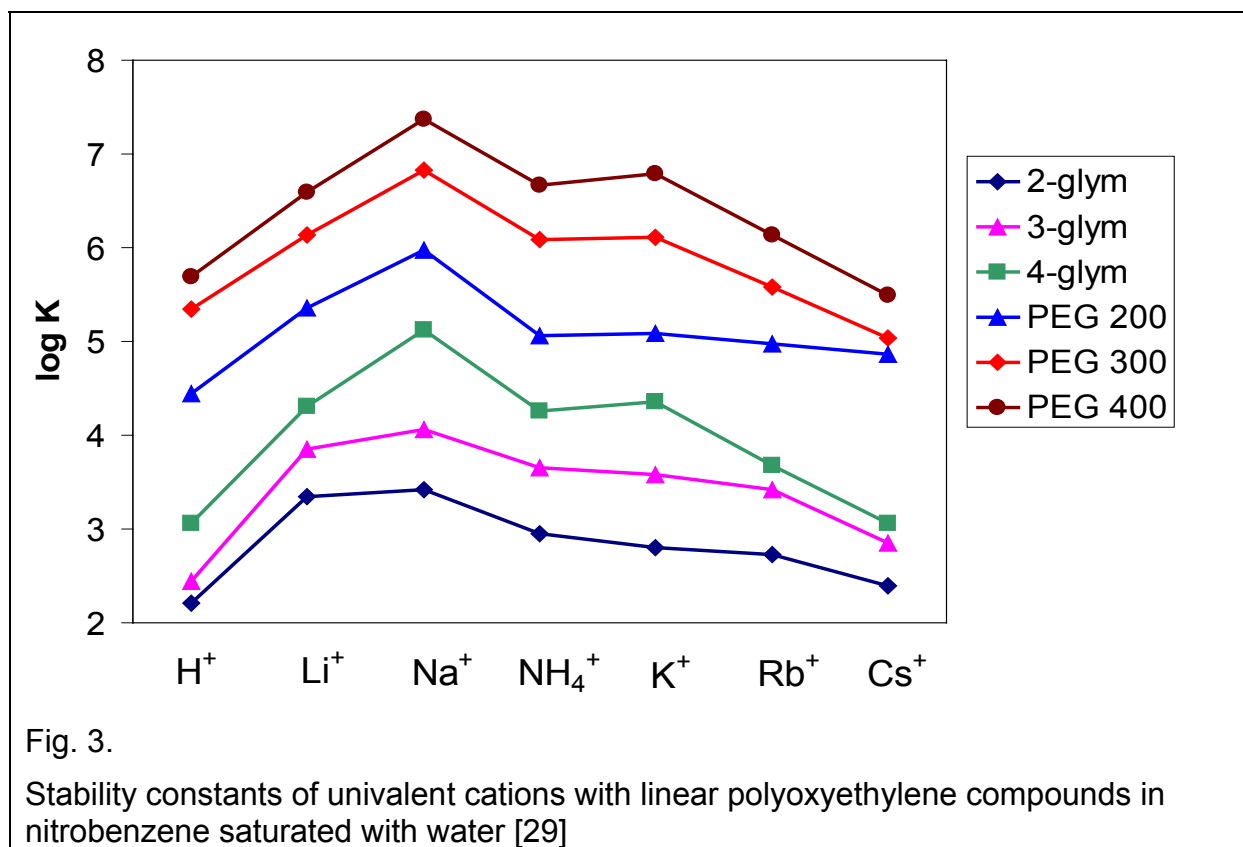


Fig. 3.

Stability constants of univalent cations with linear polyoxyethylene compounds in nitrobenzene saturated with water [29]

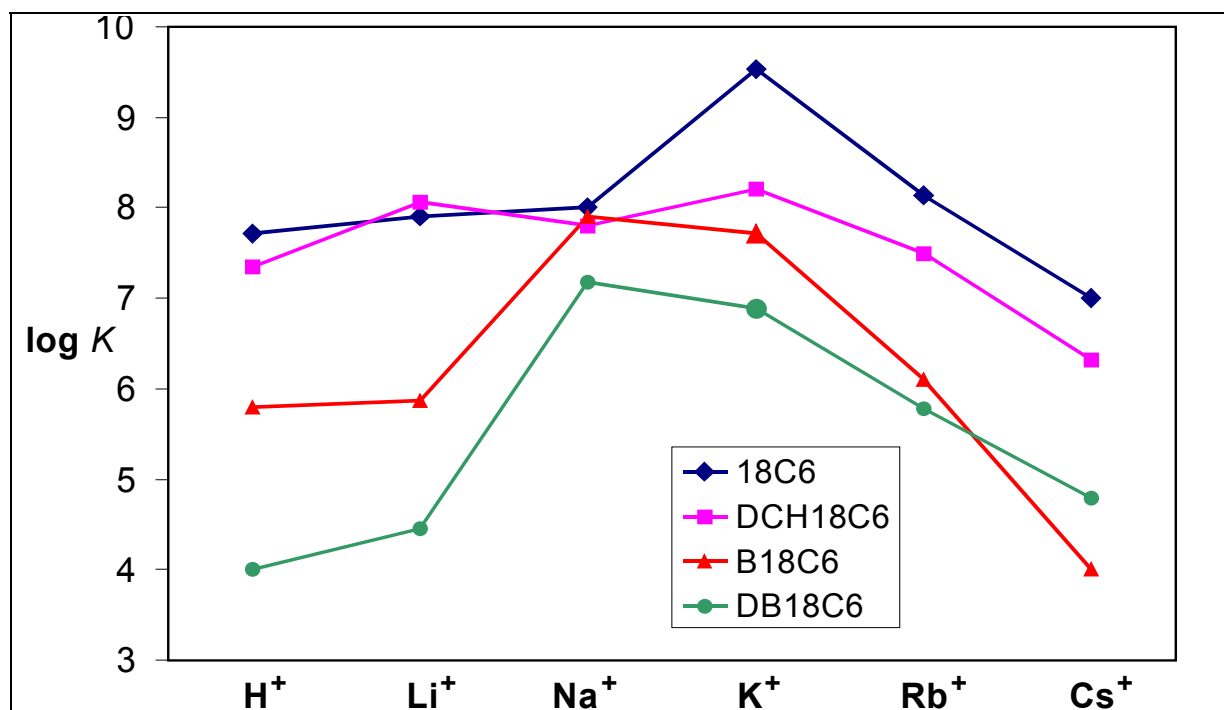
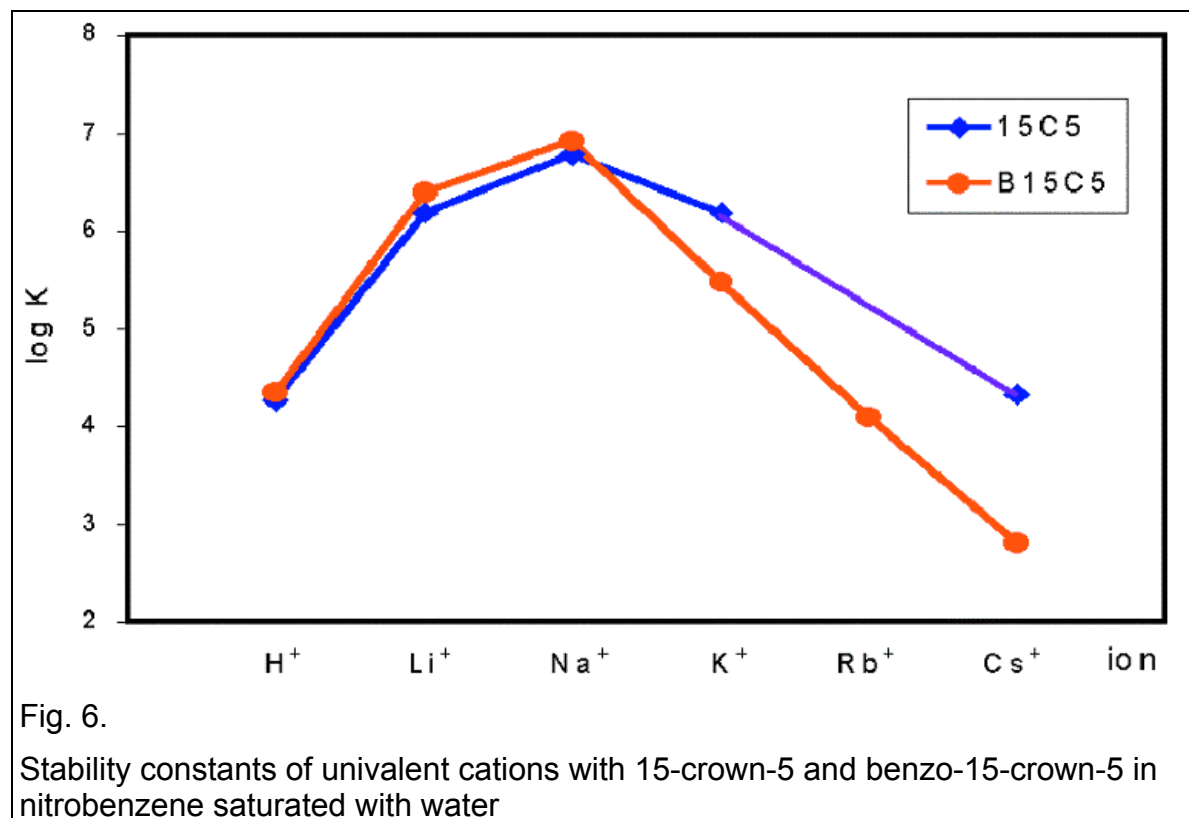
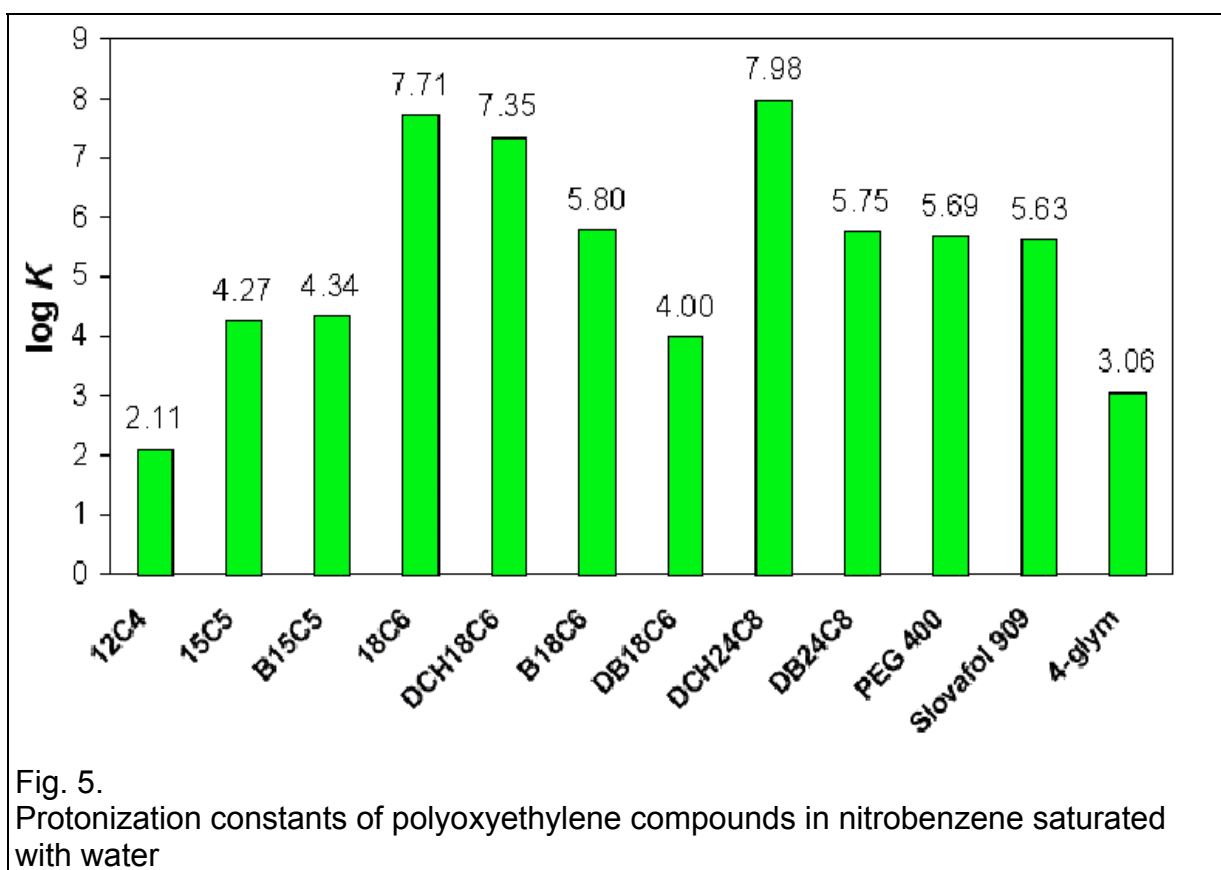


Fig. 4.

Stability constants of univalent cations with six-membered crowns in nitrobenzene saturated with water



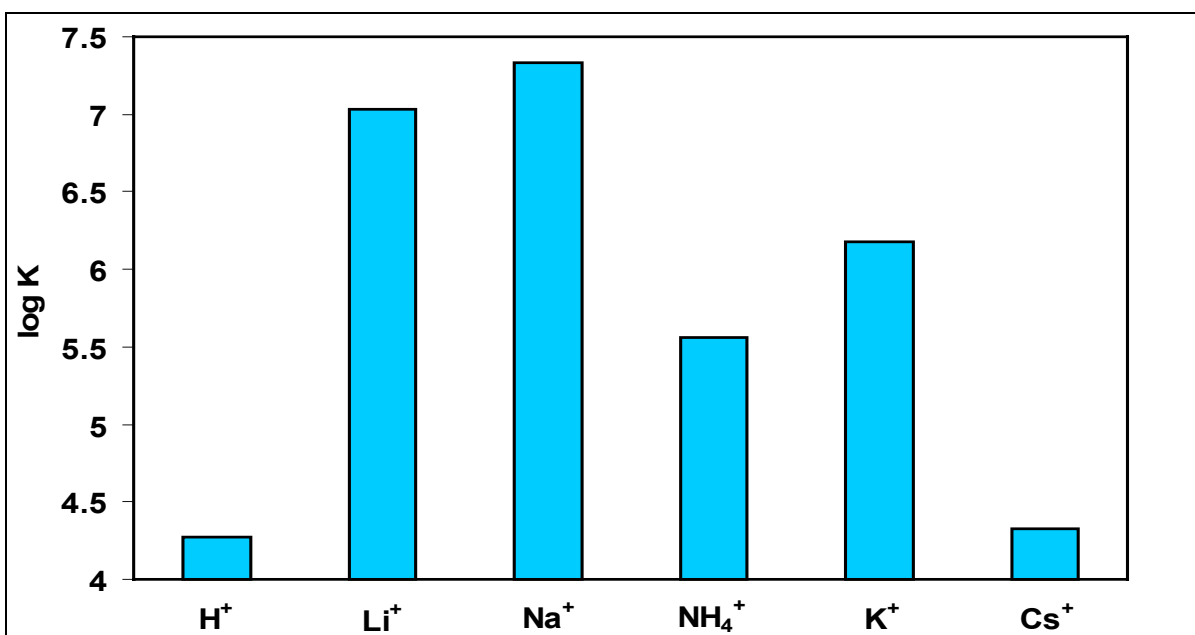


Fig. 7.

Stability constants of univalent cations with 15-crown-5 in nitrobenzene saturated with water

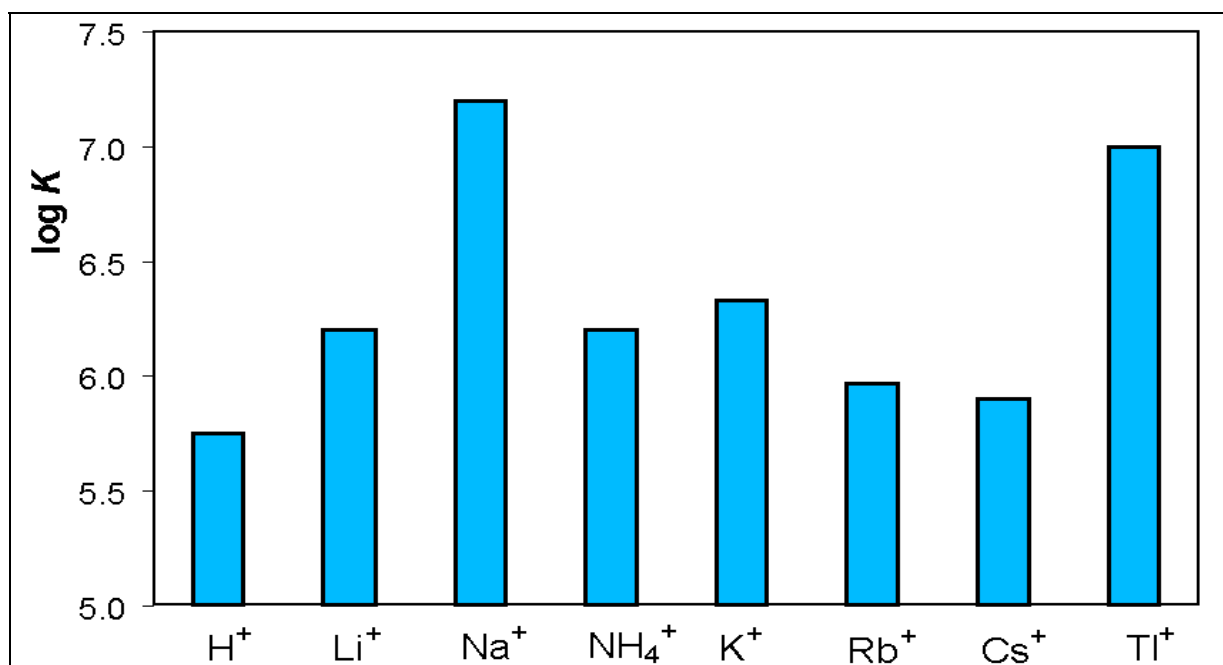


Fig. 8.

Stability constants of univalent cations with DB24C8 in nitrobenzene saturated with water

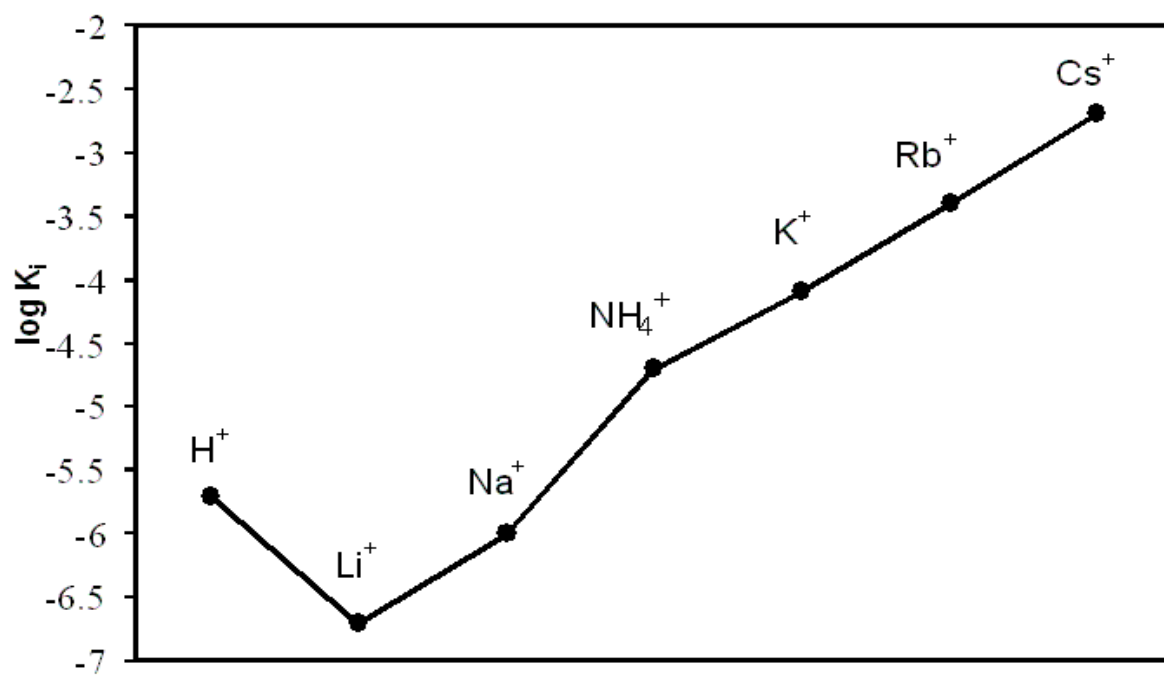


Fig. 9.

Individual extraction constants of univalent cations in the system water - nitrobenzene [7].

References

- [1] Rais J., Selucký P., Kyrš M.: *J. Inorg. Nucl. Chem.* 38, 1376 (1976).
- [2] Rais J., Šebestová E., Selucký P., Kyrš M.: *J. Inorg. Nucl. Chem.* 38, 1742 (1976).
- [3] Makrlík E., Vaňura P.: *Talanta* 32, 423 (1985).
- [4] Romanovskiy V.N., Smirnov I.V., Babain V. A., Todd T., Herbst R. S., Law J. D., Brewer K. N.: *Solvent Extr. Ion Exch.* 19, 1 (2001).
- [5] Herbst R. S., Law J. D., Todd T. A., Romanovskii V. N., Babain V. A., Esimantovski V. M., Zaitsev B. N., Smirnov I. V.: *Separ. Sci. Tech.* 37, 1807 (2002).
- [6] Makrlík E., Rais J., Baše K., Plešek J., Vaňura P.: *J. Radioanal. Nucl. Chem., Articles*, 198, 359 (1995).
- [7] Rais J.: *Collect. Czech. Chem. Commun.* 36, 3253 (1971).
- [8] Valentová Z., Vaňura P., Makrlík E.: *J. Radioanal. Nucl. Chem.* 223, 45 (1997).
- [9] Sillén L.G., Warnqvist B.: *Arkiv Kemi* 31, 315 (1969).
- [10] Vaňura P., Juklíková I.: *Collect. Czech. Chem. Commun.* 58, 483 (1993).
- [11] Vaňura P., Makrlík E.: *J. Radioanal. Nucl. Chem.* 240, 187 (1999).
- [12] Makrlík E., Vaňura P.: *J. Radioanal. Nucl. Chem.* 240, 339 (1999).
- [13] Makrlík E., Vaňura P.: *J. Radioanal. Nucl. Chem.* 240, 579 (1999).
- [14] Daňková M., Vaňura P., Makrlík E.: *J. Radioanal. Nucl. Chem.* 240, 747 (1999).
- [15] Makrlík E., Vaňura P.: *J. Radioanal. Nucl. Chem.* 241, 197 (1999).
- [16] Makrlík E., Vaňura P.: *Models in Chemistry* 136, 343 (1999).
- [17] Kudo Y., Takeda Y., Matsuda H.: *J. Electroanal. Chem.* 396, 333 (1995).
- [18] Kudo Y., Takeda Y., Kanamori K., Matsuda H.: *Anal. Sci.* 11, 119 (1995).
- [19] Kudo Y., Miyakawa T., Takeda Y., Matsuda H., Yajima S.: *J. Inclusion Phenom. Mol. Recognit. Chem.* 26, 331 (1996).
- [20] Kudo Y., Kobayashi K., Katsuta S., Takeda Y.: *Anal. Sci.* 18, 1047 (2002).
- [21] Koryta J., Kozlov Yu. N., Skalický M.: *J. Electroanal. Chem.* 234, 355 (1987).
- [22] Iwachido T., Minami M., Kimura M., Sadakane A., Kawasaki M., Toei K.: *Bull. Chem. Soc. Jpn.* 53, 703 (1980).
- [23] Makrlík E., Vaňura P., Bečková V.: *J. Radioanal. Nucl. Chem.* 241, 659 (1999).
- [24] Makrlík E., Vaňura P.: *Collect. Czech. Chem. Commun.* 51, 498 (1986).
- [25] Vaňura P., Makrlík E.: *J. Radioanal. Nucl. Chem.* 254, 217 (2002).
- [26] Vaňura P., Jedináková-Křížová V.: *Czechoslovak J. Phys.* 53 (Suppl. A), A459 (2003).
- [27] Wilke S.: *J. Electroanal. Chem.* 504, 184 (2001).
- [28] Makrlík E., Vaňura P.: *Models in Chemistry* 136, 519 (1999).
- [29] Makrlík E., Hálová J., Vaňura P.: *Collect. Czech. Chem. Commun.* 57, 276 (1992).

- [30] Makrlík E., Vaňura P., Daňková M.: *Z. Phys. Chem.* 212, 107 (1999).
- [31] Vaňura P., Makrlík E., Vobecký M.: *Chemical Papers* 57, 108 (2003).
- [32] Vaňura P., Makrlík E., Valentová Z.: *J. Radioanal. Nucl. Chem.* 241, 457 (1999).
- [33] Vaňura P., Jedináková-Křížová V., Yoshioka A.: *J. Radioanal. Nucl. Chem.* 251, 511 (2002).
- [34] Vaňura P., Makrlík E.: *J. Radioanal. Nucl. Chem.* 250, 369 (2001).
- [35] Makrlík E., Vaňura P.: *J. Radioanal. Nucl. Chem.* 250, 169 (2001).
- [36] Makrlík E., Vaňura P.: *J. Radioanal. Nucl. Chem., Letters*, 223, 229 (1997).
- [37] Vaňura P.: *Solv. Extr. Ion Exch.* 10, 145 (1994).
- [38] Vaňura P., Makrlík E.: *Collect. Czech. Chem. Commun.* 50, 581 (1985).
- [39] Vaňura P., Rais J., Selucký P., Kyrš M.: *Collect. Czech. Chem. Commun.* 44, 157 (1979).
- [40] Vaňura P., Makrlík E.: *Collect. Czech. Chem. Commun.* 63, 2001 (1998).
- [41] Vaňura P., Makrlík E.: *Chem. Papers* 57, 225 (2003).
- [42] Nový P., Vaňura P., Makrlík E.: *J. Radioanal. Nucl. Chem., Articles*, 207, 237 (1996).
- [43] Vaňura P., Makrlík E., Valentová Z.: *J. Radioanal. Nucl. Chem.* 253, 527 (2002).
- [44] Vaňura P., Makrlík E., Vobecký M.: *J. Radioanal. Nucl. Chem.* 256, 599 (2003).
- [45] Vaňura P., Jedináková-Křížová V., Ivanová P.: *J. Radioanal. Nucl. Chem., Articles*, 208, 271 (1996).
- [46] Vaňura P., Makrlík E., Rais J., Kyrš M.: *Collect. Czech. Chem. Commun.* 47, 1444 (1982).
- [47] Vaňura P., Jedináková-Křížová V.: *Proceedings "Radioanalytické metody IAA 02,"* p. 18, *Spektroskopická společnost Jana Marka Marci (Vobecký M., ed.)*, 2003.
- [48] Vaňura P., Makrlík E., Vobecký M.: *J. Radioanal. Nucl. Chem.* 257, 437 (2003).
- [49] Vaňura P.: *J. Radioanal. Nucl. Chem.* 241, 493 (1999).
- [50] Vaňura P., Makrlík E.: *J. Radioanal. Nucl. Chem.* 237, 11 (1998).
- [51] Nový P., Vaňura P., Makrlík E.: *J. Radioanal. Nucl. Chem.* 231, 65 (1998).
- [52] Vaňura P., Makrlík E.: *Collect. Czech. Chem. Commun.* 63, 338 (1998).
- [53] Daňková M., Makrlík E., Vaňura P.: *J. Serb. Chem. Soc.* 65, 275 (2000).
- [54] Vaňura P., Makrlík E.: *Collect. Czech. Chem. Commun.* 58, 1324 (1993).
- [55] Kyrš M., Selucký P.: *J. Radioanal. Nucl. Chem., Articles*, 172, 213 (1993).
- [56] Vaňura P.: *Czechoslovak J. Phys.*, 49 (Suppl. S1) 761 (1999).
- [57] Vaňura P., Stibor I.: *Collect. Czech. Chem. Commun.* 63, 2009 (1998).
- [58] Vaňura P.: *J. Radioanal. Nucl. Chem.* 228, 43 (1998).
- [59] Vaňura P., Jedináková-Křížová V.: *Solvent Extr. Ion Exch.* 10, 847 (1992).
- [60] Vaňura P., Jedináková-Křížová V., Juklíková I.: *Solvent Extr. Ion Exch.* 10, 439 (1994).

[61] Vaňura P., Makrlík E., Rais J., Kyrš M.: Poster 80-124, ISEC 80, Assoc. Ing. Univ. Liege, Liege, Belgium, 1980.

[62] Vaňura P., Jedináková-Křížová V., Valentová Z.: J. Radioanal. Nucl. Chem. Articles, 208, 283 (1996).