Extraction of some univalent and divalent cations into nitrobenzene in the presence of calcium ionophore I

https://doi.org/10.1515/ract-2023-0128
Received January 16, 2023; accepted September 19, 2023; published online October 5, 2023

Abstract: The stability constants of the Calcium ionophore I (i.e., \( N\N' = \text{di}[11\text{-ethylcarboxylinyl}] \text{undecyl} - N\N'4,5\text{-tetramethyl} - 3,6 \text{-dioxoacetamide} \)) complexes with \( M^n \) (\( M^n = \text{Li}^+, \text{H}_2\text{O}^+, \text{Na}^+, \text{NH}_4^+, \text{Ag}^+, \text{K}^+, \text{Rb}^+, \text{Tl}^+, \text{Cs}^+, \text{Ca}^{2+}, \text{Sr}^{2+}, \text{Ba}^{2+}, \text{Pb}^{2+}, \text{Cu}^{2+}, \text{Zn}^{2+} \)) in nitrobenzene saturated with water were determined by the extraction method. These constants were found to increase in the series of \( \text{Cs}^+ < \text{Rb}^+ < \text{K}^+ < \text{NH}_4^+ < \text{Na}^+ < \text{Tl}^+ < \text{H}_2\text{O}^+ < \text{Ag}^+ < \text{Li}^+ \) and \( \text{Ba}^{2+} < \text{Zn}^{2+} < \text{Sr}^{2+} < \text{Pb}^{2+} < \text{Cu}^{2+} < \text{Ca}^{2+} \).

Keywords: ionophores; complexation; stability constants; extraction; water/nitrobenzene system; univalent and divalent cations

1 Introduction

The dicarbollylcobaltate anion and some of its halogen derivatives are very useful reagents for the extraction of alkali metal cations (especially \( \text{Cs}^+ \)). These reagents can be used, in the presence of polyoxyethylene compounds, also for the extraction of univalent, divalent, and trivalent cations from aqueous solution into a polar organic phase, both under laboratory conditions for purely theoretical or analytical purposes [1, 2], and on the technological scale for the separation of some high-activity isotopes in the reprocessing of spent nuclear fuel [3, 4]. Several naturally occurring as well as synthetic substances have been found which increase the ion permeability of biological and artificial membranes [5–7]. These mediators of ion translocation fall into one of two groups: they are either ion carriers or channel formers. Thus, the series of acyclic compounds derived from 3,6-dioxoacetate-dicarboxylic acid was prepared. Among these, \( N\N' – \text{di}[11\text{-ethylcarboxylinyl}] \text{undecyl} – N\N'4,5\text{-tetramethyl} – 3,6 \text{-dioxoacetamide} \), also called Calcium ionophore I or ETH 1001 (1, see Scheme 1), exhibits a high selectivity for \( \text{Ca}^{2+} \) when used as the neutral carrier in \( n\text{-octoxy-o-nitrobenzene} \) as the membrane component in a poly(vinylchloride) matrix of the ion-selective electrode [8–10]. This ligand is able to mediate the transport of \( \text{Ca}^{2+} \) ions across the synthetic phospholipid bilayers and can therefore act as a \( \text{Ca}^{2+} \) ion carrier. The evidence available indicates that 1:2 complexes (cation to ligand) of \( \text{Ca}^{2+} \) are formed in the bulk of the membrane [7].

In our previous work, the extraction of \( ^{152,154}\text{Eu}^{3+} \) and \( ^{241}\text{Am}^{3+} \) by the nitrobenzene solution of bis-1,2-dicarbollylcobaltate in the presence of Calcium ionophore I was investigated. It was found that the particles \( \text{EuL}_2^{3+}, \text{EuL}_3^{3+}, \text{AmL}_2^{3+}, \text{AmL}_3^{3+} \) are formed in the organic phase [11]. The distribution ratios \( D \) and the separation factor \( e(\text{Am}^{3+}/\text{Eu}^{3+}) \) are very high. However, up to now, the stabilities of the Calcium ionophore I complexes with univalent and divalent cations have not been investigated. Some of these cations, especially \( \text{Cs}^+, \text{Ag}^+, \text{Rb}^+, \text{Sr}^{2+} \) and \( \text{Ba}^{2+} \) (and, of course, nitric acid, i.e., cation \( \text{H}^+ \)) represent a significant component of the raffinate from the reprocessing of spent nuclear fuel by the PUREX process.

Nitrobenzene was the first highly polar diluent investigated for the extraction of fission products and transplutonium elements from the PUREX process raffinate. Most equilibrium data and stability constants are available for this diluent. More suitable polar solvents were later found, but the extraction behavior of these solvents is like that of nitrobenzene. The individual extraction constants (see below) are available only for water-nitrobenzene and water-phenyl trifluoromethyl sulfoxide systems.

Therefore, in the current work, the stability constants of the 1,1M\( ^{n+} \) complex species, where \( M^{n+} = \text{Li}^+, \text{H}_2\text{O}^+, \text{Na}^+, \text{NH}_4^+, \text{Ag}^+, \text{K}^+, \text{Rb}^+, \text{Tl}^+, \text{Cs}^+, \text{Ca}^{2+}, \text{Sr}^{2+}, \text{Ba}^{2+}, \text{Zn}^{2+}, \text{Cu}^{2+}, \text{Pb}^{2+} \) and 1 is Calcium ionophore I (Scheme 1), in nitrobenzene saturated with water were determined by the solvent extraction method.

2 Experimental

Calcium ionophore I (1) was purchased from Fluka, Buchs, Switzerland. Cesium dicarbollylcobaltate (CsDCC) was synthesized by means of the
method described by Hawthorne et al. [12]. Acros Organics purchased the nitrobenzene (99%, extra pure) were of reagent grade purity. A nitrobenzene solution of 0.2 mol/L hydrogen dicarbollylcobaltate in nitrobenzene (HDCC, see Scheme 2) was prepared from CsDCC by the procedure published elsewhere [13]. The concentration of HDCC was determined by the potentiometric two-phase titration by the carbonate-free sodium hydroxide in a nitrogen atmosphere. A Radiometer RTS 822 automatic titrator with a G 2040 glass electrode and K 4040 calomel electrode was used for this titration. The equilibration of the nitrobenzene solution of HDCC with stoichiometric NaOH, which was dissolved in an aqueous solution of NaCl (0.2 mol/L), yielded the corresponding sodium dicarbollylcobaltate (NaDCC) solution in nitrobenzene while the equilibration of HDCC solution with aqueous 1 mol/L strontium acetate yielded the strontium dicarbollylcobaltate (Sr(DCC)₂) solution in nitrobenzene. The concentrations of the NaDCC and Sr(DCC)₂ solutions correspond to the concentration of the original HDCC solution. It was simply checked by the distribution of ²²Na, respectively ⁸⁵Sr, in the systems aqueous solution of 0.2 mol/L NaCl in water – 0.2 mol/L solution of NaDCC in nitrobenzene respectively 0.1 mol/L SrCl₂ in water – 0.1 mol/L Sr(DCC)₂ in nitrobenzene (distribution ratio $D = 1$).

The radionuclides ²²Na and ⁸⁵Sr (DuPont, Belgium) and ¹³³Ba (Polatom, Poland) were of standard radiochemical purity. The acidic solutions of these radionuclides were evaporated to dryness and afterwards dissolved in distilled water.

The extraction experiments were performed in 10 mL glass test tubes with polyethylene stoppers. 2 mL of an aqueous and organic phase were shaken for 2 h at 25 ± 1°C, using a laboratory shaker. Under these conditions, the equilibria in the systems under study were established after approximately 20 min of shaking (the distribution ratios, measured after 20 min and 40 min of shaking are the same as that measured after 2 h of shaking). Then the phases were separated by centrifugation (5 min, 3000 rpm). 1 mL samples were taken from each phase. At first 1 mL of upper aqueous phase were taken using 1 mL Plastomed macro pipette with a polyethylene tip. Afterwards, 1 mL sample was taken from lower, nitrobenzene phase. The pipetting of the organic phase was done so that the aqueous phase did not stain the inside of the polyethylene tip. Afterwards, the outside of the tip was carefully wiped with a cotton swab.

The stability constants of Na⁺ and Ba²⁺ with 1 were determined from the extraction of sodium (NaPic) and barium (Ba(Pic)₂) picrates by the extraction of sodium (NaPic) and barium (Ba(Pic)₂) picrates by the solution of Calcium ionophore I. The concentration of NaPic varied from 5 × 10⁻³ to 2 × 10⁻³ mol/L and the concentration of Ba(Pic)₂ varied from 1 × 10⁻⁴ to 2 × 10⁻⁴ mol/L. The concentration of Calcium ionophore I in nitrobenzene varied from 0.001 to 0.005 mol/L. In all experiments, the concentration of 1 in nitrobenzene was higher than the concentration of the extracted picrate salt in water.

The aqueous solutions of MNO₃ (M = Li⁺, H⁺, NH₄⁺, Ag⁺, K⁺, Rb⁺, Tl⁺, Cs⁺) respectively M(NO₃)₂ (M²⁺ = Cu²⁺, Ba²⁺, Zn²⁺, Cd²⁺, Pb²⁺) of a concentration in the range from 5 × 10⁻⁴ to 3 × 10⁻³ mol/L and microamounts of ²²Na respectively ⁶⁵Sr were added to 2 mL of a nitrobenzene solution of 1 and NaDCC, respectively Sr(DCC)₂, whose initial concentrations also varied from 5 × 10⁻⁴ to 3 × 10⁻³ mol/L. In all experiments, the initial concentration of 1 in nitrobenzene, $c_{1 nb}$ was equal to the initial concentration of NaDCC respectively Sr(DCC)₂ in this medium, $c_{NaDCC} nb$ respectively $c_{Sr(DCC)} nb$, and also to the concentration of metal or ammonium nitrate in the aqueous phase.

The equilibrium distribution ratios, $D$, of ²²Na, ⁶⁵Sr, or ¹³³Ba were determined as the ratios of the measured radioactivities in the nitrobenzene and aqueous samples.

### 3 Results and discussion

The stability constants of the cation complexes of calcium ionophore I ligand in nitrobenzene, i.e., the equilibrium constants of the reactions

$$M^{n+} (nb) + 1(nb) \rightleftharpoons 1.M^{n+} (nb) \quad K(1.M^{n+}) \quad (1)$$

are defined as

$$K(1 · M^{n+}) = \frac{[1 · M^{n+}]}{[M^{n+} ][1]} \quad (2)$$

These constants were determined for all investigated cations by the extraction methods described below. Aq and nb denote the presence of the species in the aqueous and nitrobenzene phases, respectively.
Regarding the results of our previous papers [14, 15], the two-phase water–MAₙ (M = Na⁺, Ba²⁺, A⁻ = piciprate)–nitrobenzene extraction system can be described by the equilibrium (3)

\[ M^{n⁺} (aq) + nA⁻ (aq) ⇌ M^{n⁺} (nb) + nA⁻ (nb) \]

\[ K_{ex} (M^{n⁺}, nA⁻) \]

with the corresponding extraction constant \( K_{ex} (M^{n⁺}, nA⁻) \);

\[ K_{ex} (M^{n⁺}, nA⁻) = \frac{[M^{n⁺}]_{nb}[A⁻]^n_{nb}}{[M^{n⁺}]_{aq}[A⁻]^n_{aq}} \]

(4) 

For the constant \( K_{ex} (M^{n⁺}, nA⁻) \) one can write [16].

\[ \log K_{ex} (M^{n⁺}, nA⁻) = \log K_{1M^{n⁺}} + n\log K_{A⁻} \]  

(5)

where \( K_{1M^{n⁺}} \) and \( K_{A⁻} \) are the individual extraction constants for \( M^{n⁺} \) and \( A⁻ \) in the water–nitrobenzene system. Knowing the values \( \log K_{1M^{n⁺}} = -6.0 \) [16], \( \log K_{A⁻} = -10.5 \) [17], and \( \log K_{A⁻} = 0.8 \) (A⁻ = piciprate) [16], the extraction constants were simply calculated from Eq. (5) as \( \log K_{ex} (Na⁺, A⁻) = -5.2 \) and \( \log K_{ex} (Ba^{²⁺}, 2A⁻) = -8.9 \).

The two-phase water–MAₙ (A⁻ = piciprate)–nitrobenzene – 1 (Calcium Ionophore I) extraction system, chosen for the determination of the stability constant of the complexes 1.Na⁻ and 1.Ba²⁺ (see Experimental), can be described by the main chemical equilibrium

\[ M^{n⁺} (aq) + nA⁻ (aq) + 1 (nb) ⇌ 1.M^{n⁺} (nb) + nA⁻ (nb) \]

(6)

with the equilibrium extraction constant \( K_{ex} (1.M^{n⁺}, nA⁻) \) in the form

\[ K_{ex} (1.M^{n⁺}, nA⁻) = \frac{[1.M^{n⁺}]_{nb}[A⁻]^n_{nb}}{[M^{n⁺}]_{aq}[A⁻]^n_{aq}} \]

(7)

At this point, it is necessary to emphasize that \( 1 \) is a considerably lipophilic ligand, practically present in the nitrobenzene phase only, where this ligand forms – with the univalent and divalent cations very stable complexes, as given below.

Employing the conditions of electroneutrality in the organic and aqueous phases of the system under study, the mass balances of 1 and NaA, respective Ba₂A at equal volumes of the nitrobenzene and aqueous phases, as well as the measured equilibrium distribution ratios \( D \), combined with Eq. (7), we gain the final expression for the extraction constants \( K_{ex} (1.Na⁺, A⁻) \) and \( K_{ex} (1.Ba^{²⁺}, 2A⁻) \) in the form

\[ K_{ex} (1.M^{n⁺}, nA⁻) = D^{n+1} \left( C_{1}^{in,nb} - \frac{D}{1 + D} C_{1}^{in,aq} \right) \]

(8)

where \( D \) is the distribution ratio of \(^{22}\)Na respectively \(^{133}\)Ba in the systems under study. Eq. is valid, because the distribution ratios of \(^{22}\)Na and \(^{133}\)Ba in the absence of a ligand are negligible, so \([1.Na^{⁺}]_{lab} ≫ [Na⁺]_{nb} \) and \([1.Ba^{²⁺}]_{lab} ≫ [Ba^{²⁺}]_{nb} \).

Furthermore, the stability constants of the complexes 1.Na⁻ and 1.Ba²⁺ in water-saturated nitrobenzene at 25 °C can be simply calculated from the extraction data by Eq.

\[ \log K_{nb} (1.M^{n⁺}) = \log K_{ex} (1.M^{n⁺}, nA⁻) \]

\[ - \log K_{ex} (M^{n⁺}, nA⁻) \]

(9)

as \( \log K_{nb} (1.Na⁻) = 6.1 \) and \( \log K_{nb} (1.Ba^{²⁺}) = 14.8 \).

The previous results [18, 19] indicated that the two-phase water–M(NO₃)ₙ (M = Li⁺, H⁺, NH₄⁺, A⁺, K⁺, Rb⁺, Tl⁺, Cs⁺, Ca²⁺, Ba²⁺, Pb²⁺, Cu²⁺, Zn²⁺)-nitrobenzene–1–NDCCₙ extraction system (\( \text{N}^{n⁺} = \text{Na}⁺, \text{Sr}^{²⁺} \)) (see Experimental), chosen for the determination of stability of the complexes 1.Mⁿ⁺ in water-saturated nitrobenzene, can be characterized by the main chemical equilibrium (10) to which the general equilibrium extraction constant expressed by Eq. (11) corresponds.

\[ M^{n⁺} (aq) + 1.N^{n⁺} (nb) ⇌ 1.M^{n⁺} (nb) + nN^{n⁺} (aq) \]

(10)

\[ K_{ex} (M^{n⁺}, 1.N^{n⁺}) \]

(11)

Applying the conditions of electroneutrality in the organic and aqueous phases of the system under study, the mass balances of 1, Mⁿ⁺ and Nⁿ⁺ at equal volumes of the nitrobenzene and aqueous phases, as well as the measured equilibrium distribution ratio \( D \) combined with Eq. (11), we gain the final expression for the extraction constant \( K_{ex} (M^{n⁺}, 1.N^{n⁺}) \) in the form

\[ K_{ex} (M^{n⁺}, 1.N^{n⁺}) = \frac{1}{D (1 + D)} C_{\text{in,q}}^{1.M^{n⁺}} C_{\text{in,nb}}^{1.N^{n⁺}} - C_{\text{in,nb}}^{1.M^{n⁺}} \]

(12)

Eq. (12) is valid if conditions \([1.M^{n⁺}]_{nb} ≫ [M^{n⁺}]_{nb} \) and \([1.N^{n⁺}]_{nb} ≫ [N^{n⁺}]_{nb} \) are valid, which means for \( \log K (1.M^{n⁺}) > 5 \) and \( \log K (1.N^{n⁺}) > 5 \).

In the absence of the ligand, the extraction proceeds by Eq. (13) as

\[ M^{n⁺} (aq) + N^{n⁺} (nb) ⇌ M^{n⁺} (nb) + N^{n⁺} (aq) \]

(13)

\[ K_{ex} (M^{n⁺}, N^{n⁺}) \]

For the constant \( K_{ex} (M^{n⁺}, N^{n⁺}) \) one can write Eq. (14), where \( K_{1M^{n⁺}} \) and \( K_{1N^{n⁺}} \) are the individual extraction constants for \( M^{n⁺} \) and \( N^{n⁺} \) in the water/nitrobenzene system.
log $K_{ex}(M^{n+}, N^{n+}) = log K_{M+}^{i} - log K_{N+}^{i}$.

(14)

Knowing $K_{ex}(M^{n+}, 1-N^{n+})$ and $K_{ex}(M^{n-}, N^{n-})$ the stability constants of Calcium ionophore I – metal complex can be simply calculated as

$$
\log K_{nb}(1.M^{n+}) = \log K_{nb}(1.N^{n+}) + \log K_{ex}(M^{n+}, 1.N^{n+}) - \log K_{ex}(M^{n+}, N^{n+})
$$

(15)

where $M^{n+} = Li^{+}, H_{2}O^{+}, NH_{4}^{+}, Ag^{+}, K^{+}, Rb^{+}, Tl^{+}, Cs^{+}, Ca^{2+}, Pb^{2+}, Cu^{2+}, Zn^{2+}$ and $N^{n-} = Na^{+}$ and $Sr^{2+}$.

The stability constants of the complex $1.Sr^{2+}$, used for the calculations of the stability constants of divalent cations by Eq. (15), has been calculated using the analogical equation

$$
\log K_{nb}(1.Sr^{2+}) = \log K_{nb}(1.Ba^{2+}) + \log K_{ex}(Sr^{2+}, 1.Ba^{2+}) - K_{nb}(Sr^{2+}, Ba^{2+})
$$

(16)

All resulting stability constants are summarized in Tables 1 and 2. It must be pointed out that the stability constants of the complexes $1.K^{+}, 1.Rb^{+}$ and $1.Cs^{+}$ are lower than $10^{-5}$, so Eq. (12) is not fully valid. Therefore, these stability constants were refined using the computer program Haltapall [21]. Table 1 contains these refined values.

It is clear from Table 1 that the stability constants of the univalent cations in nitrobenzene saturated with water, $K_{nb}(1.M^{+})$, increase in the order $Cs^{+} < Rb^{+} < K^{+} < NH_{4}^{+} < Na^{+} < Tl^{+} < H_{2}O^{+} < Ag^{+} < Li^{+}$. The log $K_{nb}(1.M^{+})$ values of the alkali metal cation and $H_{2}O^{+}$ decrease almost linearly with the crystallographic radius of the respective cation $M^{+}$, as depicted in Figure 1. On the other hand, the stability constants of $NH_{4}^{+}$ and soft univalent cations $Ag^{+}$ and $Tl^{+}$ are higher than the stability constants of the alkali metal cation with similar ionic radius. This is probably caused by the presence of nitrogen atoms in the molecule of Calcium ionophore I. It must be pointed out that the protonation constant of Calcium ionophore I in nitrobenzene, determined in the present work, log $K_{nb}(1.H_{2}O^{+}) = 6.4$, agrees with that determined in our previous work from the extraction of Eu$^{3+}$ and Am$^{3+}$ (log $K_{nb}(1.H_{2}O^{+}) = 6.2$ [11]).

It is possible to prove that the affinity of the extracted cation to the nitrobenzene phase is proportional to the

**Table 2:** Equilibrium constants for the $M^{2+}$ and $1-M^{2+}$ cations in the two–phase water/nitrobenzene extraction system at 25 °C ($M^{2+} = Ca^{2+}, Sr^{2+}, Ba^{2+}, Pb^{2+}, Cu^{2+}, Zn^{2+}$; 1 = Calcium ionophore I). For the meaning of the constants, see text. The standard deviations of the constants log $K$ are lower than 0.1 (three measurements).

<table>
<thead>
<tr>
<th>Quantity</th>
<th>$M^{2+}$</th>
<th>$Ca^{2+}$</th>
<th>$Sr^{2+}$</th>
<th>$Ba^{2+}$</th>
<th>$Pb^{2+}$</th>
<th>$Cu^{2+}$</th>
<th>$Zn^{2+}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>log $K_{M+}^{i}$</td>
<td>-11.2</td>
<td>-10.7</td>
<td>-10.5</td>
<td>-10.6</td>
<td>-11.5</td>
<td>-11.6</td>
<td></td>
</tr>
<tr>
<td>log $K_{nb}(1-M^{2+})$</td>
<td>20.0</td>
<td>16.1</td>
<td>14.8</td>
<td>18.2</td>
<td>19.0</td>
<td>15.0</td>
<td></td>
</tr>
<tr>
<td>log $K_{M+}^{i}$ + log $K_{nb}(1-M^{2+})$</td>
<td>8.8</td>
<td>5.4</td>
<td>4.3</td>
<td>7.6</td>
<td>7.5</td>
<td>3.4</td>
<td></td>
</tr>
</tbody>
</table>

*aRef. [17].

**Figure 1:** Dependence of the logarithm of the stability constant of the $1-M^{+}$ complex cation ($M^{+} = Li^{+}, Na^{+}, K^{+}, Rb^{+}, Cs^{+}, Ca^{2+}, Ag^{+}, Pb^{2+}, Cu^{2+}, Zn^{2+}$; 1 = calcium ionophore I) in nitrobenzene saturated with water, log $K_{nb}(1-M^{+})$, on the crystallographic radius of the cation $M^{+}$, r(A).

**Table 1:** Equilibrium constants for the $M^{+}$ and $1-M^{+}$ cations in the two–phase water/nitrobenzene extraction system at 25 °C ($M^{+} = Li^{+}, Na^{+}, H_{2}O^{+}, NH_{4}^{+}, Ag^{+}, K^{+}, Rb^{+}, Tl^{+}, Cs^{+}$; 1 = calcium ionophore I). For the meaning of the constants see text. The standard deviations of the constants log $K$ are lower than 0.1 (three measurements).

<table>
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<tr>
<th>Quantity</th>
<th>$M^{+}$</th>
<th>$Li^{+}$</th>
<th>$Na^{+}$</th>
<th>$H_{2}O^{+}$</th>
<th>$NH_{4}^{+}$</th>
<th>$Ag^{+}$</th>
<th>$K^{+}$</th>
<th>$Rb^{+}$</th>
<th>$Tl^{+}$</th>
<th>$Cs^{+}$</th>
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<tbody>
<tr>
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<td>-4.5</td>
<td>-4.1</td>
<td>-3.4</td>
<td>-3.4</td>
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</tr>
<tr>
<td>log $K_{nb}(1-M^{+})$</td>
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<td>6.14</td>
<td>6.4</td>
<td>5.1</td>
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<td>4.7</td>
<td>3.8</td>
<td>6.3</td>
<td>3.4</td>
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</tr>
<tr>
<td>log $K_{M+}^{i}$ + log $K_{nb}(1-M^{+})$</td>
<td>0.9</td>
<td>0.14</td>
<td>0.7</td>
<td>0.4</td>
<td>2.0</td>
<td>0.6</td>
<td>0.4</td>
<td>2.9</td>
<td>0.7</td>
<td></td>
</tr>
</tbody>
</table>

*aRef. [16], Ref. [20].
product of its individual extraction constant and the stability constant of its complex with Calcium Ionophore I in nitrobenzene. These products for the univalent cations are also summarized in Table 1. It is clear from Table 1 that the maximum affinity to nitrobenzene phase have the ‘soft’ cations Ag⁺ and Tl⁺. The same products in Table 2 indicates that the highest affinity to nitrobenzene has the cation Ca⁺.

The stability constants of divalent cations in the system under study increase in the sequence Ba²⁺ < Zn²⁺ < Pb²⁺ < Sr²⁺ < Cu²⁺ < Ca²⁺. The stability constants of Ca²⁺ with 1 is very high log $K_{nb}(1.Ca^{2+}) = 20$. We cannot find the reason for the extraction behavior of Cu²⁺ and Zn²⁺. On the other hand, the extraction of alkali earth metal cations Ca²⁺, Sr²⁺ and Ba²⁺ and also of the cation Pb²⁺ decrease with the crystallographic radius of the respective cation M²⁺ as depicted in Figure 2. Calcium cation has the highest affinity to the nitrobenzene phase (Table 2).

4 Conclusions

In the present work, the solvent extraction of univalent cations Li⁺, H₂O⁺, Na⁺, Ag⁺, K⁺, NH₄⁺, Tl⁺, Rb⁺, Cs⁺ and divalent cations Ca²⁺, Sr²⁺, Ba²⁺, Pb²⁺, Cu²⁺, Zn²⁺ in a water – nitrobenzene extraction system has been studied. Furthermore, the stability constants of the proven cationic complexes with Calcium ionophore I in nitrobenzene saturated with water were evaluated. The stability constants of univalent cations decrease with the ionic radius, but the stability constants of ammonium and especially of the “soft” cations Ag⁺ and Tl⁺ are higher than that of the alkali metal cation with similar ionic radius. The stability constant of Ca²⁺ with Calcium ionophore I is very high, log $K_{nb}(1.Ca^{2+}) = 20$.

Because Calcium ionophore I is a very efficient extraction reagent also for Eu³⁺ and Am³⁺ [11] the present work is a valuable contribution also for the handling of reprocessing raffinate.

Research ethics: Not applicable.
Author contributions: Both the authors have accepted responsibility for the entire content of this submitted manuscript and approved submission.
Competing interests: The authors declare no conflicts of interest regarding this article.
Research funding: This work was supported by the Grant Agency of Faculty of Environmental Sciences, Czech University of Life Sciences, Prague, Project No.: 42900/1312/3114, and by the Czech Ministry of Education, Youth, and Sports (Project 20/2015).
Data availability: The raw data can be obtained on request from the corresponding author.

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