Determination of formation constants of uranyl(VI) complexes with a hydrophilic SO$_3$-Ph-BTP ligand, using liquid-liquid extraction

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Abstract. Complex formation between uranyl ion, UO$_2^{2+}$, and a hydrophilic anionic form of SO$_3$-Ph-BTP$^{4-}$ ligand, L$^{4-}$, in water was studied by liquid-liquid extraction experiments performed over a range of the ligand and HNO$_3$ concentrations in the aqueous phase, at a constant concentration of nitrate anions at 25°C. The competition for UO$_2^{2+}$ ions between the lipophilic TODGA extractant and the hydrophilic L$^{4-}$ ligand leads to the decrease in the uranyl distribution ratios, D, with an increasing L$^{4-}$ concentration. The model of the solvent extraction process used accounts – apart from uranyl complexation by TODGA and SO$_3$-Ph-BTP$^{4-}$ – also for uranyl complexation by nitrates and for the decrease in the concentration of the free L$^{4-}$ ligand in the aqueous phase, due to its protonation, bonding in the uranyl complex and the distribution between the two liquid phases. The unusually strong dependence of the D values on the acidity, found in the experiment, could hardly be explained as due to L$^{4-}$ protonation merely. Three hypotheses were experimentally tested, striving to interpret the data in terms of additional extraction to the organic phase of ion associates of protonated TODGA cation with either partly protonated anionic L$^{4-}$ ligands or anionic UO$_2^{2+}$ complexes with NO$_3^-$ or L$^{4-}$. None of them has been confirmed. The analysis of the results, based on the formal correction of free ligand concentrations, points to the formation of 1:1 and 1:2 uranyl–SO$_3$-Ph-BTP complexes in the aqueous phase. The conditional formation constant of the 1:1 complex has been determined, log$\beta_{L,1} = 2.95 \pm 0.15$.

Key words: uranyl ion • hydrophilic poly-N-dentate ligands • complexes • solvent extraction • stripping • formation constant

Introduction

Uranium(VI) is the main (by mass) component of spent nuclear fuel (SNF). The PUREX process with its further modifications is commonly used for the recovery of uranium (and plutonium) [1]. Two decades ago a novel concept partitioning and transmutation (P&T) appeared for the technology of nuclear waste reprocessing. Separation of long-lived minor actinides (MA), in particular americium, from the waste, followed by its transmutation by fast neutrons to short-lived and stable nuclides would result in a significant shortening of the period of significant radiotoxicity of the waste [1, 2]. In the last years, a new process, GANEX (grouped actinide separation), was developed by CEA [3], and then modified using different extractants and stripping agents [4-6]. The process consists of two cycles. In the first cycle, the almost whole uranium is selectively extracted from an SNF solution in ca. 4 M HNO$_3$, by N,N-di-(ethyl-2-hexyl)isobutyramide (DEHiBA) extractant. In the second cycle, the actinides are extracted from the raffinate to the novel organic phase, e.g. a mixture of N,N'-dimethyl-N,N'...
Model of solvent extraction process

To calculate the formation constants of the uranyl SO$_3$-Ph-BTP$^-$ complexes, we considered the following chemical model of solvent extraction process of UO$_2^{2+}$ ion from an acidic aqueous phase containing nitrate ions and a hydrophilic anionic ligand, L$^-$ (L = SO$_3$-Ph-BTP), into the organic phase containing the lipophilic neutral ligand, TODGA, as extractant:

\[
\begin{align*}
(1) & \quad \text{UO}_2^{2+} + i \text{TODGA}_{\text{org}} + j \text{NO}_3^- \quad \xrightleftharpoons{K_{\text{ex}}} \quad \text{UO}_2(\text{TODGA})_i(\text{NO}_3)_j^{2-\text{org}} \\
(2) & \quad \text{UO}_2^{2+} + i \text{L}^+ \quad \xrightleftharpoons{K_{\text{L}}} \quad \text{UO}_2(\text{NO}_3)_j^{2-\text{i}} \\
(3) & \quad \text{UO}_2^{2+} + j \text{NO}_3^- \quad \xrightleftharpoons{K_{\text{NO}_3_L}} \quad \text{UO}_2(\text{NO}_3)_j^{2-} \\
(4) & \quad \text{L}^+ + n \text{H}^+ \quad \xrightleftharpoons{K_{\text{H}}} \quad \text{H}_n\text{L}^{n-4}
\end{align*}
\]

where subscript ‘org’ denotes the species in the organic phase, and lack of a subscript – the species in the aqueous phase. The experiments were performed at relatively high acidities (0.3 < pH < 3) and at a constant ionic strength (I = 1 M). Under these conditions, we can expect that: (i) UO$_2^{2+}$ is not hydrolyzed but is moderately complexed by nitrates; (ii) HNO$_3$ is almost totally dissociated; and (iii) the thermodynamic constants are the conditional constants related to an aqueous solution of 1 M HNO$_3$ + NaNO$_3$. We also assume that the Na$^+$ ions present in the aqueous phase do not interact with the SO$_3$-Ph-BTP$^-$ ligand. Therefore, we consider the following equilibrium constants:

\[
\begin{align*}
(5) & \quad K_{\text{ex}} \equiv \frac{[\text{UO}_2(\text{TODGA})_i(\text{NO}_3)_j^{2-\text{org}}]}{[\text{UO}_2^{2+}][\text{TODGA}]_i^{\text{org}}[\text{NO}_3^-]^j} \\
(6) & \quad \beta_{\text{L}} \equiv \frac{[\text{UO}_2(\text{NO}_3)_j^{2-}]}{[\text{UO}_2^{2+}][\text{L}]^n} \\
(7) & \quad \beta_{\text{NO}_3_L} \equiv \frac{[\text{UO}_2(\text{NO}_3)_j^{2-}]}{[\text{UO}_2^{2+}][\text{NO}_3^-]^n} \\
(8) & \quad K_{\text{H}} \equiv \frac{[\text{H}_n\text{L}^{n-4}]}{[\text{L}^+]^n[\text{H}^+]^n}
\end{align*}
\]

The square brackets denote molar concentrations of the given species, approximate to their thermodynamic activities. Subscript ‘org’ denotes the species in the organic phase, while no subscript – in the aqueous phase. In particular, [L$^-$] denotes the concentration of the ‘free’ (unbound, unprotonated) L$^-$ ligand in the aqueous phase. The $\beta_L$, $\beta_{\text{NO}_3_L}$ and $K_H$ values denote the apparent formation constants of UO$_2^{2+}$ complexes with the SO$_3$-Ph-BTP$^-$ ligand, with nitrate ions, and the protonation constants of L$^+$, respectively. The mass balance correlation can be expressed as (subscript ‘tot’ denotes the initial concentration of the given species in the aqueous phase, or total concentration in the system):

\[
\begin{align*}
(9) & \quad C_{\text{U, tot}} = \sum_{i,j} \frac{[\text{UO}_2(\text{TODGA})_i(\text{NO}_3)_j^{2-}]}{[\text{UO}_2^{2+}][\text{TODGA}]_i^{\text{org}}[\text{NO}_3^-]^j} \\
& \quad + \sum_{i,j} \frac{[\text{UO}_2(\text{NO}_3)_j^{2-}]}{[\text{UO}_2^{2+}][\text{L}]^n} + \sum_{i,j} \frac{[\text{UO}_2(\text{NO}_3)_j^{2-}]}{[\text{UO}_2^{2+}][\text{NO}_3^-]^n} \\
& \quad + \sum_{i,j} \frac{[\text{UO}_2(\text{NO}_3)_j^{2-}]}{[\text{UO}_2^{2+}][\text{L}]^n[\text{H}^+]^n} \\
& \quad + \sum_{i} \frac{[\text{UO}_2(\text{NO}_3)_j^{2-}]}{[\text{UO}_2^{2+}][\text{L}]^n[\text{H}^+]^n} \\
(10) & \quad C_{\text{L, tot}} = [\text{L}^+] + \sum_{i} [\text{UO}_2(\text{NO}_3)_j^{2-}] + \sum_{i} [\text{LH}^{n-4}]
\end{align*}
\]

where [L$^-$]$_{\text{org}}$ denotes the total concentration of L in the organic phase. It was expected and verified experimentally in the present work that the ligand was not extracted into the organic phase, i.e. [L$^-$]$_{\text{org}} = 0$. Using Eqs. (6) and (8), we obtain:

\[
\begin{align*}
(11) & \quad C_{\text{L, tot}} = [\text{L}^+] \left(1 + \sum_{n} K_{\text{H}}[\text{H}^+]^n \right) \\
& \quad + \sum_{i,j} \frac{[\text{UO}_2(\text{NO}_3)_j^{2-}]}{[\text{UO}_2^{2+}][\text{L}]^n[\text{H}^+]^n} \\
\end{align*}
\]
The distribution ratio of uranyl in the system studied, $D = \frac{C_{U,\text{org}}}{C_{U,\text{aq}}}$, can be expressed as:

$$D = \frac{\sum_{j=1}^{n} \left[ \text{UO}_2^{2+} \right] \left[ \text{TODGA} \right]_{j} \left[ \text{NO}_3^{-} \right]_{s}^{2-}}{\left[ \text{UO}_2^{2+} \right] + \sum_{j=1}^{n} \left[ \text{UO}_2^{2+} \right] \left[ \text{NO}_3^{-} \right]_{j}^{2-} + \sum_{l=1}^{m} \left[ \text{UO}_2^{2+} \right] \left[ \text{L}^{2-} \right]_{l}^{4-}}$$

where, in the absence of L, we have $D = D_0$, and $\sum_{j=1}^{n} \left[ \text{UO}_2^{2+} \right] \left[ \text{TODGA} \right]_{j} \left[ \text{NO}_3^{-} \right]_{s}^{2-}$

$$D_0 = \frac{\sum_{j=1}^{n} \left[ \text{UO}_2^{2+} \right] \left[ \text{TODGA} \right]_{j} \left[ \text{NO}_3^{-} \right]_{s}^{2-}}{\left[ \text{UO}_2^{2+} \right] + \sum_{j=1}^{n} \left[ \text{UO}_2^{2+} \right] \left[ \text{NO}_3^{-} \right]_{j}^{2-}}$$

The combination of Eqs. (6), (7), (12) and (13) leads to the equation:

$$\sum_{i=1}^{k} \beta_{i.N} \left[ \text{L}^{2-} \right] = \left( \frac{D_0}{D} - 1 \right) \left( 1 + \sum_{i=1}^{r} \beta_{i.NO_3} \left[ \text{NO}_3^{-} \right] \right)$$

However, the above model does not account in full for the effect of acidity of the solution on the $D$ values. The stoichiometry of the extracted metal-diglycolamide complexes depends on the nature and the concentration of acid, and on the diluent. The review by Manchanda et al. [9] summarizes the works on the protonation and acid-driven aggregation of TODGA, which is responsible for the unusual dependencies observed in the extraction of trivalent metal ions. Similar effects were also observed in UO$_2^{2+}$ extraction. Although solid UO$_2^{2+}$ compounds contain only one tridentate DGA ligand in the molecule [10], the slope values of the log $D$ vs. log[DGA] relationships in UO$_2^{2+}$ extraction from HNO$_3$ solutions by DGA extractants are between 2 and 3 [11, 12]. It seems clear that in the complexes formed in solutions not all the DGA ligands coordinate the UO$_2^{2+}$ cation in the tridentate manner.

**Experimental**

The extractant and the hydrophilic ligand studied, TODGA and SO$_3$-Ph-BTP, were purchased from Technocom Ltd. (UK). TODGA was used as received. The SO$_3$-Ph-BTP sample was additionally purified from the remaining free H$_2$SO$_4$, according to the following procedure: the acidic material was dissolved in water. The solution was neutralized with NaOH to pH 7 and evaporated under reduced pressure. The residue was dissolved in methanol, the solution was filtered and evaporated under reduced pressure. This was repeated three times. Finally, the methanol was evaporated and the residue (as sodium form) was dried at 70°C.

Solutions of TODGA and SO$_3$-Ph-BTP were prepared from precisely weighed amounts of the reagents. The aqueous phase of a constant ionic strength contained nitric acid (POCH Gliwice) and sodium nitrate (Merck, ACS Reagent) of total concentration in deionized water equal to 1.00 M. It also contained the SO$_3$-Ph-BTP ligand; 5 to 80 mM. The initial uranium concentration in the aqueous phase was equal to 1·10$^{-4}$ M (stock solution of uranyl nitrate was prepared from solid UO$_2$(NO$_3$)$_2$·6H$_2$O, 99.7%, Chemapol Ltd., Czech Republic). The organic phase consisted of 0.6 M TODGA in 5 vol.% octanol-kerosene. Such high concentration of the extractant was used because of only moderate extractability of U(VI) in the TODGA/HNO$_3$ system [11–13]. Chemical- and analytical-grade kerosene and 1-octanol (both Sigma-Aldrich) were used as the diluent and modifier, respectively.

Because of the significant HNO$_3$ extraction to organic solutions of TODGA [14], the organic phase was pre-equilibrated with the aqueous phase containing no SO$_3$-Ph-BTP and U(VI). Solvent extraction experiments were carried out in plastic vials of Eppendorf type. The volumes of the organic and aqueous phase were equal to 0.4 mL each. The vials with the two phases were mechanically shaken in a thermomixer for 30 min (the shaking rate was 1400 rpm) at 25 ± 0.1°C to achieve equilibrium (preliminary studies have shown that the D values are reproducible when shaking the phases from 15 to 90 min). After shaking, the phases were centrifuged at 7000 rpm for 5 min and separated. Two aliquots of the aqueous phase, of 0.1 mL each, were taken for further analysis. The concentration of uranium in the aqueous phases at equilibrium $C_{U,\text{aq}}$ and at the equilibrium, $C_{U,\text{eq}}$, – was determined spectrophotometrically with ARSENAZO III [15]. Absorbance was measured and absorption spectra were recorded using a T50 UV-VIS spectrophotometer (Enwag) equipped with a quartz cell of 1 cm path length. The measurements were carried out in duplicates.

With the equal volumes of the organic and aqueous phases, the distribution ratio of uranyl was calculated as:

$$D = \frac{C_{U,\text{org}} - C_{U,\text{aq}}}{C_{U,\text{eq}}}$$

In the preliminary work we tested the radiotracer method with U-235 measured by liquid scintillation counting. The determined D values well corresponded to those obtained using the spectrophotometric method, and the mass balance was correct within >90%. We decided to further use the less laborious spectrophotometric technique. The radiometric data have not been reported, because the unpurified SO$_3$-Ph-BTP ligand was used in that experiment.

To determine the concentration of the SO$_3$-Ph-BTP ligand in the organic phase at equilibrium a spectrophotometric method was developed. We made use of the formation of very strong and intensively coloured (charge transfer bands) Fe(II) complexes with aromatic poly-N-dentate ligands [16]. A 0.25 mL aliquot of the organic phase was shaken with 1 mL of an aqueous solution of the composition: 1 M HCl, 0.05 M hydroxylamine and 0.01 M Fe$^{2+}$, and then the aqueous phase was analyzed. The molar absorptivities of the three characteristic bands at 466, 575, and 631 nm in 1 M HCl in respect to ligand under the excess of Fe$^{2+}$ ions were equal to 7.58·10$^3$, 6.16·10$^3$, and 4.66·10$^3$ L·mol$^{-1}$·cm$^{-1}$, respectively. The calibration curve remained linear in the studied range 2.68·10$^{-6}$ – 1.0·10$^{-4}$ M SO$_3$-Ph-BTP.
The dependences of the uranium(VI) distribution ratios $D$ on the initial (total) concentration of SO$_3$-Ph-BTP in the aqueous phase, $[L]_{tot,aq}$, determined at various acidities at 25°C, are shown in Fig. 1.

A bunch of curves is observed, with different $D_0$ values slightly increasing with increasing the acidity of the aqueous phase: red – 0.001 M; green – 0.01 M; blue – 0.12 M and triangle – 0.15 M HNO$_3$, at a constant nitrate concentration, 1 M NO$_3^-$, 25°C. The organic phase – 0.6 M TODGA in 5 vol.% octanol-kerosene.

Results and discussion

The dependences of the uranium(VI) distribution ratios $D$ on the initial (total) concentration of SO$_3$-Ph-BTP in the aqueous phase, $[L]_{tot,aq}$, determined at various acidities at 25°C, are shown in Fig. 1.

A bunch of curves is observed, with different $D_0$ values slightly increasing with increasing the acidity of the aqueous phase: $D_0 = 9.1 \pm 0.4, 9.8 \pm 0.7, 10.7 \pm 0.4$ and $10.8 \pm 0.3$, for 0.001, 0.01, 0.12, and 0.15 M HNO$_3$, respectively. The competition for UO$_2^{2+}$ ions between the extractant (lipophilic ligand) TODGA and the hydrophilic ligand SO$_3$-Ph-BTP (L) leads to the decrease in the $D$ values with increasing concentration of L. Moreover, the significant increase in the $D$ values with increasing HNO$_3$ concentration is observed. This unusually strong dependence of the $D$ values from the acidity would point to a significant change of the protonation of L$^+$ in the examined range of acidity (Eqs. (4) and (8)). The protonated (at the donor N atoms of pyridine [17]) hydrophilic HL$^+$ ligands do not complex the UO$_2^{2+}$ ions in the aqueous phase. Therefore, at higher acidities the $D$ values become less prone to decrease with increasing the concentration of L (Fig. 1).

To conclude on the complex formation of the UO$_2^{2+}$ ions with L$^+$ in the aqueous phase, we plotted the log($D_0/D - 1$) values as a function of log([L$^+$] 

\[ \log \left( \frac{D_0}{D - 1} \right) + \log \left( 1 + \sum \beta_{NO_3^-} \left[ NO_3^- \right] \right) = i \log [L^+] + \log \beta_{L,i} \]

Equation (16) shows that both protonation of L$^+$ ions and their complex formation with UO$_2^{2+}$ decrease [L$^+$] at the given $C_{L,tot}$, [H$^+$] and $C_{U,aq}$ values. In order to calculate the [L$^+$] values (as functions of $\beta_{L,i}$) for each set of variables, $C_{L,tot}$ and [H$^+$], we had used this equation with the following parameters: $n = 1$ [18], $i = 1$ (Fig. 3) and $C_{U,aq} = C_{U,in}/(D + 1) = 10^{-7}/(D + 1)$. Surprisingly, the calculations we had made taking the protonation constant of SO$_3$-Ph-BTP in water, determined by Ruff from the UV-Vis spectra, log$K_{H,1}$ = p$K_a = 0.5 \pm 0.1$ [19], did not allow the $D$ values determined at various acidities to fit the same relationship $F = \log (D_0/D - 1)$ vs. log([L$^+$]) for $i = 1$. Therefore, we undertook attempts to unify the [L$^+$] values by finding the optimum log$K_{H,1}$ value which would ensure the best fit of this relationship to the experimental points. An iterative procedure was used to calculate the [L$^+$] and ($\beta_{L,i}$) values using Eq. (11) with the parameters as above, for each pair of the experimental variables, [H$^+$] and $C_{L,tot}$. Among a dozen log$K_{H,1}$ values from the arbitrarily selected range of 1.00 to 2.70 we have found the log$K_{H,1}$ and [L$^+$] values which minimize the sum of weighted $(F_{exp} - F_{calc})^2$ values in the range of linearity of F (the slope of 1), i.e. log([L$^+$]) $< -2.0$ (Fig. 3). The uncertainties were calculated according to the procedure of error propagation of experimental data [20]. The minimum $\Sigma_{i=1}^{13} (F_{exp,i} - F_{calc,i})^2$ value ($i = 1+13$) of 1.23 (normalized $w_i$) has been obtained at log$K_{H,1} = 1.88$. The use of this ‘best fit’ value allowed us for a formal adjustment of the free ligand concentrations to the values that made it possible to plot all the experimental log($D_0/D - 1$) values on the same curve – the function of log([L$^+$]) (Fig. 3). The effect of this apparent protonation constant on the decrease in the L$^+$ concentration dominates in all the systems investigated, except from those of the lowest acidities and highest $C_{L,tot}$, where the contribution from the complex formation becomes comparable.

On the contrary, our further studies on the complexation of Am$^{3+}$ with SO$_3$-Ph-BTP$^+$ resulted in the similar ‘best fit’ adjustment of the [L$^+$] values at log$K_{H,1} = 0.5$ [21], i.e. the value equal to that determined by spectrophotometry [19]. This result confirms that the ‘best fit’ value found in the uranyl system, log$K_{H,1} = 1.88$, is the apparent one. A question arises, whether the free ligand concentrations, [L$^+$], calculated with the use of this apparent $K_{H,1}$ value are genuine or artifactual values. The former might be true if another factor, different from the protonation, would decrease the aqueous phase concentra-
\[ L^4- \] The above could take place, e.g. when the protonated \( \text{SO}_3\text{-Ph-BTP} \) ligand alone is extracted into the organic phase, probably as an ion associate (ion pair) of its anionic form with the protonated TODGA cation, at the high (0.6 M) concentration of the extractant. To test this hypothesis, an experiment was carried out by shaking an aqueous solution (0.05 M \( \text{SO}_3\text{-Ph-BTP} \) in 0.15 M HNO\(_3\) + 0.85 M NaNO\(_3\)) with an equal volume of 0.6 M TODGA in 5 vol.% octanol-kerosene. Then the loaded organic phase was shaken with 1 M HCl to strip the extracted \( \text{SO}_3\text{-Ph-BTP} \). Spectrophotometric analysis of the new aqueous phase has shown that the concentration of the \( \text{SO}_3\text{-Ph-BTP} \) ligand in the organic phase was less than 3.2\( \times \)10\(^{-6}\), i.e. the extraction of hydrophilic \( \text{SO}_3\text{-Ph-BTP} \) was negligible. The hypothesis was thus rejected and another reason for the above discrepancy had to be sought.

This other reason could be due to an oversimplification of the model of uranyl extraction, i.e. to assuming the extraction of uranyl in the form of TODGA complexes merely. We turned attention to the anionic uranyl species which could form extractable ion associates with protonated TODGA: (i) homoleptic \( \text{UO}_2^{2+} - L^4- \) or heteroleptic \( \text{UO}_2^{2+} - \text{TODGA} - L^4- \) complexes; and (ii) trinitratouranyl anion, \( \text{UO}_2(\text{NO}_3)_3^- \). In the former case, a significant amount of the \( \text{SO}_3\text{-Ph-BTP} \) ligand would be co-extracted with uranyl to the organic phase. However, detection of no \( \text{SO}_3\text{-Ph-BTP} \) ligand in the 0.6 M TODGA organic phase loaded with nearly 2\( \times \)10\(^{-4}\) M uranium extracted from the aqueous solution (0.06 M \( \text{SO}_3\text{-Ph-BTP} \) in 0.15 M HNO\(_3\) + 0.85 M NaNO\(_3\)) resulted in rejecting this hypothesis as well.

The last hypothesis was formulated in view of efficient extraction of \( \text{UO}_2(\text{NO}_3)_3^- \) as ion pairs with protonated ketones [22], amides [23] and diamides [24] from strongly acidic HNO\(_3\) solutions. In spite of the fact that in our experiments the acidities of the aqueous phases were relatively low and the effect of acidity on the \( D \) values was weak, we have measured the UV-Vis spectrum of the organic phase after extraction of uranyl from the standard aqueous phase containing 0.013 M \( \text{UO}_2^{2+} \) and 0.06 M \( \text{SO}_3\text{-Ph-BTP} \). Figure 2 shows no spectral evidence [22–24] for the presence of \( \text{UO}_2(\text{NO}_3)_3^- \) in the organic phase, therefore this hypothesis has been rejected as well.

After having failed all the hypotheses striving to find a factor responsible for the discrepancy between the experimental and the apparent \( K_{H,1} \) values, we had to state formally that the thermodynamic activity of \( L^4- \) in the aqueous phase strongly decreases with increasing concentration of \( L \) and HNO\(_3\), and that the \( [L^4-] \) values calculated with the use of this adjusted apparent \( K_{H,1} \) value do correspond to the genuine thermodynamic activities of \( L^4- \) in the aqueous phase. This peculiarity of the extraction system studied can result, at least in a part, from the relatively high concentrations of the \( \text{SO}_3\text{-Ph-BTP} \) ligand, which increases the ionic strength of the aqueous phase over 1.0 to a significant extent.

The plot of \( \log(D/D - 1) \) as a function of \( \log[L^4-] \) has been shown in Fig. 3. The plot is not exactly linear. The slope of the dependence of \( \log(D/D - 1) \)

\[ \log(D/D - 1) = 2.73 \pm 0.14 \]

Formation constant of the \( \text{UO}_2\text{NO}_3^- \) complex at 25°C, calculated from UV-Vis spectra, was reported to be \( \log(\beta_{\text{NO}_3}) = -0.19 \pm 0.02 \) [25]. Taking \( r = 1 \) and \( [\text{NO}_3^-] = 1 \) M, we obtain \( \log(1 + \beta_{\text{NO}_3}[\text{NO}_3^-]) = 0.216 + 0.008 \).

Therefore, we have \( \log(\beta_{\text{L,1}}) = 2.95 \pm 0.15 \) for the \( \text{UO}_2\text{NO}_3^- - \text{SO}_3\text{-Ph-BTP} \) complex.

The determined value \( \log(\beta_{\text{L,1}}) = 2.95 \pm 0.15 \) for \( \text{UO}_2\text{NO}_3^- \) is rather low when comparing to the literature \( \log(\beta_{\text{L,1}}) \) values for \( \text{SO}_3\text{-Ph-BTP} \) complexes of \( \text{Cm}^{3+} \) and \( \text{Eu}^{3+} \), equal to 5.4 ± 0.1 and 5.2 ± 0.1, respectively [26]. Due to the lack of literature data found on \( \log([L^4-]) \) equal to one, corresponding to the 1:1 complex, is observed in the range of \( \log([L^4-]) \) values between –3 and –2. The deviations from the linearity, observed at \( \log([L^4-]) > -2 \) can be attributed to the 1:2 complex. The value of \( \log(D/D - 1) \) calculated by extrapolation of the straight line with the slope of 1.0 to the \( \log([L^4-]) = 0 \) is equal to 2.73 ± 0.14.

Fig. 2. UV-Vis absorption spectrum of the organic phase (0.6 M TODGA in 5 vol.% octanol-kerosene) after extraction of 0.013 M uranyl (see text). Quartz cell of 1 cm path length, room temperature.

Fig. 3. \( \log(D/D - 1) \) for \( \text{UO}_2\text{NO}_3^- \) in the system studied, as a function of \( \log([L^4-]) \) values at various concentrations of HNO\(_3\): –0.001 M; –0.01 M; –0.12 M and –0.15 M. \( I = 1.0 \) M NO\(_3^-\), 25°C. The \( \log([L^4-]) \) values have been calculated assuming \( \log(K_{H,1}) = 1.88 \).
on uranyl complexes with hydrophilic BTP ligands, we analyzed the coordination ability of SO$_3$-Ph-BTP in respect to uranyl only in light of available information on uranyl complexes with related lipophilic ligands. X-ray crystal structures of 1:1 complexes of uranyl with lipophilic R-BTPs (R = Me, n-Pr), [UO$_2$(NO$_3$)$_2$(R-BTP)], reveal a geometry with seven coordinating atoms around the UO$_2$ fragment. The large steric crowding in the equatorial girdle forces the bidentate NO$_3$ ligands to be almost perpendicular to the equatorial plane, inducing bending of the UO$_2$ fragment [27]. Such structural distortion can cause the affinity of BTP ligands to UO$_2^{2+}$ to be lower than to Cm$^{3+}$/Eu$^{3+}$ ions. The effect of steric hindrance of bulky ligands has also been concluded based on DFT calculations of [UO$_2$L$_2$(NO$_3$)$_2$] complexes even at CN6 (two monodentate amide ligands, L) [28]. Unfortunately, no data are available on UO$_2^{2+}$-BTP complexes in solution. Related hemi-BTP (6-(5,6-dipentyl-1,2,4-triazin-3-yl)-2,2'-bipyridine) ligand in methanol forms uranyl complexes (1:1) of nearly the same stability as those of -bipyridine) ligand in methanol forms uranyl complexes (1:1) of nearly the same stability as those of Am$^{3+}$ and Eu$^{3+}$ ions [30].

Conclusions

The conditional formation constant of the 1:1 complex formed by uranyl ion, UO$_2^{2+}$, and a hydrophilic SO$_3$-Ph-BTP$^{2-}$ ligand in aqueous 1 M nitrate solution at 25°C, log$b_{11}$ = 2.95 ± 0.15, has been determined by the liquid-liquid extraction method, with the use of a lipophilic TODGA extractant. Also the 1:2 complex is formed in the aqueous phase at higher concentrations of SO$_3$-Ph-BTP$^{2-}$.

Unusually strong dependence of uranyl distribution ratios on the acidity has been observed in the extraction system studied. The decrease in the thermodynamic activity of the SO$_3$-Ph-BTP$^{2-}$ ligand in the aqueous phase, caused by its protonation, is insufficient to explain the data. The reason of this discrepancy is still unknown.

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