



Determination of formation constants of uranyl(VI) complexes with a hydrophilic SO₃-Ph-BTP ligand, using liquid-liquid extraction

Lukasz Steczek,
Jerzy Narbutt,
Marie-Christine Charbonnel,
Philippe Moisy

Abstract. Complex formation between uranyl ion, UO₂²⁺, and a hydrophilic anionic form of SO₃-Ph-BTP⁺ ligand, L⁻, in water was studied by liquid-liquid extraction experiments performed over a range of the ligand and HNO₃ concentrations in the aqueous phase, at a constant concentration of nitrate anions at 25°C. The competition for UO₂²⁺ ions between the lipophilic TODGA extractant and the hydrophilic L⁻ ligand leads to the decrease in the uranyl distribution ratios, D, with an increasing L⁻ concentration. The model of the solvent extraction process used accounts – apart from uranyl complexation by TODGA and SO₃-Ph-BTP⁺ – also for uranyl complexation by nitrates and for the decrease in the concentration of the free L⁻ 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⁻ 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⁻ ligands or anionic UO₂²⁺ complexes with NO₃⁻ or L⁻. 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 – SO₃-Ph-BTP complexes in the aqueous phase. The conditional formation constant of the 1 : 1 complex has been determined, logβ_{L,1} = 2.95 ± 0.15.

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

L. Steczek[✉]
Centre for Radiochemistry and Nuclear Chemistry,
Institute of Nuclear Chemistry and Technology,
16 Dorodna Str., 03-195 Warsaw, Poland,
and RadioChemistry & Processes Department,
Nuclear Energy Division, CEA,
F-30207 Bagnols sur Cèze, France,
E-mail: L.Steczek@ichtj.waw.pl

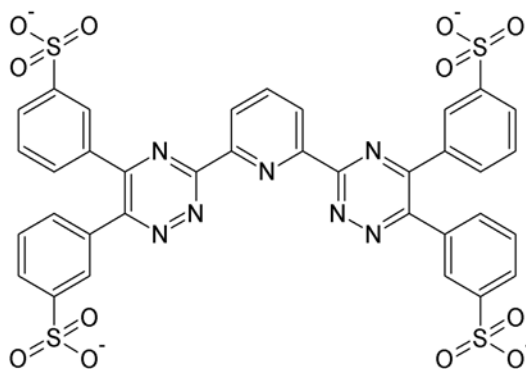
J. Narbutt
Centre for Radiochemistry and Nuclear Chemistry,
Institute of Nuclear Chemistry and Technology,
16 Dorodna Str., 03-195 Warsaw, Poland

M.-Ch. Charbonnel, Ph. Moisy
RadioChemistry & Processes Department,
Nuclear Energy Division, CEA,
F-30207 Bagnols sur Cèze, France

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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 HNO₃, 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'*-

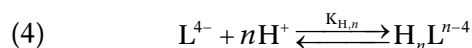
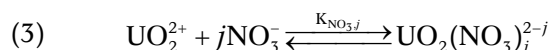
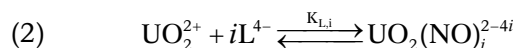
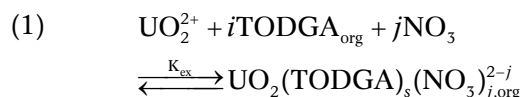


Scheme 1. Structural formula of the $\text{SO}_3\text{-Ph-BTP}^-$ anion.

-dioctylhexylethoxymalonamide (DMDOHEMA) and *N,N,N',N'*-tetraoctyldiglycolamide (TODGA) extractants in a kerosene diluent [4–6], and then separated from the co-extracted fission products (in particular lanthanides) by stripping the actinides to a fresh aqueous solution. An interesting actinide-selective stripping agent is a hydrophilic, anionic BTP ligand, 2,6-bis(5,6-di(sulfophenyl)-1,2,4-triazin-3-yl)pyridine ($\text{SO}_3\text{-Ph-BTP}^-$ – Scheme 1), developed for the innovative SANEX (selectively actinides extraction) process [7, 8]. The knowledge of complexing properties of ligands used in the separation processes is of paramount importance for designing novel separation schemes. Though extensive studies focus on the An(III)/Ln(III) complexation by $\text{SO}_3\text{-Ph-BTP}$, no data are published on U(VI), small amounts of which remain in the raffinate of the 1st cycle of GANEX. The aim of the present work was to determine formation constants of uranyl complexes with the $\text{SO}_3\text{-Ph-BTP}^-$ ligand in acidic (HNO_3) solutions. The liquid-liquid distribution method was used to reach this goal.

Model of solvent extraction process

To calculate the formation constants of the uranyl $\text{SO}_3\text{-Ph-BTP}^-$ 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^{4-} ($\text{L} = \text{SO}_3\text{-Ph-BTP}$), into the organic phase containing the lipophilic neutral ligand, TODGA, as extractant:



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 ($0.3 < \text{pH} < 3$)

and at a constant ionic strength ($I = 1 \text{ M}$). 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 $\text{HNO}_3 + \text{NaNO}_3$. We also assume that the Na^+ ions present in the aqueous phase do not interact with the $\text{SO}_3\text{-Ph-BTP}^-$ ligand. Therefore, we consider the following equilibrium constants:

$$(5) \quad K_{\text{ex}} = \frac{[\text{UO}_2(\text{TODGA})_i(\text{NO}_3)_j]_{\text{org}}}{[\text{UO}_2^{2+}][\text{TODGA}]_{\text{org}}^i[\text{NO}_3^-]_{\text{aq}}^j}$$

$$(6) \quad \beta_{\text{L},i} = \frac{[\text{UO}_2\text{L}_i^{2-4i}]}{[\text{UO}_2^{2+}][\text{L}^{4-}]^i}$$

$$(7) \quad \beta_{\text{NO}_3,j} = \frac{[\text{UO}_2(\text{NO}_3)_j^{2-j}]}{[\text{UO}_2^{2+}][\text{NO}_3^-]^j}$$

$$(8) \quad K_{\text{H},n} = \frac{[\text{H}_n\text{L}^{n-4}]}{[\text{L}^{4-}][\text{H}^+]^n}$$

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, $[\text{L}^{4-}]$ denotes the concentration of the ‘free’ (unbound, unprotonated) L^{4-} ligand in the aqueous phase. The β_{L} , β_{NO_3} and K_{H} values denote the apparent formation constants of UO_2^{2+} complexes with the $\text{SO}_3\text{-Ph-BTP}$ ligand, with nitrate ions, and the protonation constants of L^{4-} , 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):

$$(9) \quad C_{\text{U,tot}} = [\text{UO}_2^{2+}] + \sum_{j=1}^r [\text{UO}_2(\text{NO}_3)_j^{2-j}] + \sum_{i=1}^k [\text{UO}_2\text{L}_i^{2-4i}] + \sum_{j=1}^s [\text{UO}_2(\text{TODGA})_j(\text{NO}_3)_2]_{\text{org}}$$

$$(10) \quad C_{\text{L,tot}} = [\text{L}^{4-}] + \sum_{i=1}^k i [\text{UO}_2\text{L}_i^{2-4i}] + \sum_{n=1}^z [\text{LH}_n^{n-4}] + \sum [\text{L}]_{\text{org}}$$

where $[\text{L}]_{\text{org}}$ 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. $[\text{L}]_{\text{org}} = 0$. Using Eqs. (6) and (8), we obtain:

$$(11) \quad C_{\text{L,tot}} = [\text{L}^{4-}] \left(1 + \sum_{n=1}^z K_{\text{H},n} [\text{H}^+]^n \right) + [\text{UO}_2^{2+}] \sum_{i=1}^k i \beta_{\text{L},i} [\text{L}^{4-}]^i$$

The distribution ratio of uranyl in the system studied, $D = C_{U,org}/C_{U,aq}$, can be expressed as:

$$(12) \quad D = \frac{\sum_{j=1}^s [\text{UO}_2(\text{TODGA})_j(\text{NO}_3)_2]_{\text{org}}}{[\text{UO}_2^{2+}] + \sum_{j=1}^r [\text{UO}_2(\text{NO}_3)_j]^{2-j} + \sum_{i=1}^k [\text{UO}_2\text{L}_i]^{2-4i}}$$

where, in the absence of L, we have $D = D_0$,

$$(13) \quad D_0 = \frac{\sum_{j=1}^s [\text{UO}_2(\text{TODGA})_j(\text{NO}_3)_2]_{\text{org}}}{[\text{UO}_2^{2+}] + \sum_{j=1}^r [\text{UO}_2(\text{NO}_3)_j]^{2-j}}$$

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

$$(14) \quad \sum_{i=1}^k \beta_{L,i} [\text{L}^{4-}]^i = \left(\frac{D_0}{D} - 1 \right) \left(1 + \sum_{j=1}^r \beta_{\text{NO}_3,j} [\text{NO}_3^-]_j \right)$$

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 UO₂²⁺ extraction. Although solid UO₂²⁺ compounds contain only one tridentate DGA ligand in the molecule [10], the slope values of the log D vs. log[DGA] relationships in UO₂²⁺ extraction from HNO₃ 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 UO₂²⁺ cation in the tridentate manner.

Experimental

The extractant and the hydrophilic ligand studied, TODGA and SO₃-Ph-BTP, were purchased from Technocomm Ltd. (UK). TODGA was used as received. The SO₃-Ph-BTP sample was additionally purified from the remaining free H₂SO₄, 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 SO₃-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 SO₃-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 UO₂(NO₃)·6H₂O, 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/HNO₃ 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 HNO₃ extraction to organic solutions of TODGA [14], the organic phase was pre-equilibrated with the aqueous phase containing no SO₃-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 phase – initial, C_{U,in}, and at the equilibrium, C_{U,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:

$$(15) \quad D = \frac{C_{U,in} - C_{U,eq}}{C_{U,eq}}$$

In the preliminary work we tested the radiotracer method with U-233 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 SO₃-Ph-BTP ligand was used in that experiment.

To determine the concentration of the SO₃-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 Fe²⁺, 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 Fe²⁺ ions were equal to 7.58·10⁵, 6.16·10⁵, and 4.66·10⁵ L·mol⁻¹·cm⁻¹, respectively. The calibration curve remained linear in the studied range 2.68·10⁻⁶ – 1.0·10⁻⁴ M SO₃-Ph-BTP.

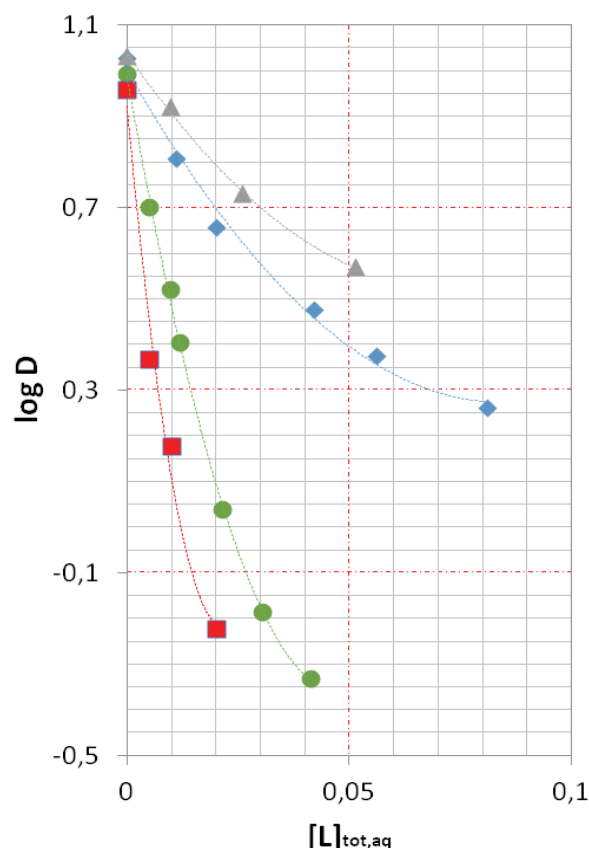


Fig. 1. Distribution ratio of uranyl(VI), D , as a function of the initial (total) concentration of $\text{SO}_3\text{-Ph-BTP}$ in the aqueous phase, $[\text{L}]_{\text{tot,aq}}$, and of the acidity of the aqueous phase: \blacksquare – 0.001 M; \bullet – 0.01 M; \blacklozenge – 0.12 M and \blacktriangle – 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 $\text{SO}_3\text{-Ph-BTP}$ in the aqueous phase, $[\text{L}]_{\text{tot,aq}}$, 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 ± 0.7 , 10.7 ± 0.4 and 10.8 ± 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 $\text{SO}_3\text{-Ph-BTP}$ (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^{3+} 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 $\log[\text{L}^+]$ [18]. In the regions of ligand concentration where only one form of the complex (e.g. 1 : 1) predominates, Eq. (14) can be simplified and expressed in the logarithmic form, where the slope is equal to the number, i , of the ligand molecules complexing the metal ion:

$$(16) \quad \log\left(\frac{D_0}{D} - 1\right) + \log\left(1 + \sum_{j=1}^r \beta_{\text{NO}_3,j} [\text{NO}_3^-]^j\right) \\ = i \log[\text{L}^+] + \log \beta_{\text{L},i}$$

Equation (11) shows that both protonation of L^+ ions and their complex formation with UO_2^{2+} decrease $[\text{L}^+]$ at the given $C_{\text{L,tot}}$, $[\text{H}^+]$ and $C_{\text{U,aq}}$ values. In order to calculate the $[\text{L}^+]$ values (as functions of $\beta_{\text{L},i}$) for each set of variables, $C_{\text{L,tot}}$ and $[\text{H}^+]$, we had used this equation with the following parameters: $n = 1$ [18], $i = 1$ (Fig. 3) and $C_{\text{U,aq}} = C_{\text{U,ini}} / (D + 1) = 10^{-4} / (D + 1)$. Surprisingly, the calculations we had made taking the protonation constant of $\text{SO}_3\text{-Ph-BTP}$ in water, determined by Ruff from the UV-Vis spectra, $\log K_{\text{H},1} = \text{pKa} = 0.5 \pm 0.1$ [19], did not allow the D values determined at various acidities to fit the same relationship $F = \log(D_0/D - 1)$ vs. $\log[\text{L}^+]$ for $i = 1$. Therefore, we undertook attempts to unify the $[\text{L}^+]$ values by finding the optimum $\log K_{\text{H},1}$ value which would ensure the best fit of this relationship to the experimental points. An iterative procedure was used to calculate the $[\text{L}^+]$ (and $\beta_{\text{L},1}$) values using Eq. (11) with the parameters as above, for each pair of the experimental variables, $[\text{H}^+]$ and $C_{\text{L,tot}}$. Among a dozen $\log K_{\text{H},1}$ values from the arbitrarily selected range of 1.00 to 2.70 we have found the $\log K_{\text{H},1}$ and $[\text{L}^+]$ values which minimize the sum of weighted $(F_{\text{exp}} - F_{\text{calc}})^2$ values in the range of linearity of F (the slope of 1), i.e. $\log[\text{L}^+] < -2.0$ (Fig. 3). The uncertainties were calculated according to the procedure of error propagation of experimental data [20]. The minimum $\sum w_i (F_{\text{exp},i} - F_{\text{calc},i})^2$ value ($i = 1 \div 13$) of 1.23 (normalized w_i) has been obtained at $\log K_{\text{H},1} = 1.88$. 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 $\log[\text{L}^+]$ (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 $C_{\text{L,tot}}$, where the contribution from the complex formation becomes comparable.

On the contrary, our further studies on the complexation of Am^{3+} with $\text{SO}_3\text{-Ph-BTP}^{4-}$ resulted in the similar 'best fit' adjustment of the $[\text{L}^+]$ values at $\log K_{\text{H},1} = 0.5$ [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, $\log K_{\text{H},1} = 1.88$, is the apparent one. A question arises, whether the free ligand concentrations, $[\text{L}^+]$, calculated with the use of this apparent $K_{\text{H},1}$ value are genuine or artificial values. The former might be true if another factor, different from the protonation, would decrease the aqueous phase concen-

tration of L⁺. The above could take place, e.g. when the protonated SO₃-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 SO₃-Ph-BTP in 0.15 M HNO₃ + 0.85 M NaNO₃) 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 SO₃-Ph-BTP. Spectrophotometric analysis of the new aqueous phase has shown that the concentration of the SO₃-Ph-BTP ligand in the organic phase was less than 3.2 · 10⁻⁶, i.e. the extraction of hydrophilic SO₃-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 UO₂²⁺ – L⁺ or heteroleptic UO₂²⁺ – TODGA – L⁺ complexes; and (ii) trinitratouranyl anion, UO₂(NO₃)₃⁻. In the former case, a significant amount of the SO₃-Ph-BTP ligand would be co-extracted with uranyl to the organic phase. However, detection of no SO₃-Ph-BTP ligand in the 0.6 M TODGA organic phase loaded with nearly 2 · 10⁻⁴ M uranium extracted from the aqueous solution (0.06 M SO₃-Ph-BTP in 0.15 M HNO₃ + 0.85 M NaNO₃) resulted in rejecting this hypothesis as well.

The last hypothesis was formulated in view of efficient extraction of UO₂(NO₃)₃⁻ as ion pairs with protonated ketones [22], amides [23] and diamides [24] from strongly acidic HNO₃ 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 D₀ 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 UO₂²⁺ and 0.06 M SO₃-Ph-BTP). Figure 2 shows no spectral evidence [22–24] for the presence of UO₂(NO₃)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⁺ in the aqueous phase strongly decreases with increasing concentration of L and HNO₃, and that the [L⁺] values calculated with the use of this adjusted apparent K_{H,1} value do correspond to the genuine thermodynamic activities of L⁺ 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 SO₃-Ph-BTP ligand, which increases the ionic strength of the aqueous phase over 1.00 to a significant extent.

The plot of log(D₀/D – 1) as a function of log[L⁺] has been shown in Fig. 3. The plot is not exactly linear. The slope of the dependence of log(D₀/D – 1)

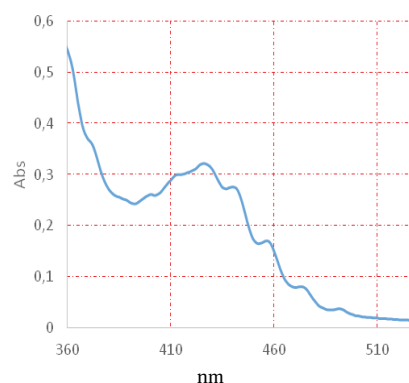


Fig. 2. UV-Vis absorption spectrum of the organic phase (0.6 M TODGA in 5 vol.% octanol-kerosene) after extraction of 0.013 M uranyl (see text). Quartz cell of 1 cm path length, room temperature.

on log[L⁺] equal to one, corresponding to the 1 : 1 complex, is observed in the range of log[L⁺] values between –3 and –2. The deviations from the linearity, observed at log[L⁺] > –2 can be attributed to the 1 : 2 complex. The value of log(D₀/D – 1) calculated by extrapolation of the straight line with the slope of 1.0 to the log[L⁺] = 0, is equal to 2.73 ± 0.14. Formation constant of the UO₂²⁺ – NO₃⁻ complex at 25°C, calculated from UV-Vis spectra, was reported to be logβ_{NO₃,1} = –0.19 ± 0.02 [25]. Taking r = 1 and [NO₃⁻] = 1 M, we obtain log(1 + β_{NO₃,j}[NO₃⁻]) = 0.216 + 0.008.

Therefore, we have logβ_{L,1} = 2.95 ± 0.15 for the UO₂²⁺–SO₃-Ph-BTP⁺ complex.

The determined value logβ_{L,1} = 2.95 ± 0.15 for UO₂²⁺ is rather low when comparing to the literature logβ_{L,1} values for SO₃-Ph-BTP complexes of Cm³⁺ and Eu³⁺, equal to 5.4 ± 0.1 and 5.2 ± 0.1, respectively [26]. Due to the lack of literature data found

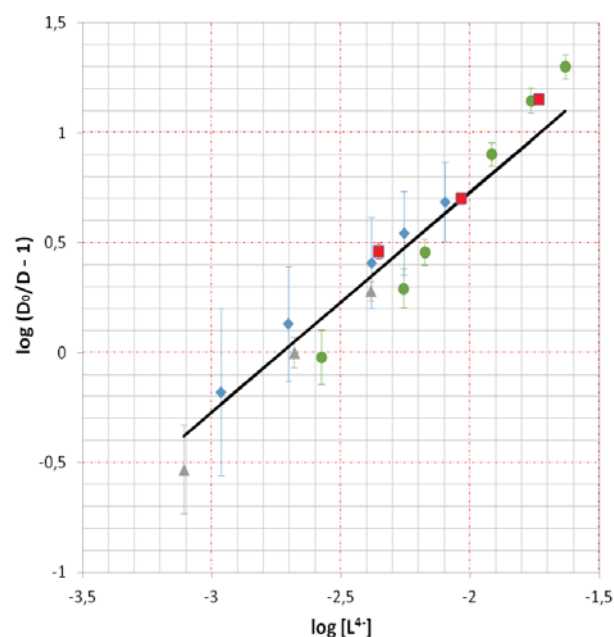


Fig. 3. Log(D₀/D – 1) for UO₂²⁺ in the system studied, as a function of the log[L⁺] values at various concentrations of HNO₃: ■ – 0.001 M; ● – 0.01 M; ◆ – 0.12 M and ▲ – 0.15 M. I = 1.0 M NO₃⁻, 25°C. The log[L⁺] values have been calculated assuming logK_{H,1} = 1.88.

on uranyl complexes with hydrophilic BTP ligands, we analyzed the coordination ability of $\text{SO}_3\text{-Ph-BTP}$ 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 ($\text{R} = \text{Me}, n\text{-Pr}$), $[\text{UO}_2(\text{NO}_3)_2(\text{R-BTP})]$, 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 $\text{Cm}^{3+}/\text{Eu}^{3+}$ ions. The effect of steric hindrance of bulky ligands has also been concluded based on DFT calculations of $[\text{UO}_2\text{L}_2(\text{NO}_3)_2]$ 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 Eu^{3+} ion, and the same relationship was observed in the complexes of a BTBP ((6,6'-bis(5,6-dipentyl-1,2,4-triazin-3-yl)-2,2'-bipyridine) ligand [29]. On the other hand, pentadentate bitopic *N,O*-bearing *N,N,N',N'*-tetraethyl-6,6''-(2,2' : 6,6''-terpyridine) diamide ligand in methanol-water solution forms a weak 1 : 1 uranyl complex of low formation constant ($\log\beta_{L,1} = 2.4$) by one-two orders of magnitude lower than those for Am^{3+} and Eu^{3+} ions [30].

Further studies on the complexation of other actinides by $\text{SO}_3\text{-Ph-BTP}$ are in progress.

Conclusions

The conditional formation constant of the 1 : 1 complex formed by uranyl ion, UO_2^{2+} , and a hydrophilic $\text{SO}_3\text{-Ph-BTP}^+$ ligand in aqueous 1 M nitrate solution at 25°C, $\log\beta_1 = 2.95 \pm 0.15$, 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 $\text{SO}_3\text{-Ph-BTP}^+$.

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 $\text{SO}_3\text{-Ph-BTP}^+$ 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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