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Luminescence of uranium(VI) after liquid-liquid extraction from HCl by Aliquat® 336 in *n*-dodecane:1-decanol by time-resolved laser-induced luminescence spectroscopy

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Abstract: To investigate the extraction of uranium(VI) in HCl media by Aliquat® 336 in 1:99 (v:v) 1-decanol:*n*-dodecane mixture, our objective is to identify the complexe(s) in the organic phase by time-resolved laser-induced luminescence spectroscopy (TRLS). The extraction mechanism is supposed to involve the formation of $[\text{UO}_2\text{Cl}_4^{2-} \cdot (\text{R}_4\text{N}^+)_2]$ in the organic phase. The occurrence of such a species leads to the presence of the $\text{UO}_2\text{Cl}_4^{2-}$ species in the organic solution, which luminescence shows particular features. The luminescence spectra and decay time evolutions are obtained in the organic phase as a function of HCl concentration in the aqueous phase (0.5–6 M). The extraction of $\text{UO}_2\text{Cl}_4^{2-}$ is confirmed by the particular spectrum of uranium(VI) in the organic phase, and the typical splitting of the luminescence bands, due to the crystal field effect, is clearly evidenced. The stoichiometry is verified using luminescence intensity variation as a function of the activity of Cl^- , and extraction constants are calculated both using the specific interaction theory and Pitzer model. A decomposition of the spectrum of the extracted complex in the organic phase is also proposed. The decay time variation as a function of temperature allows estimating the activation energy of the luminescence process of the extracted complex.

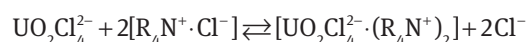
Keywords: Uranium, Solvent extraction, Luminescence, Fluorescence.

1 Introduction

To develop a hydrometallurgical process, it is necessary to have thermodynamic and kinetic data for an extraction process of a metal, typically in aqueous solution,

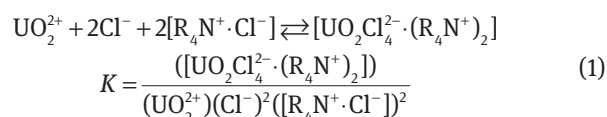
by an extracting molecule, typically in organic phase. Solvent extraction is a ubiquitous separation technique in the nuclear industry, from front- to back-end fuel cycle. The extraction of uranium(VI) by tertiary ammonium is occurring *via* an ion-exchange mechanism. This reaction has been used in several studies with Aliquat® 336 [1–3], with Cyphos IL 101 [4], or in mixture of extractant [5]. Recently, applications in microfluidic extraction were reported [6, 7].

The typical ion-exchange mechanism of $\text{UO}_2\text{Cl}_4^{2-}$ at the surface of ion-exchange resins usually involves the following reaction [1].

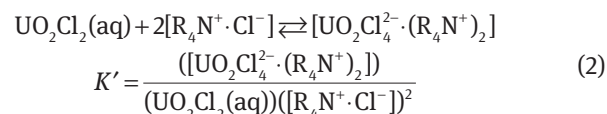


where $[]$ are denoting ion-exchanged species.

The presence of $\text{UO}_2\text{Cl}_4^{2-}$ anion during U(VI) extraction from highly concentrated HCl [8], or Cl^- in 0.25 M H_2SO_4 [9], at the surface of ion-exchange resins has been shown, but its existence has not been univocally evidenced in aqueous solution. One can nevertheless propose the equivalent mechanism,



or as proposed otherwise [10],



where $()$ are denoting activities.

The latter expression depends on the thermodynamic data of the chloro complexes of uranium(VI), whereas the former does not.

Due to its use in the nuclear industry, a large body of data is existing on the chemistry of uranium. Commonly accepted reviews of uranium thermodynamic data [11, 12] provide also a general framework to account for activity correction through the specific ion interaction theory (SIT) [11–13]. Nevertheless, the SIT is limited to moderately high ionic strength – typically 3–4 M. Knowing the high concentration of acid used in extraction processes of uranium(VI), it can be useful to compare the results

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obtained using the SIT to more widely applicable Pitzer model [14] – comparison between the application of the two models can be found in Grenthe et al. [15]. The recommended thermodynamic data only account for UO_2Cl^+ and $\text{UO}_2\text{Cl}_2(\text{aq})$ complexes [11–13]. Nevertheless, the formation UO_2Cl_3^- was proposed in more concentrated HCl solutions [16]. Up to now, no formation constant for $\text{UO}_2\text{Cl}_4^{2-}$ complex in aqueous solution has been proposed.

Usually, spectroscopic data on uranyl(VI) complexes are obtained at rather high total concentration of uranium [1, 3, 4, 10, 17–21] – typically using absorption spectroscopy. Taking advantage of Time-Resolved Laser-induced Spectroscopy (TRLS) [22, 23], one can observe these phenomena at lower total uranium concentration.

Following previous microfluidic studies [6, 7], the aim of this work is to study the extraction mechanism of uranyl from HCl solution by Aliquat® 336 in 1:99 (v:v) 1-decanol:*n*-dodecane mixture, using TRLS in batch experiments. The luminescence evolution of the extracted uranium, followed in terms of luminescence spectra and decay time, will allow: (i) estimating the symmetry of the extracted complex; (ii) determining both the stoichiometry and extraction constant of the complex through slope analysis; and (iii) varying the temperature of the luminescence acquisition to determine the activation energy of the luminescence process of the extracted complex.

2 Materials and methods

2.1 Materials

All aqueous solutions were prepared using HCl Ultrex 37 % (Sigma Aldrich). Uranyl chloride solutions were prepared from a $10,000 \text{ mg}_\text{U} \text{ kg}_\text{w}^{-1}$ SPEX solution (Jobin Yvon) diluted with $18 \text{ M}\Omega$ deionized water produced by a Milli-Q water purification system (Millipore, Bedford, MA, USA). The commercial extractant Aliquat® 336 (98 %) was purchased from Alfa Aesar, and was used as received. 1-decanol (99 %) and *n*-dodecane were supplied by Sigma Aldrich. Organic extractant solutions were prepared by dissolving weighed amounts of the desired compounds in the diluent. Aqueous and organic phases were mutually pre-saturated by contact under agitation for 3 h.

2.2 Extraction procedure

The extractions were performed using a classical batch experiment where $400 \mu\text{L}$ of an HCl solution at

concentration varying between 0.5 and 6 M – i. e. 0.505 and $6.63 \text{ mol kg}_\text{water}^{-1}$ –, containing U for a final concentration of 10^{-5} M , was agitated with an equal volume of an organic solution – 99:1 (v:v) *n*-dodecane:1-decanol – containing Aliquat® 336 at 10^{-2} M in a thermomixer apparatus under the following conditions: $T = (293 \pm 1) \text{ K}$; 1400 rpm; agitation time = 48 h. After centrifugation, the concentration of U remaining in the aqueous phase was determined by inductively coupled plasma mass spectrometry (ICP-MS) using a quadrupole ICP-MS spectrometer 7700x (Agilent Technologies). Duplicate experiments showed that the reproducibility of these measurements was within 10 %. After separation, the solutions were analysed in TRLS in 1 cm fluorescence cuvette (Hellma QS-111-10-40).

2.3 Time-resolved luminescence spectroscopy

The TRLS set-up has already been fully described elsewhere [24]. Taking advantage of the time-resolution, the luminescence spectra were obtained at $\lambda_\text{exc} = 450 \text{ nm}$, at a delay $D = 100 \text{ ns}$ after the laser flash, during a gate width $W = 2\text{--}3 \mu\text{s}$, and during 1000 accumulation. The fittings of the decay times and decomposition of the spectra were done using the Solver from Microsoft Excel as already explained elsewhere [24, 25], and the fitting uncertainties and correlation matrices were calculated using the SolverAid macro [26].

3 Results and discussions

3.1 Uranium luminescence in organic phase as a function of HCl concentration

3.1.1 Spectral evolution

The evolution of the uranium time-resolved luminescence spectra between 0.5 and 6 M are shown in Figure 1a. The luminescence intensity of uranium increases with the extraction in the organic phase. As awaited from the very high quenching of uranyl(VI) luminescence from chloride ions [27, 28], no luminescence signal can be detected in the corresponding HCl solutions. For the HCl concentrations lower than 2 M, no exploitable signal was obtained in the organic phase. For the HCl concentrations higher than 2 M, the signal increases in the organic phase and the shape of the spectra are mostly the same from 2 to 6 M as shown on the spectra normalized to their total areas

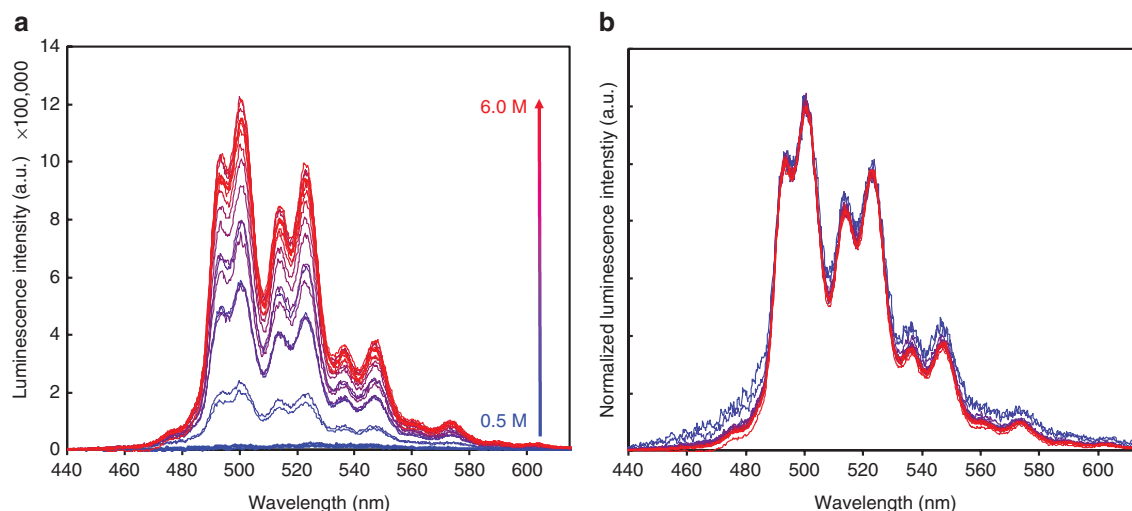


Figure 1: Comparisons of luminescence spectra of uranyl(VI) extracted from HCl by Aliquat® 336 in 99:1 (v:v) *n*-dodecane:1-decanol. Luminescence spectra of uranyl(VI) extracted from HCl solutions by Aliquat® 336 in 99:1 (v:v) *n*-dodecane:1-decanol: (a) spectra for HCl concentrations from 0.5 to 6 M, $\lambda_{\text{exc}} = 450$ nm, $D = 100$ ns, $W = 3$ μ s, 1000 accumulations; and (b) normalized spectra to their total areas from 2 to 6 M.

in Figure 1b. The spectra are showing a typical pattern already observed for extraction from HCl of uranyl in organic solvent [10] and in ionic liquid [17, 18] – this can be clearly seen in Fig. S1 of the Supplementary Information (SI), which is showing the comparison of these results and other spectra from the literature [10, 17, 18]. This apparent splitting of the luminescence bands has been interpreted as a consequence of the removing of the twofold degeneracy of the cylindrical symmetry of UO_2^{2+} ion during complexation [10].

3.1.2 Decomposition of the luminescence spectrum at HCl 6 M.

In order to propose more precise positions of the peaks wavelengths, and of the $\Delta\bar{\nu}$ values, the decomposition in Gaussian peaks of the spectra obtained at HCl 6 M is shown in Figure 2, following:

$$F_i(\lambda) = F_{\text{max},i} \exp\left(-\frac{4 \ln(2)(\lambda - \lambda_{0,i})^2}{w_i}\right) \quad (3)$$

where $F_i(\lambda)$ is the luminescence intensity at a particular wavelength, $F_{\text{max},i}$ is the luminescence at the maximum intensity, $\lambda_{0,i}$ is the centre wavelength, and w_i is the half-width

Due to the resolution of the apparatus – particularly the use of the 300 mm^{-1} grating – only relatively wide components are obtained. However, the fitting parameters

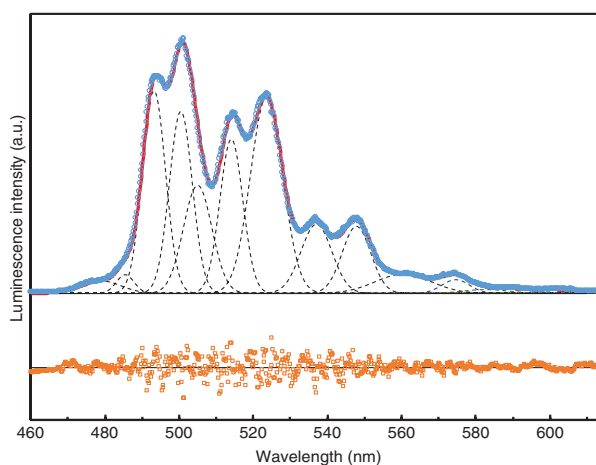


Figure 2: Decomposition in Gaussian components (dashed lines) of the luminescence spectrum (blue circles), using 300 mm^{-1} grating, of uranyl(VI) extracted from HCl 6 M by Aliquat® 336 in 99:1 (v:v) *n*-dodecane:1-decanol (upper part), and residuals of the fit (lower part, squares) between the experimental spectrum and sum of components (red plain line): $\lambda_{\text{exc}} = 450$ nm, $D = 100$ ns, $W = 3$ μ s, 1000 accumulations.

obtained in Table 1 can be discussed in relation with previous identification of transitions – correlation matrix in Table S1 of the SI. Görller-Walrand et al. [10] proposed 20 peaks between ca. 485 and 610 nm and tentatively identified the transition in $D_{\infty h}$ and D_{4h} point symmetry groups. These transitions are definitely combined in the different components that we are proposing. Transition F_2 can be affected to D_{4h} transition $E_g - v_b$, F_4 to $E_g - v_b - v_s$, F_6 to $E_g - v_b - 2v_s$, and F_8 to $E_g - v_b - 3v_s$. All other components are

Table 1: Fitting parameters of the decomposition of the spectra in Figure 2.

Fitting parameter		Wave number (cm ⁻¹)	Identification from ref. [10]
$F_{\max,0}$	$(4.90 \pm 0.19) 10^5$		
$\lambda_{0,0}$	$(479.04 \pm 0.60) \text{ nm}$	$\bar{\nu}_0$	$(20875.1 \pm 26.1) \text{ cm}^{-1}$
w_0	12.53 ± 0.86		
$F_{\max,1}$	$(7.34 \pm 0.73) 10^5$		
$\lambda_{0,1}$	$(485.45 \pm 0.16) \text{ nm}$	$\bar{\nu}_1$	$(20595.6 \pm 6.8) \text{ cm}^{-1}$
w_1	5.62 ± 0.40		
$F_{\max,2}$	$(7.99 \pm 0.13) 10^6$		
$\lambda_{\max,2}$	$(493.22 \pm 0.09) \text{ nm}$	$\bar{\nu}_2$	$(20274.9 \pm 3.5) \text{ cm}^{-1}$
w_2	7.30 ± 0.16		$E_g - v_b$
$F_{\max,3}$	$(7.17 \pm 5.70) 10^6$		
$\lambda_{0,3}$	$(500.46 \pm 0.68) \text{ nm}$	$\bar{\nu}_3$	$E_g - v_{10} - v_{11}$ $E_g - v_b - v_{11}$
w_3	7.29 ± 0.87		
$F_{\max,4}$	$(4.26 \pm 3.39) 10^6$		
$\lambda_{0,4}$	$(504.99 \pm 3.88) \text{ nm}$	$\bar{\nu}_4$	$(19802.4 \pm 152.0) \text{ cm}^{-1}$
w_4	9.05 ± 4.33		$E_g - v_s$
$F_{\max,5}$	$(6.08 \pm 0.31) 10^6$		
$\lambda_{0,5}$	$(514.08 \pm 0.14) \text{ nm}$	$\bar{\nu}_5$	$(19452.2 \pm 5.2) \text{ cm}^{-1}$
w_5	7.31 ± 0.19		$E_g - v_b - v_s$
$F_{\max,6}$	$(7.74 \pm 0.01) 10^6$		
$\lambda_{0,6}$	$(523.58 \pm 0.03) \text{ nm}$	$\bar{\nu}_6$	$(19099.3 \pm 1.0) \text{ cm}^{-1}$
w_6	10.22 ± 0.09		$E_g - v_{10} - v_{11} - v_s$ $E_g - v_b - v_{11} - v_s$ $E_g - 2v_s$ $E_g - v_b - 2v_s$
$F_{\max,7}$	$(2.72 \pm 0.01) 10^6$		
$\lambda_{0,7}$	$(537.02 \pm 0.04) \text{ nm}$	$\bar{\nu}_7$	$(18621.3 \pm 1.5) \text{ cm}^{-1}$
w_7	9.85 ± 0.18		
$F_{\max,8}$	$(2.64 \pm 0.07) 10^6$		
$\lambda_{0,8}$	$(547.82 \pm 0.05) \text{ nm}$	$\bar{\nu}_8$	$(18254.2 \pm 1.6) \text{ cm}^{-1}$
w_8	9.06 ± 0.18		$E_g - v_{10} - v_{11} - 2v_s$ $E_g - v_b - v_{11} - 2v_s$ $E_g - 3v_s$ $E_g - v_b - 3v_s$
$F_{\max,9}$	$(7.55 \pm 0.08) 10^5$		
$\lambda_{0,9}$	$(560.45 \pm 0.35) \text{ nm}$	$\bar{\nu}_9$	$(17842.8 \pm 11.1) \text{ cm}^{-1}$
w_9	17.85 ± 1.97		
$F_{\max,10}$	$(5.38 \pm 1.74) 10^5$		
$\lambda_{0,10}$	$(574.62 \pm 0.32) \text{ nm}$	$\bar{\nu}_{10}$	$(17402.8 \pm 9.6) \text{ cm}^{-1}$
w_{10}	8.74 ± 0.98		$E_g - v_{10} - v_{11} - 3v_s; E_g - v_b - v_{11} - 3v_s$
$F_{\max,11}$	$(1.48 \pm 1.43) 10^5$		
$\lambda_{0,11}$	$(582.73 \pm 5.03) \text{ nm}$	$\bar{\nu}_{11}$	$(17160.6 \pm 148.0) \text{ cm}^{-1}$
w_{11}	14.63 ± 12.27		$E_g - 4v_{11}$
$F_{\max,12}$	$(1.44 \pm 0.33) 10^5$		
$\lambda_{0,12}$	$(598.39 \pm 7.41) \text{ nm}$	$\bar{\nu}_{12}$	$(16711.5 \pm 206.9) \text{ cm}^{-1}$
w_{12}	26.98 ± 11.17		

the results of convolutions of different transitions – see tentative attribution in Table 1.

The fitting parameters, including wavelengths of the components – both in λ (nm) and in $\bar{\nu}$ (cm⁻¹) –, allow estimating the maxima of the different peaks in Table 1 and the $\Delta\bar{\nu}$ values of the progressions.

3.2 Estimation of the extraction stoichiometry relative to chloride in hydrochloric solution

The evolution of the uranyl(VI) luminescence in extraction solution as a function of HCl molality, calculated from Novotny and Sohnel [29], is given in Figure 3. It is

interesting to compare this evolution with the calculated theoretical speciation of uranyl(VI) in HCl in Fig. S2 of the SI in the conditions of Figure 3 – according to the thermodynamic data and SIT parameters from Guillaumont et al. [12]. It is noteworthy that no complex with higher stoichiometry than $\text{UO}_2\text{Cl}_2(\text{aq})$ in aqueous solution is selected in the evaluation of uranium thermodynamic data – UO_2Cl_3^- was proposed in concentrated HCl [16], and $\text{UO}_2\text{Cl}_4^{2-}$ was observed in organic solvent [10]. Considering the strong luminescence quenching of uranyl(VI) by Cl^- [28], these species cannot be – and have not been – observed in TRLS under our experimental conditions.

As a comparison, Fig. S3 of the SI shows the difference in the activity coefficient of Cl^- calculated both using the SIT [12] – using $\epsilon(\text{H}^+, \text{Cl}^-) = 0.12 \text{ kg}_w \text{ mol}^{-1}$ to

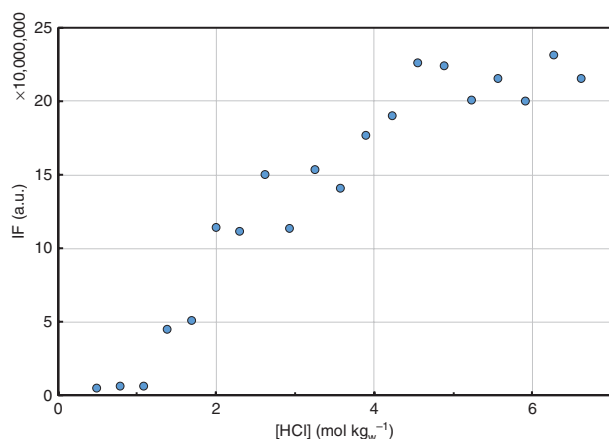


Figure 3: Evolution of the luminescence of uranyl(VI) extracted from HCl by Aliquat® 336 in 99:1 (v:v) *n*-dodecane:1-decanol vs. molality of HCl calculated from the molarity [29].

calculate $\log_{10}\gamma_{\text{Cl}^-}$ – and Pitzer's model [14] – $\beta_{\text{HCl}}^{(0)} = 0.1775$, $\beta_{\text{HCl}}^{(1)} = 0.2945$, and $C_{\text{HCl}}^{\Phi} = 0.0008$, to calculate $\log_{10}\gamma_{\text{HCl}}^{\mp}$. The deviation for ionic strengths higher than 4 mol kg⁻¹ is clearly shown. It must be noted that additional parameters should be used for concentration higher than 6 mol kg⁻¹ using Pitzer model [14], which is not the case here.

The stoichiometry of the extraction process regarding Cl⁻ is verified in Figure 4. In both cases, the extraction of two Cl⁻ from HCl during the process is confirmed. One can also note that the increase of uranyl(VI) luminescence is in agreement with the progressive increase in the theoretical $\text{UO}_2\text{Cl}_2(\text{aq})$ proportion in HCl. One can note that the positive slope indicates that Cl⁻ is extracted to, and not released from, the organic phase. Then the mechanism relative to uranyl extraction leads to equilibrium (1).

Other expressions could be proposed, e.g. considering UO_2Cl_3^- or $\text{UO}_2\text{Cl}_4^{2-}$. However, thermodynamic constants are scarce and can be questioned. Soderholm et al. [16] proposed constants for $\text{UO}_2\text{Cl}_n^{2-n}$ with $n=\{1;2;3\}$ in 5.3 mol kg⁻¹ HClO_4/HCl media. The variation of media condition would require a reinterpretation of the data within the framework of SIT for an application to our conditions, which is outside the scope of this study.

If one assumes that the proposed mechanism involves 2 tertiary amines from the organic phase $[\text{R}_4\text{N}^+\text{Cl}^-]$, then the exchange could be modelled as the logarithmic expression of equation (1).

$$\log_{10} \frac{([\text{UO}_2\text{Cl}_4^{2-} \cdot (\text{R}_4\text{N}^+)_2])}{(\text{UO}_2^{2+})} = \log_{10} D = \log_{10} K + 2\log_{10} ([\text{R}_4\text{N}^+, \text{Cl}^-]) + 2\log_{10} (\text{Cl}^-) \quad (4)$$

$$\log_{10} D = b + 2\log_{10} (\text{Cl}^-)$$

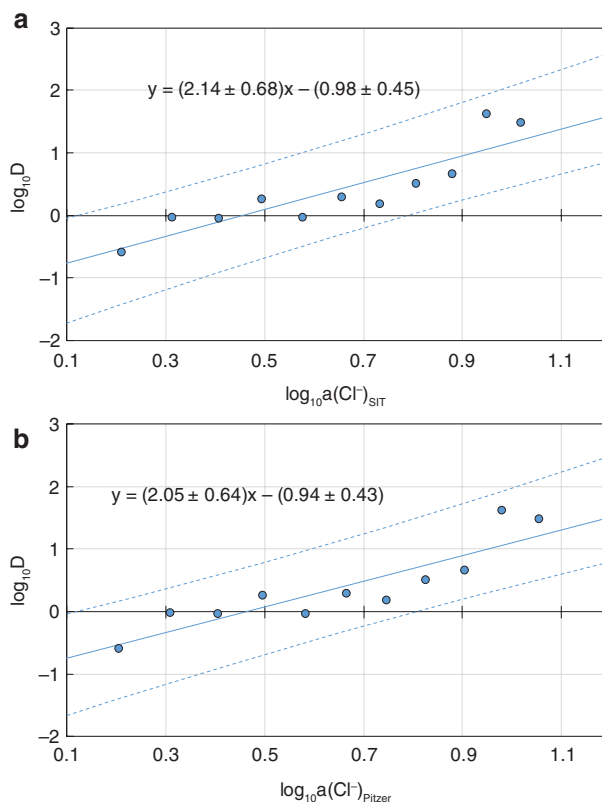


Figure 4: Stoichiometry and conditional constant determination of U(VI) extraction from HCl in *n*-dodecane by Aliquat® 336. Slope analysis of the uranium distribution coefficient vs. the activity of Cl⁻ in hydrochloric solutions, according to (a) the SIT [12], and (b) the Pitzer model [14].

Here D is defined only referring to UO_2^{2+} in order to have a direct access the stoichiometry relative to Cl⁻ in hydrochloric solution.

The free concentration of $[\text{R}_4\text{N}^+ \cdot \text{Cl}^-]$ in the organic phase is obtained through the mass balance on Aliquat® 336, which is in high excess compared to the total concentration of uranium.

$$([\text{R}_4\text{N}^+ \cdot \text{Cl}^-]) = C_{\text{Aliquat}} - ([\text{UO}_2\text{Cl}_4^{2-} \cdot (\text{R}_4\text{N}^+)_2]) \cong C_{\text{Aliquat}} \quad (5)$$

Knowing that Aliquat® 336 is in high excess, $\log_{10} K$ can be estimated as follows.

$$\log_{10} K = b - 2\log_{10} ([\text{R}_4\text{N}^+ \cdot \text{Cl}^-]) \cong b - 2\log_{10} C_{\text{Aliquat}} \quad (6)$$

From the obtained intercepts b , values of $\log_{10} K_{\text{SIT}} = 3.02 \pm 0.45$ ($\Delta_r G = -17.24 \pm 2.57$ kJ mol⁻¹) and $\log_{10} K_{\text{Pitzer}} = 3.07 \pm 0.43$ ($\Delta_r G = -17.47 \pm 2.45$ kJ mol⁻¹) can be obtained – note that the $\Delta_r G$ are not referring to the standard state at infinite dilution. These values cannot be considered significantly different.

3.3 Estimation of the activation energy of the luminescence process

The fact that the luminescence of $[\text{UO}_2\text{Cl}_4^{2-} \cdot (\text{R}_4\text{N}^+)_2]$ in the organic phase can be observed is indicative of lesser quenching compared to the one that is occurring in hydrochloric solution, and that the luminescence decay time (τ) can be determined. The luminescence decay time of $[\text{UO}_2\text{Cl}_4^{2-} \cdot (\text{R}_4\text{N}^+)_2]$ extracted from HCl 5.5 M by Aliquat® 336 in 99:1 (v:v) *n*-dodecane:1-decanol was acquired vs. temperature between 15 and 35 °C – see Fig. S4 and Table S2 of the SI. Here, the gate width is $W = 3 \mu\text{s}$ – leaving the delay and accumulation unchanged compared to § 3.1. All determination are giving mono-exponential decays. The Arrhenius plot of the radiative constants, which is the reciprocal of the luminescence decay time ($k_r = 1/\tau$), is shown in Figure 5 yielding an activation energy of the luminescence process of the extracted complex of $E_a = (18.8 \pm 0.2) \text{ kJ mol}^{-1}$. This can be compared to the higher values *ca.* 40–50 kJ mol^{-1} in 0.01 to HClO_4 1 M [27].

Hence, it appears that if the extracted luminescence of $[\text{UO}_2\text{Cl}_4^{2-} \cdot (\text{R}_4\text{N}^+)_2]$ in 99:1 *n*-dodecane:1-decanol is less intense than UO_2^{2+} in HClO_4 , the influence of temperature on the luminescence of the extracted species is less important in organic solution. It is not possible to propose an interpretation of this phenomenon with these experiments only. One has to determine the amount of water, which is

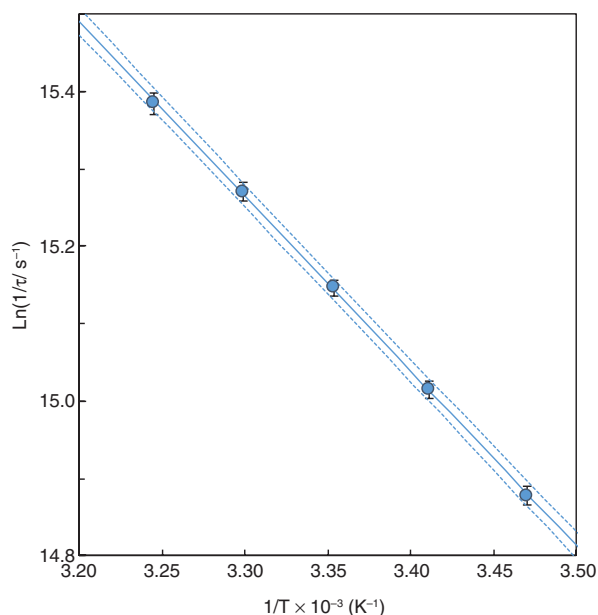


Figure 5: Arrhenius plot of the luminescence decay of $[\text{UO}_2\text{Cl}_4^{2-} \cdot (\text{R}_4\text{N}^+)_2]$ species extracted from HCl 5.5 M by Aliquat® 336 in 99:1 (v:v) *n*-dodecane:1-decanol; error bars are 2σ of the fitting uncertainty; dotted lines are the 95 % confidence intervals of the regression.

extracted with the complex in organic solution. The possibility of the quenching of uranium(VI) could then be dependent on the amount of water, and the Brownian motion within the complex.

4 Conclusions

During extraction from HCl aqueous solutions by Aliquat® 336 in 99:1 (v:v) *n*-dodecane:1-decanol mixture, uranyl is extracted as $[\text{UO}_2\text{Cl}_4^{2-} \cdot (\text{R}_4\text{N}^+)_2]$, from its free ion form UO_2^{2+} associated with two Cl^- ions from HCl and two extractant molecules $[\text{R}_4\text{N}^+, \text{Cl}^-]$ to assure the electroneutrality. The evolution of the luminescence spectra is confirming that these species seems the only one that is forming during the extraction process from HCl 2 to 6 M. The extraction constants are not significantly different either using the SIT or Pitzer model to account for activity correction of chloride ions. These values allow simulating the extraction process. The influence of temperature on the luminescence process of $[\text{UO}_2\text{Cl}_4^{2-} \cdot (\text{R}_4\text{N}^+)_2]$ seems less intense than for UO_2^{2+} in HClO_4 but allows observing the luminescence even in the presence of highly quenching Cl^- .

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