

MODELING OF THE SOLVENT EXTRACTION EQUILIBRIUM OF URANIUM (VI) SULFATE WITH ALAMINE 336

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Abstract - The present study investigated the solvent extraction of uranium from sulfate acid solutions using Alamine 336 as an extractant dissolved in commercial kerosene Exxsol D-100 and 5% v/v of tridecanol as a modifying agent at room temperature (25±2) °C and an aqueous/organic volumetric ratio of unity. Experiments were carried out at typical concentration levels like those used at the uranium plant of INB (*Indústrias Nucleares do Brasil*), Brazil. Data fitting using the slope analysis method revealed that uranium is extracted by Alamine 336 as UO_2SO_4 and $\text{UO}_2(\text{SO}_4)_2^{2-}$ species, forming $(\text{R}_3\text{NH}^+)_2\text{UO}_2(\text{SO}_4)_2^{2-}$ in the organic phase; the extraction of the species $\text{UO}_2(\text{SO}_4)_3^{4-}$ seems improbable for the operating conditions investigated. The extraction of uranium is significantly reduced when the concentrations of sulfate and chloride ions in the aqueous phase are increased.

Keywords: Solvent extraction; Uranium sulfate; Alamine 336; Equilibrium.

INTRODUCTION

The nuclear energy industry was the major user of the solvent extraction technique for metals separation before base metals recovery was implemented in the late 1960s, when the first large copper plants came into operation. A number of extractants have been used for uranium extraction from acid solutions. Such extractants are classified into four main types (Kumar *et al.*, 2011): (i) nitrogen-based extractants, that cover predominantly the amide and amine functional group containing extractants, such as Alamine 336 (N,N-dioctyl-octan-1-amine) and Adogen 363 (tri-octyl methylammonium chloride); (ii) phosphorous-based

extractants, including tri-butyl-phosphate (TBP), di(2-ethylhexyl) phosphoric acid (D2EHPA), 2-ethylhexyl mono-2-ethylhexyl phosphonic acid (PC88A), tri-n-octyl-phosphine oxide (TOPO or Cyanex 923), and bis(2,4,4-trimethyl pentyl) phosphinic acid (Cyanex 272); (iii) sulfur-based extractants, mainly sulfoxides and other sulfur-containing extractants; and (iv) other extractants. The performance of a number of alkyl-diammonium extractants in the extraction of uranium from sulfuric, nitric, and hydrochloric media was compared with that of Aliquat 336 (tri-octyl-methylammonium chloride) and Alamine 336 in an attempt to simulate the conditions employed in the mining industry (du Preez *et al.*, 1985).

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Tertiary amines are the most common extractant types used to treat industrial solutions resulting from the sulfuric acid leaching of uranium-bearing ores (Yakubu and Dudeney, 1987; Lakshmi *et al.*, 2004). The selectivity order of amines for some ions is (MacKenzie, 1997): $\text{UO}_2(\text{SO}_4)_3^{4-} > \text{NO}_3^- > \text{Cl}^- > \text{HSO}_4^- > \text{Fe}(\text{SO}_4)_2^-$. The extraction of a neutral uranium (VI) sulfate species in an adduct type of mechanism is also plausible (Ritcey, 2006). The degree to which either the extraction of an anionic or neutral uranium species is involved would seem to depend on the uranium species present, which in turn depends on the sulfate concentration and pH of the aqueous phase. The major impurity that is preferentially extracted from uranium by Alamine 336 is molybdenum. The synergistic extraction of uranium using tertiary amines can be accomplished by adding TOPO to the solvent phase to enhance kinetics; however, stripping is difficult (IAEA, 1993).

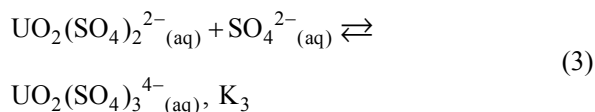
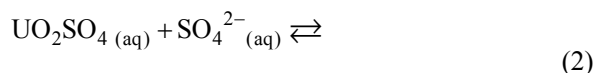
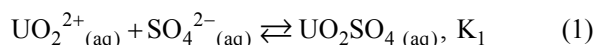
In Brazil, uranium is solely produced by INB (*Indústrias Nucleares do Brasil S.A.*), the state-owned company responsible for uranium extraction and its transformation into nuclear energy. The current production consists of 400 tons of uranium per year. The purification of the sulfate leach liquors is carried out by solvent extraction, using Alamine 336 as an extractant. Uranium is stripped from the extract stream by contacting it with a sodium chloride (NaCl) solution. The water used in this process is fully recycled/recirculated within the plant after treatment, given that this industrial plant is located in the semi-arid regions of Northeast Brazil. As water treatment does not include a chloride removal step, the increase in chloride concentrations in the aqueous solutions has affected uranium purification efficiency through solvent extraction with Alamine 336 (Gomiero *et al.*, 2009). Stripping studies using ammonium sulfate ($(\text{NH}_4)_2\text{SO}_4$) revealed a viable alternative stripping agent (Morais and Gomiero, 2005), so this reagent could replace NaCl in the stripping step, avoiding the presence of chloride ions in the aqueous streams of the industrial plant.

In this context, the present study aimed to evaluate the solvent extraction equilibrium of uranium from sulfate solutions using Alamine 336 under typical operating conditions of the INB industrial process and at room temperature. The study has two main purposes: (i) develop a thermodynamic model and validate it to assess the sulfate aqueous solutions without chloride ions in concentrated systems, and (ii) evaluate experimentally the effect of the presence of chloride ions on uranium extraction from sulfate

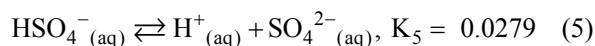
solutions. The model was developed in the absence of chloride aiming to identify the uranium (VI) sulfate species that is (are) extracted with Alamine 336 in the normal operating conditions of the industrial plant of INB. However, due to the scarcity of water, that results in an increase of chloride content in the recirculated aqueous streams of the industrial plant, experiments were also done to quantify the deleterious effect of chloride on the uranium extraction process.

DEVELOPMENT OF THE THERMODYNAMIC MODEL

Uranium (VI) dissociates in sulfate media according to the following reactions (NEA, 2004; Vercouter *et al.*, 2008; Vopálka *et al.*, 2010):



The theoretical distribution of uranium (VI) species within the studied operating conditions (concentration range limited by the vertical gray lines) is shown in Figure 1. Calculations were done using stability constants (K_1 to K_3) from distinct authors portrayed in Table 1. The concentrations of HSO_4^- and SO_4^{2-} ions in the aqueous phase were determined assuming dissociation of sulfuric acid according to the following reactions (Free, 2013):



The predictions using the stability constants given by the NEA database (NEA, 2004) and Vopálka *et al.* (2010) are quite similar for a broad operating range ($[\text{SO}_4^{2-}] \leq 1.0 \text{ M}$); after this limit, however, deviations are verified in the speciation of the anionic species because the stability constants K_3 differ sig-

nificantly. On the other hand, a huge discrepancy for any concentration level is observed by comparing the predictions for all aqueous species by using the stability constants given by Vercouter *et al.* (2008); according to these authors, the fluorescence features of the sulfate complexes were observed to depend on the ionic conditions and changes in the coordination mode (mono- and bidentate) of the sulfate ligands may explain such observations.

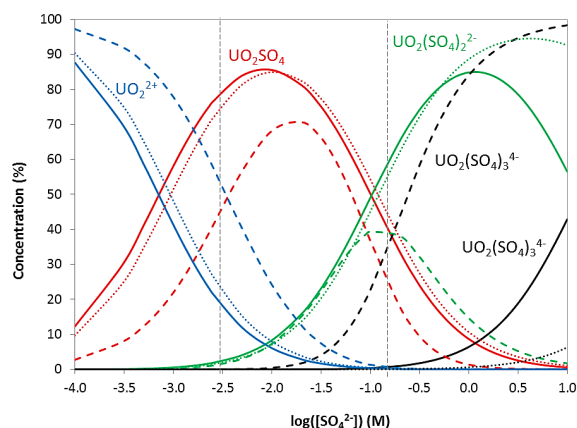


Figure 1: Speciation diagram of uranium (VI) sulfate: NEA (2004) – continuous curves; Vopálka *et al.* (2010) – dotted curves; Vercouter *et al.* (2008) – dashed curves ($[U]_{\text{total}} = 0.01 \text{ M}$; $T = 25 \text{ }^\circ\text{C}$; stability constants listed in Table 1).

Table 1: Stability constants of uranium (VI) sulfate in the aqueous phase ($I = 0$; $T = 25 \text{ }^\circ\text{C}$).

	NEA (2004)	Vopálka <i>et al.</i> (2010)	Vercouter <i>et al.</i> (2008)
$\log(K_1)$	3.15 ± 0.02	3.03 ± 0.31	2.45 ± 0.05
$\log(K_2)$	0.99 ± 0.07	0.92 ± 0.25	1.03 ± 0.04
$\log(K_3)$	-1.12 ± 0.38	-2.17 ± 0.25	0.76 ± 0.20

According to the theoretical distribution shown in Figure 1, the predominance of species UO_2SO_4 and $\text{UO}_2(\text{SO}_4)_2^{2-}$ is expected. The occurrence of UO_2^{2+} and $\text{UO}_2(\text{SO}_4)_3^{4-}$ is significant only if calculations are done using the stability constants given by Vercouter *et al.* (2008). Therefore, neutral and both anionic species may preferentially compete to be extracted by Alamine 336, given that it is a water insoluble extractant that is capable of forming oil soluble salts of anionic species at a low pH. As shown in Figure 2, species HSO_4^- and SO_4^{2-} predominate in the aqueous phase at $0 \leq \text{pH} \leq 0.54$, so these species may compete to protonate the molecules of Alamine 336 (Shmidt, 1971).

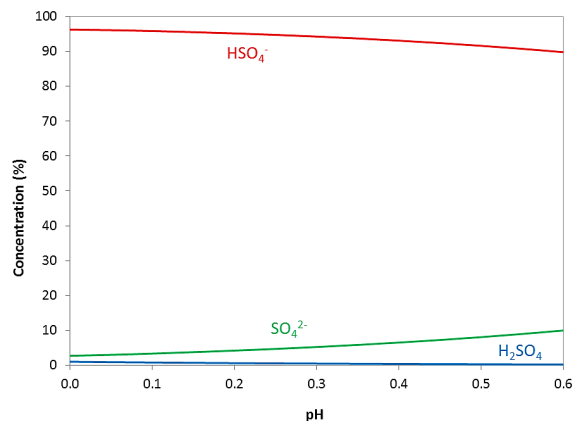
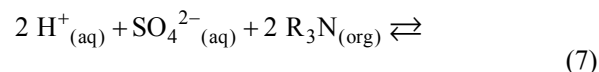
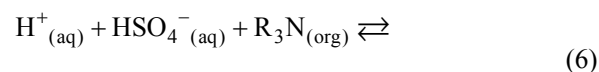


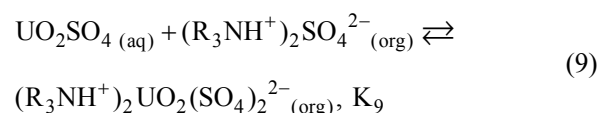
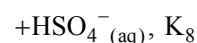
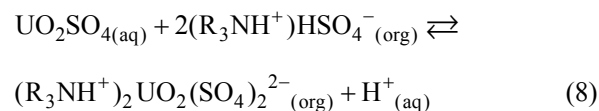
Figure 2: Speciation diagram of sulfuric acid ($[S]_{\text{total}} = 0.5 \text{ M}$; stability constants given by Eqs. (4) and (5); $T = 25 \text{ }^\circ\text{C}$).

Based on such assumptions, the following reactions were considered to occur in the solvent extraction of uranium (VI) with Alamine 336:

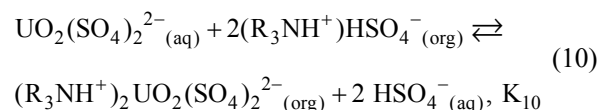
- Protonation of Alamine 336 with dissociated sulfuric acid species HSO_4^- and SO_4^{2-}

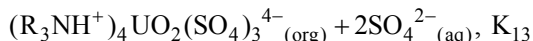
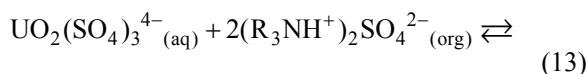
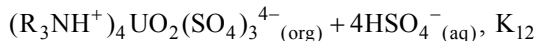
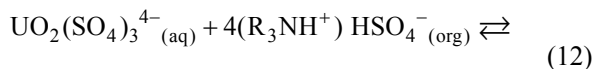
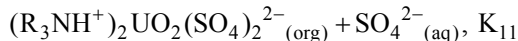
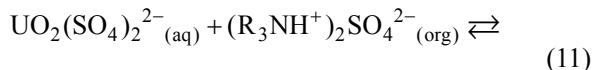


- Reactions between the protonated amine species with neutral species of uranium (VI) sulfate



- Reactions between the protonated amine species with anionic species of uranium (VI) sulfate





According to the reaction scheme considered, the distribution coefficient of uranium (D_U) is determined by the following equation:

$$D_U = \frac{[(\text{R}_3\text{NH}^+)_2\text{UO}_2(\text{SO}_4)_2^{2-}] + [(\text{R}_3\text{NH}^+)_4\text{UO}_2(\text{SO}_4)_3^{4-}]}{[\text{UO}_2^{2+}] + [\text{UO}_2\text{SO}_4] + [\text{UO}_2(\text{SO}_4)_2^{2-}] + [\text{UO}_2(\text{SO}_4)_3^{4-}]} \quad (14)$$

Equations (8) and (10), as well as Eqs. (9) and (11), are not independent and can be derived by combining them with Eq. (2). Substituting Eqs. (1)-(13) in Eq. (14), the following expression is derived:

$$D_U = \frac{K_a[\text{R}_3\text{N}]^2[\text{H}^+]^2 + K_b[\text{R}_3\text{N}]^4[\text{H}^+]^4[\text{SO}_4^{2-}]}{\frac{1}{K_1K_2[\text{SO}_4^{2-}]^2} + \frac{1}{K_2[\text{SO}_4^{2-}]} + 1 + K_3[\text{SO}_4^{2-}]} \quad (15)$$

where (i) $K_a = K_6^2K_8/(K_2K_5) = K_6^2K_{10}$ if equilibrium is governed by Eq. (8) or Eq. (10), (ii) $K_a = K_7K_9/K_2 = K_7K_{11}$ if equilibrium is governed by Eq. (9) or Eq. (11), (iii) $K_b = K_3K_6^4K_{12}$ if equilibrium is governed by Eq. (12), and (iv) $K_b = K_3K_7^2K_{13}$ if equilibrium is governed by Eq. (13). Equation (15) depends on the concentration of the extractant, protons, and sulfate ions in the equilibrium and must be fitted to experimental data. Stability constants K_1 to K_3 are given by the NEA database (NEA, 2004) values shown in Table 1, while K_a and K_b are parameters to be determined by data fitting. No activity coefficient was considered and the model does not presume the aggregation of amine salts in the organic phase.

The concentration of free extractant in the organic phase is proportional to the mass balance of total uranium extracted from the aqueous phase given by:

$$[\text{R}_3\text{N}] = [\text{R}_3\text{N}]_{\text{initial}} - m([\text{U}]_{\text{initial}} - [\text{U}]) \quad (16)$$

where $m = 1, 2$ or 4 corresponds to the stoichiometric coefficient of extractant in Eqs. (8) to (13).

EXPERIMENTAL D_U MEASUREMENTS UNDER INDUSTRIAL CONDITIONS

Reagents

The aqueous solutions were obtained by dissolving an uranium concentrate (a mixture of $\text{NH}_4\text{U}_2\text{O}_7$ and $\text{Na}_2\text{U}_2\text{O}_7$) supplied by INB (82.4%w/w of U_3O_8) in sulfuric acid (Vetec, purity of 98%w/w) dissolved in deionized water. The organic solutions were prepared by dissolving Alamine 336 (N,N-dioctyl-octan-1-amine, Cognis Brazil S.A., purity of 95-100%, used without further purification) in kerosene Exxsol D-100 (Exxon Chemicals, 100% aliphatic) and 5% v/v of tridecanol (Cognis Brazil S.A., commercial grade) as a modifier agent. The concentration of the modifier was determined using a titration method (Ritcey, 2006). All other chemicals used in the experiments were of analytical grade.

Extraction Conditions

The batch solvent extraction experiments were carried out by bringing equal volumes of aqueous and organic solutions (30 mL each) into contact in a glass reactor (A/O volumetric ratio of unity), at room temperature (25 ± 2) °C and $0 \leq \text{pH} \leq 0.54$. Both phases were combined for 5 minutes by mechanical stirring (180 rpm) using a glass marine-type impeller. After equilibration, phase separation was carried out using a separating funnel.

In the tests without chloride ions in the aqueous phase, the initial concentrations of uranium and sulfate ions in the aqueous phase varied respectively from 2×10^{-3} to 9×10^{-3} M (concentration levels $[\text{U}] = 0.46, 1.0, 1.6$ and 2.1 g.L^{-1} were used), and from 0.25 to 1.00 M (concentration levels $[\text{SO}_4^{2-}] = 23, 46, 68$ and 95 g.L^{-1} were used). In the tests with chloride ions in the aqueous phase, the initial concentration of uranium in the aqueous phase was kept constant at 9×10^{-3} M ($[\text{U}] = 2.1 \text{ g.L}^{-1}$), while those of sulfate and chloride ions varied from 0.25 to 1.00 M (concentration levels $[\text{SO}_4^{2-}] = 23, 46, 68$ and 95 g.L^{-1} were used), and from 0.03 to 0.20 M (concentration levels $[\text{Cl}^-] = 1, 3, 5$ and 7 g.L^{-1} were used), respectively. The following initial concentrations of Alamine 336 in the organic phase were used: 0.05, 0.10, 0.15 and 0.20 M. Such concentration levels in both phases are similar to those verified at the INB uranium plant in the city of Caetité, Brazil.

Analytical Methods

The total concentration of uranium in the aqueous phase was determined using the method of retarded neutrons (IPR R-1 Triga Mark research reactor of CDTN, accuracy 95%). The uranium concentration in the organic phase was calculated by mass balance difference. Analysis of total sulfate species in the aqueous phase was carried out by a gravimetric method (Weast and Astle, 1983), while chloride ion concentrations were measured using an ion selective electrode (Orion). The pH of the aqueous phase was measured before and after equilibration using a pH meter (Digimed, model DM-20). No third phase formation could be observed.

RESULTS AND DISCUSSION

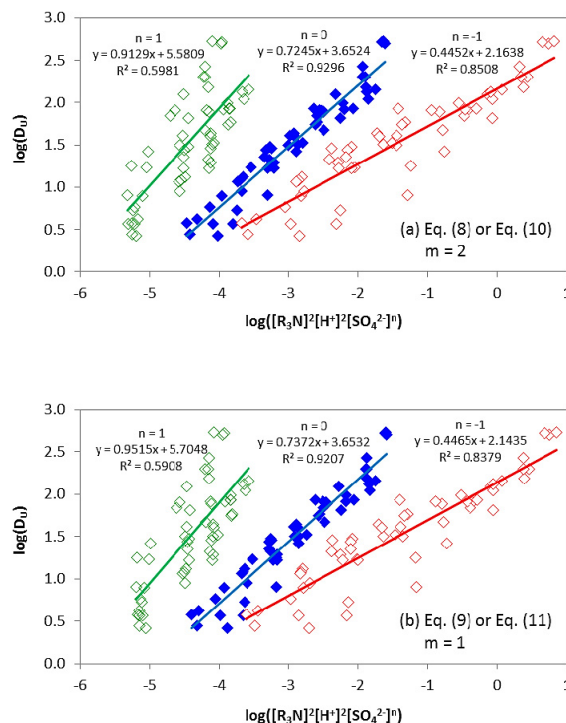
Data Fitting Results

In an attempt to obtain the unknown equilibrium constants K_a and K_b , experimental data were fitted to Eq. (15), using the Statistica software; however, no successful fitting was obtained. In fact, different results were obtained according to the optimization method used (Quasi-Newton, Hooke-Jeeves, Rosenbrock, and Simplex methods were tested) as well as to the initial guess value, thus indicating the existence of correlated constants in the proposed model.

Hence, to identify the predominant species involved in the extraction of uranium using Alamine 336, Eq. (15) was then fitted in parts, i.e., it was assumed that equilibrium occurs with only one species in the organic phase and only one species in the aqueous phase. In this manner, 16 distinct equations can be derived from Eqs. (15) and (16). Taking the logarithms of those equations, fitting was carried out by plotting $\log(D_U)$ data versus $\log([R_3N]^2[H^+]^2[SO_4^{2-}]^n)$ if species $(R_3NH^+)_2UO_2(SO_4)_2^{2-}$ is predominant in the organic phase according to (i) Eq. (8) or Eq. (10) ($m = 2$), or (ii) Eq. (9) or Eq. (11) ($m = 1$), or as $\log(D_U)$ versus $\log([R_3N]^4[H^+]^4[SO_4^{2-}]^{n+2})$ if species $(R_3NH^+)_4UO_2(SO_4)_3^{4-}$ is predominant in the organic phase according to (iii) Eq. (12) ($m = 4$), or (iv) Eq. (13) ($m = 2$). In those fittings, $n = 2$ if equilibrium occurs with species UO_2^{2+} in the aqueous phase, $n = 1$ if it occurs with UO_2SO_4 species, $n = 0$ if it occurs with $UO_2(SO_4)_2^{2-}$ species, or $n = -1$ if the $UO_2(SO_4)_3^{4-}$ species predominates in the aqueous phase.

Fitting results are shown in Figure 3, which illustrates that equilibrium may occur predominantly

between $(R_3NH^+)_2UO_2(SO_4)_2^{2-}$ and aqueous species $UO_2(SO_4)_2^{2-}$ given that, in these cases, only a straight line with an angular coefficient relatively near unity and satisfactory R^2 coefficient was obtained (see data fitting in Figures 3(a)-3(b)). It was found that the extraction of uranium (VI) sulfate with Alamine 336 is satisfactorily described by Eq. (8) or Eq. (10), as well as by Eqs. (9) or (11). However, in both cases, a better fitting is obtained when aqueous species UO_2SO_4 and $UO_2(SO_4)_2^{2-}$ are considered, giving $\log(K_a) \approx 5$, despite the relatively lower R^2 coefficient as observed in Figure 4. Perhaps all these reactions may occur simultaneously to changing extents depending on the operating condition, corroborating Ritcey (2006). Therefore, based on the present analysis, uranium (VI) could be extracted by Alamine 336 as UO_2SO_4 and/or as $UO_2(SO_4)_2^{2-}$, forming $(R_3NH^+)_2UO_2(SO_4)_2^{2-}$. According to data fitting shown in Figure 3(c)-3(d), equilibrium may not occur with the species $(R_3NH^+)_4UO_2(SO_4)_3^{4-}$ and reactions given by Eqs. (12)-(13) are not valid for the operating conditions studied. This observation is inconsistent with the previously published literature and the mechanism may depend on acidity (Sato, 1963; Schmidt, 1971; Collet *et al.*, 2009). Highly scattered data (low R^2 coefficient) were obtained with $n = 2$ (equilibrium with aqueous species UO_2^{2+}) and these data were not displayed in Figure 3.



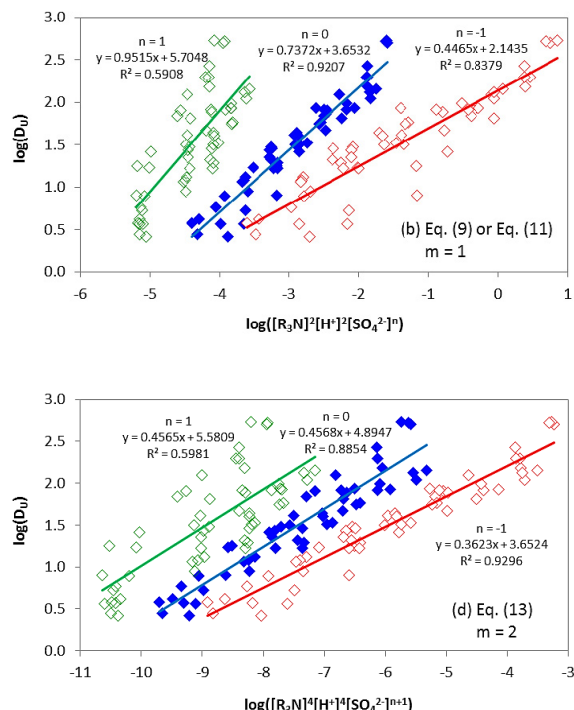


Figure 3: Data fitting presuming the predominance of only one single species in each phase: Equilibrium between $(R_3NH^+)_2UO_2(SO_4)_2^{2-}$ and UO_2SO_4 ($n = 1$, green) or $UO_2(SO_4)_2^{2-}$ ($n = 0$, blue) or $UO_2(SO_4)_3^{4-}$ ($n = -1$, red) given by (a) Eq. (8) or Eq. (10) with $m = 2$, and (b) Eq. (9) or Eq. (11) with $m = 1$; Equilibrium between $(R_3NH^+)_4UO_2(SO_4)_3^{4-}$ and UO_2SO_4 ($n = 1$, green) or $UO_2(SO_4)_2^{2-}$ ($n = 0$, blue) or $UO_2(SO_4)_3^{4-}$ ($n = -1$, red) given by (c) Eq. (12) with $m = 4$, and (d) Eq. (13) with $m = 2$ ($0 \leq \text{pH} \leq 0.54$; $T = 25^\circ\text{C}$).

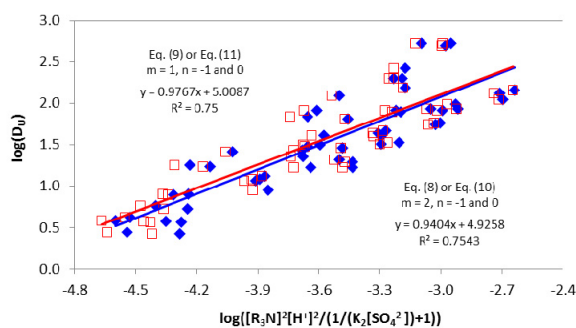


Figure 4: Data fitting presuming equilibrium between $(R_3NH^+)_2UO_2(SO_4)_2^{2-}$ in the organic phase and aqueous species UO_2SO_4 and $UO_2(SO_4)_2^{2-}$ ($0 \leq \text{pH} \leq 0.54$; $T = 25^\circ\text{C}$).

Alamine 336 is expected to be fully protonated under the operating conditions studied ($0 \leq \text{pH} \leq 0.54$). The reaction of protonation, Eq. (6), leads to

the extraction of HSO_4^- ions from the aqueous phase, thus favoring the consumption of SO_4^{2-} ions; such consumption is also expected for the protonation of Alamine according to Eq. (7). Consequently, Eq. (3) most likely occurs from the right to the left, as long as UO_2SO_4 and $UO_2(SO_4)_2^{2-}$ species are preferentially being extracted by Alamine 336.

Experimental Results

The effect of initial concentrations of Alamine 336 and sulfate ions on the extraction of uranium (VI) is shown in Figure 5. In this figure, simulations obtained using the equilibrium model, Eqs. (8) or (10), proposed by the present study are also included for comparison. In fact, a relative deviation of 8.4% was obtained between simulations and experimental data.

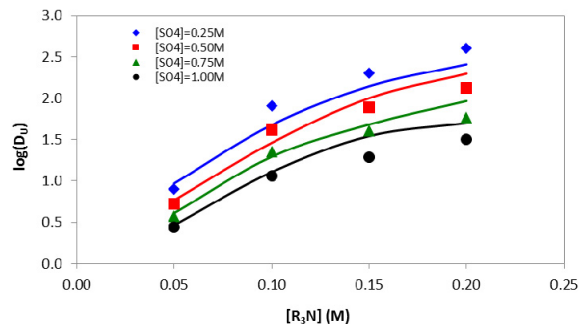


Figure 5: Effect of initial concentrations of sulfate ions and extractant on the extraction of uranium (VI) with Alamine 336 ($[U]_{\text{initial}} = 0.007\text{ M}$; $0 \leq \text{pH} \leq 0.54$; $[Cl^-] = 0\text{ M}$; $T = 25^\circ\text{C}$; continuous lines were calculated using Eq. (8) or Eq. (10)).

As expected, the higher uranium extraction observed when the extractant concentration increased is due to the larger amount of reagent in the organic phase when in contact with the aqueous phase. Higher concentrations of extractant may raise the viscosity of the organic phase and even result in the formation of molecular aggregates (Elhassadi and Do, 1986; Subba Rao *et al.*, 2002); however, none of these effects produced a negative impact on the efficiency of uranium extraction within the investigated operating conditions. On the contrary, the increase in the initial concentration of sulfate ions resulted in a reduced extraction of uranium, probably due to a competitive extraction of SO_4^{2-} and uranium (VI). As shown in Figure 1, and according to Eq. (3), a higher concentration of sulfate ions in the aqueous phase may in fact favor the formation of $UO_2(SO_4)_3^{4-}$ species, which are not preferentially extracted by Alamine

336. In addition, as given by Eq. (11), the extraction of anionic $\text{UO}_2(\text{SO}_4)_2^{2-}$ species involves the release of sulfate ions into the aqueous phase, thus contributing to a reduction in uranium extraction. The effect of initial concentration of uranium was not pronounced for the operating range investigated; therefore, tests with chloride ions in the aqueous phase were carried out at a fixed concentration level for uranium ($[\text{U}] = 2.1 \text{ g}\cdot\text{L}^{-1}$).

The effect of chloride ions on the extraction of uranium using Alamine 336 at changing concentrations of extractant and sulfate ions is shown in Figure 6. It can be observed that the presence of chloride ions is quite harmful, because the uranium extraction efficiency drops significantly when the concentration of chloride ions in the aqueous phase increases. This behavior is enhanced when the concentration of sulfate ions is increased. The same negative impact on the extraction of uranium was verified when using a mixed solvent containing D2EHPA and Alamine 336 (Quinn *et al.*, 2013). Therefore, to maintain the uranium extraction at higher levels, it is necessary to raise the concentration of Alamine 336 in the organic phase. This procedure may well result in higher operating costs, which may be prohibitive under the given conditions. The need for more extractant, aimed at maintaining the level of uranium extraction, is an indication that chloride ions may have a direct reaction with Alamine 336, possibly competing with the anionic $\text{UO}_2(\text{SO}_4)_2^{2-}$ species and/or affecting the protonation reaction. However, speciation calculations ($[\text{U}]_{\text{total}} = 0.01 \text{ M}$; $[\text{Cl}^-] = 0.10 \text{ M}$; $T = 25 \text{ }^\circ\text{C}$) including the species UO_2Cl^+ (equilibrium given by $\text{UO}_2^{2+}(\text{aq}) + \text{Cl}^-(\text{aq}) \rightleftharpoons \text{UO}_2\text{Cl}^+(\text{aq})$, $\log K = 0.170$) (NEA, 2004) and UO_2Cl_2 (equilibrium given by $\text{UO}_2\text{Cl}^+(\text{aq}) + \text{Cl}^-(\text{aq}) \rightleftharpoons \text{UO}_2\text{Cl}_2(\text{aq})$, $\log K = -1.100$) (NEA, 2004) indicate that the presence of uranium (VI) chloride species is negligible for the operating conditions studied due to the presence of sulfate ions in the aqueous solution.

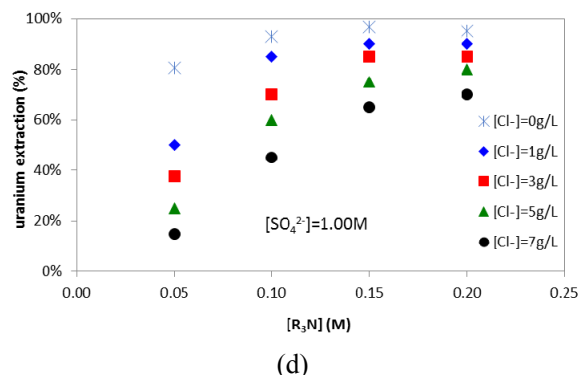
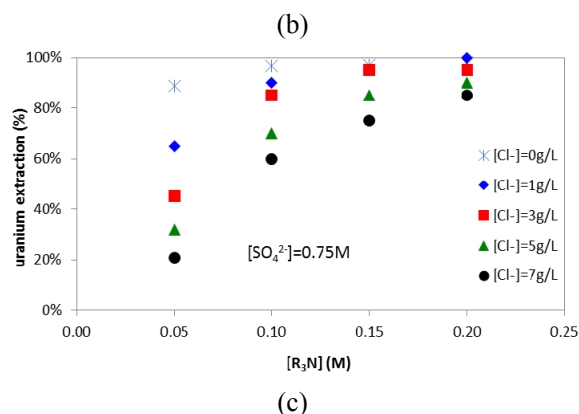
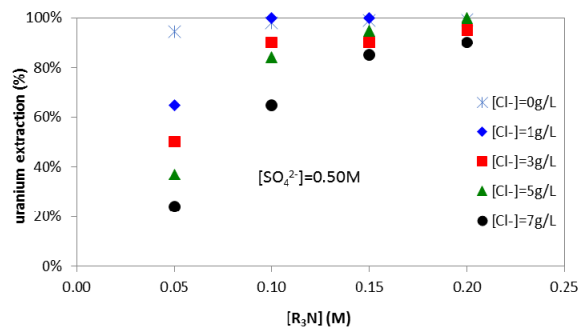
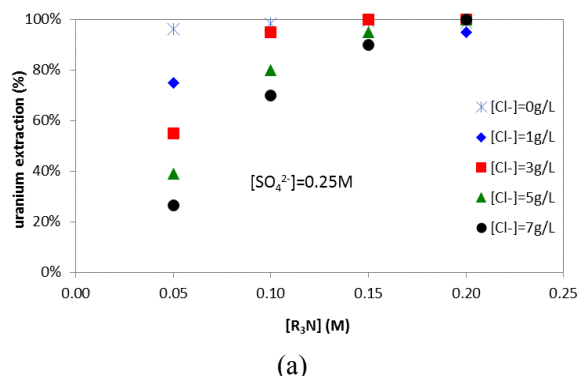


Figure 6: Effect of initial concentration of chloride ions on the extraction of uranium with Alamine 336 ($[\text{U}]_{\text{total}} = 0.002 \text{ M}$; $0 \leq \text{pH} \leq 0.54$; $T = 25 \text{ }^\circ\text{C}$).

CONCLUSIONS

The extraction of uranium from aqueous sulfate solutions using Alamine 336 as an extractant was investigated at typical concentration levels found in the uranium plant of INB (Caetité, Brazil). The following main conclusions could be drawn:

- Species distribution calculations in the aqueous phase revealed that concentrations of UO_2^{2+} , UO_2Cl^+ , and UO_2Cl_2 are negligible within the evaluated condition ($[\text{U}]_{\text{total}} = 0.01 \text{ M}$; $0 \leq \text{pH} \leq 0.54$; $[\text{Cl}^-] = 0.10 \text{ M}$; $T = 25 \text{ }^\circ\text{C}$). Species UO_2SO_4 and $\text{UO}_2(\text{SO}_4)_2^{2-}$ predominate within the operating conditions ($-2.5 \leq$

$\log([\text{SO}_4^{2-}]) \leq -0.8$ M), with an increase of $\text{UO}_2(\text{SO}_4)_3^{4-}$ species within the concentration conditions;

- Uranium (VI) is extracted by Alamine 336 as UO_2SO_4 and $\text{UO}_2(\text{SO}_4)_2^{2-}$, forming $(\text{R}_3\text{NH}^+)_2\text{UO}_2(\text{SO}_4)_2^{2-}$ in the organic phase according to Eqs. (8) or (10) and/or Eqs. (9) or (11). The extraction of species $\text{UO}_2(\text{SO}_4)_3^{4-}$ seems improbable for the operating conditions investigated;
- The efficiency of uranium extraction by Alamine 336 is significantly reduced when the concentrations of sulfate and chloride ions increase.

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