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The Simple Solution Modeling Implemented in the PAREX Code to Simulate Solvent Extraction Operations.

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ABSTRACT: The solvent extraction systems devoted to uranium purification from crude ore to spent fuel involve concentrated solutions in which deviation from ideality can not be neglected. The Simple Solution Concept based on the behaviour of isopiestic solutions has been applied to quantify the activity coefficients of metals and acids in the aqueous phase in equilibrium with the organic phase. This approach has been validated on various solvent extraction systems such as trialkylphosphates, malonamides or acidic extracting agents both on batch experiments and counter-current tests. Moreover, this concept has been successfully used to estimate the aqueous density which is useful to quantify the variation of volume and to assess critical parameters such as the number density of nuclides.

KEYWORDS: modelling, activity coefficient, simple solution, actinide, solvent extraction, separation, computer simulation.

I. INTRODUCTION

The Zdanovskii's rule was postulated in 1936, considering the experimental behaviour of electrolyte isopiestic solutions (solutions having the same water activity), [1]. This empirical rule was expressed as: "Binary solutions (i.e. one electrolyte in water) having the same water activity are mixed without any variation of this water activity value". The linear relation below (1) is the mathematical expression of empirical Zdanovskii's rule expressed in the molarity scale:

$$\sum_i \frac{C_i}{C_i^{bi}} = 1 \quad (1)$$

According to this relation, water activity of any mixture can be estimated by an iterative way if the composition of the mixture (C_i concentrations) and the binary data of each electrolyte (C_i^{bi} , a_w) are known. Previous studies have demonstrated that the deviation from ideal behaviour in the concentrated aqueous solutions could be mastered thanks to the water activity and the total concentration of dissolved species. Therefore the "simple systems" theory has been successfully applied in various fields such as: speciation studies [2], liquid-liquid extraction modelling [3, 4], binary data estimation [5, 6] and density [7, 8] or interfacial tension evaluations [9].

The use of the "simple systems" theory will be illustrated in this paper by two examples: aqueous density estimation and the modelling of solvent extraction by a monoamide.

II. Density estimation of mixtures

In 1965, Ryazanov and Vdovenko [10] demonstrated that the calculation of thermodynamic properties of mixtures is

solved most simply when Zdanovskii's rule is verified. For example, the volume of a mixture obtained from two binary solutions can be expressed as the relation (2) involving binary thermodynamic properties of the mixture's components:

$$V = \frac{C_1}{C_1^{bi}} \cdot V_1^{bi} + \frac{C_2}{C_2^{bi}} \cdot V_2^{bi} \quad (2)$$

This relation means that the mixture exhibits no excess volume. It has similarly been demonstrated that excess enthalpy of isopiestic mixtures following Zdanovskii's rule is null. Therefore, thermodynamic properties of such systems also called "simple systems" are similar to those of the "ideal systems" apart from the fact that isopiestic binary mixtures are here taken into account instead of pure components mixtures. The relation (2) has been rewritten by Ryazanov and coll. to express the density of a two electrolyte mixture as:

$$\rho = \frac{M_1 \cdot C_1 + M_2 \cdot C_2 + 1000}{\frac{C_1}{C_1^{bi}} \cdot \left(\frac{1000 + M_1 C_1^{bi}}{\rho_1^{bi}} \right) + \frac{C_2}{C_2^{bi}} \cdot \left(\frac{1000 + M_2 C_2^{bi}}{\rho_2^{bi}} \right)} \quad (3)$$

This relation can be written for a mixture of i electrolytes as:

$$\rho = \frac{\sum_i (M_i \cdot C_i) + 1000}{\sum_i \frac{C_i}{C_i^{bi}} \cdot \left(\frac{1000 + M_i \cdot C_i^{bi}}{\rho_i^{bi}} \right)} \quad (4)$$

The equation (4) is thermodynamically rigorous on condition that Zdanovskii's experimental behaviour is

confirmed. This behaviour is followed by many nitrate salts mixtures [11, 12] including the $\text{HNO}_3/\text{UO}_2(\text{NO}_3)_2/\text{H}_2\text{O}$ system. It must be pointed out that, unlike empirical dilution laws, Ryazanov-Vdovenko (RV) relation doesn't need any density measurement of the mixtures. By keeping the same form whatever the nature and the number of the electrolyte mixtures, this concept is widespread.

According to the equation (3), the density estimation of $\text{HNO}_3/\text{UO}_2(\text{NO}_3)_2/\text{H}_2\text{O}$ mixtures only requires the knowledge of the nitric acid and uranyl nitrate concentrations in the mixture (C_H , C_U) and the concentrations and densities of nitric acid and uranyl nitrate in the binary solutions having the same water activity as the mixture respectively noted as (C_H^{bi} , ρ_H^{bi}) and (C_U^{bi} , ρ_U^{bi}). The physicochemical data of binary solutions also called "binary data" are composed of the triplet (a_w , C_i , ρ_i). Therefore, each triplet is specific to an electrolyte at a given temperature. Such binary data have been tabulated by the National Bureau of Standards (NBS) for a lot of electrolytes and most often at 25°C. Once these data have been computed, the density of electrolyte mixtures is calculated according to the following steps:

- water activity of the mixture is estimated by solving Zdanovskii's rule (1) according to an iterative procedure,
- the knowledge of the water activity enables us to estimate the couples of data (C_H^{bi} , ρ_H^{bi}) and (C_U^{bi} , ρ_U^{bi}) by interpolating binary data of nitric acid and uranyl nitrate.

1. Binary data for nitric acid and uranyl nitrate solutions

An extensive study has been carried out to check binary data of nitric acid and uranyl nitrate solutions. Computation of the triplet (a_w , C_i , ρ_i) involves two sets of data. The first set consists in collecting of experimental water activity determination. Concentrations of the binary solutions often cover the entire electrolyte solubility range and are usually expressed in molality scale (m_i). This couple (a_w , m_i) is complemented by a second set of data consisting of the density of the binary electrolyte solution. Concentrations are here either written in molarity or molality scale which are related by the relation (5).

$$C_i = \frac{1000 \cdot m_i \cdot \rho}{1000 + \sum_j m_j \cdot M_j} \quad (5)$$

$$m_i = \frac{1000 \cdot C_i}{1000 \cdot \rho - \sum_j C_j \cdot M_j}$$

Nitric acid binary data (a_w , m_H) tabulated by Davis and coll. [13], Redlich [14] and, later, by Hamer and coll. [15] at 25°C, exhibit large discrepancies. For this reason, Charrin [5] has proposed revised values by adopting a new methodology taking into account recent experimental results. Density data tabulated in the International Critical

Tables (ITC) at 25°C [16] have been successfully checked and has therefore been retained.

The physicochemical data available for uranyl nitrate binary solutions were exhaustively collected by Goldberg [17] for the NBS. Water activities evaluated after a rigorous critical review of experimental data have been chosen. On the other hand, the density data compiled in the ITC are inaccurate and need to be updated because of their poor precision. More recent empirical relations were proposed by Söhnel [18] to describe concentration and temperature dependences of electrolyte solutions densities. Accuracy of such relations to estimate density of uranyl nitrate binary solutions at 25°C is unfortunately altered by the multi-temperature interpolation.

To overcome these discrepancies, the experimental densities data available for uranyl nitrate solutions at 25°C have been inventoried and interpolated with assumed polynomial expressions. Four new studies [19-22] have been taken into account in addition to the two sources from Grant [23] and Kaputinskii [24], already exploited by Söhnel [18]. Among these four references, the numerous data measured by Davis for liquid-liquid extraction with TBP extractant have been ignored because of a significant solubility of this extractant in aqueous solutions. Experimental data are reported in Figure 1 and have been interpolated with the relation (6) as followed:

$$\rho_{25} = 0.99707 + 0.32096 \cdot m_U - 0.02061 \cdot m_U^2 \quad (6)$$

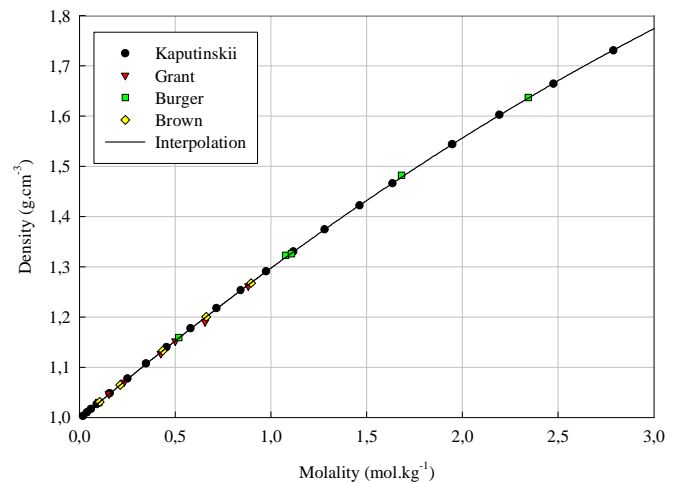


Figure 1: Density data of uranyl nitrate solution at 25°C

2. Validation of the RV relation

The validity of RV relation to estimate density of concentrated electrolyte solutions has been tested by comparing calculated and experimental data available for ternary solutions $\text{HNO}_3/\text{UO}_2(\text{NO}_3)_2/\text{H}_2\text{O}$ at 25°C. Experimental density data for these mixtures were obtained from analytical studies [19, 20, 25, 26] as well as criticality experiments [27]. Main characteristics of these experimental studies are reported in Table 1:

Table 1 - Experimental density data of HNO₃/UO₂(NO₃)₂/H₂O mixtures at 25°C

Reference	Number of data	[HNO ₃] range (mol.L ⁻¹)	[U] range (g.L ⁻¹)
Burger [21]	9	0.15-0.6	25-480
Davis [27]	17+10 (*)	1-8	25-340
Brown [24]	32+1 (*)	1-6	25-200
Spencer [28]	13+5 (*)	2-6	160-300
JAERI [29]	49	0.8-1	300-464

(*) Out of water activity range

For the most concentrated mixtures, water activity can not be estimated from Zdanovskii's rule because its value is out of the water activity range of uranyl nitrate binary data file. Deviations between experimental and calculated densities for HNO₃/UO₂(NO₃)₂/H₂O solutions at 25°C are shown in Figure 2. Calculated data are in good agreement with experimental ones, the deviations are lower than 0.6 per cent except for three dispersed points. The average estimated error on all points is less than 0.1 per cent which confirms the validity of the RV relation to estimate the density of electrolytes mixtures. Deviations become larger and more dispersed in increasing the acidity of the mixtures. This behaviour may be a consequence of increased uncertainty of analytical measurements in such concentrated mixtures. On the other hand, it must be pointed out that, unlike classical dilution laws, the best performances are observed with the solutions containing the largest amount of uranium [20, 27].

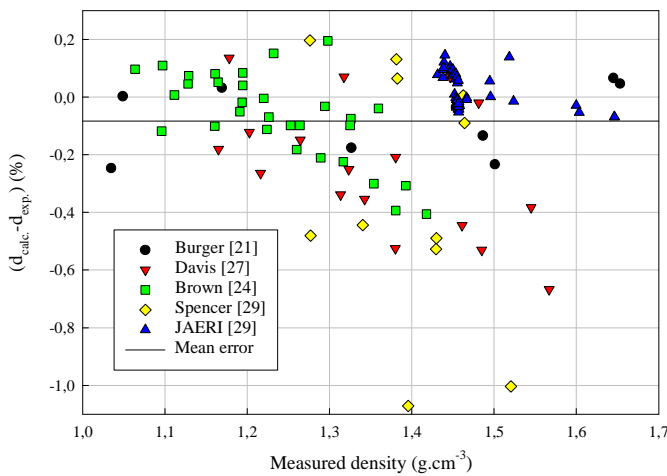


Figure 2: Comparison between experimental and calculated densities of HNO₃/UO₂(NO₃)₂/H₂O solutions at 25°C (use of RV relation)

III. The GANEX 1st cycle MODELLING

The GANEX process (Group ActiNide EXtraction) was developed by the CEA for the hydrometallurgical reprocessing of Generation IV spent nuclear fuels in the frame of the actinide homogenous recycling strategy [28]. The first cycle consists in selective extraction of uranium (VI) from the dissolution solution before the actinide group separation (Np, Pu, Am, Cm), carried out in the second cycle prior to the co-conversion step [29]. The preliminary separation of uranium in the first cycle is required in order to recover the pure actinide to match the uranium-transuranium element ratio before the actinide co-conversion. Moreover, this first step is useful to manage in the future the excess of uranium due to the reprocessing of unloaded fuels from light water and fast reactors. The separation of this major constituent of the spent fuels is finally useful to simplify the conception of process for the second extraction cycle.

The selective separation of uranium is operated by solvent extraction using a N,N-dialkylamide DEHiBA (N,N-di-(ethyl-2-hexyl)isobutyramide), depicted in Figure 3. DEHiBA was selected for the GANEX 1st cycle because it shows a good compromise between a quantitative extraction of uranium and a high U(VI)/Pu(IV) selectivity (SF_{U(VI)/Pu(IV)} ~ 80 at 3M HNO₃) [30] and a high loading capacity for uranium [31].

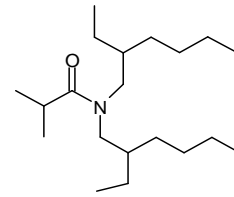
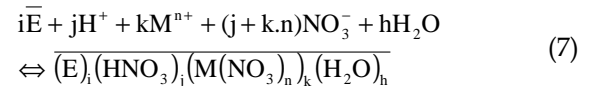


Figure 3: DEHiBA structure

Experimental distribution ratios obtained for nitric acid and uranium(VI) were described with a physicochemical model based on the application of the mass action law on each extraction equilibrium.



$$K_{ijkh} = \frac{\overline{[(E)_i(HNO_3)_j(M(NO_3)_n)_k(H_2O)_h]}}{[\bar{E}]^i \cdot a_{HNO_3}^j \cdot a_{M(NO_3)_n}^k \cdot a_{H_2O}^h} \cdot \frac{y_{ijkh}}{y_E^i} \quad (8)$$

Deviations from ideal behaviour were estimated by calculating the thermodynamic aqueous activity of each component in the aqueous phase. Due to a lack of data on the extraction of water, organic activity coefficients were neglected. The estimation of the aqueous activity involves determining the stoichiometric activity coefficients as expressed in the relation (9) below:

$$a_{M_p X_q} = \gamma_{st, M_p X_q}^{(p+q)} \cdot C_M^p \cdot C_X^q \quad (9)$$

The stoichiometric activity coefficient in binary solution ($M_p X_q / H_2O$) can be interpolated from the experimental data available in literature for many electrolytes in a wide range of concentrations. From a practical point of view, these binary data are based on the water activity determination which often involves measurements of vapor pressures of the solvent. Binary activity coefficients are evaluated through the Gibbs-Duhem relation integration.

In the case of a solution of several electrolytes, McKay [32] demonstrated that the activities of all the solutes in a mixture can be determined from only the measurement of the solvent activity. The modified relation proposed later by Majima [33] for a mixture of two electrolytes ($MX_1/MX_2/H_2O$) is reported below:

$$0,018 \cdot v_{MX_1} \cdot \ln \left(\frac{m^* \cdot \gamma_{MX_1}}{M_{MX_1} \cdot \Gamma_{MX_1}} \right) = - \int_0^{\ln(a_{H_2O})} \left\{ \frac{1}{m^*} \cdot \left(\frac{\partial m^*}{\partial \ln x_2} \right)_{a_{H_2O}} + \frac{1}{m^*} - \frac{1}{M_{MX_1}} \right\} \cdot d \ln(a_{H_2O}) \quad (10)$$

$$\text{with: } m^* = m_{MX_1} + \frac{v_{MX_2}}{v_{MX_1}} \cdot m_{MX_2} \quad \text{and} \quad x_2 = \frac{v_{MX_2}}{v_{MX_1}} \cdot \frac{m_{MX_2}}{m^*}$$

Evaluation of the integral term requires the determination of water activity for a large number of mixtures. Nevertheless, the McKay-Perring relation can be dramatically simplified when “simple solution” concept is valid. When the mixture of electrolytes follows the Zdanovskii’s rule, the integrand term is zero and the following relation between activity coefficients is obtained from the equation (10) also known as the Mikulin’s relation [34]:

$$\gamma_{MX_i} = \frac{v_{MX_i} \cdot m_{MX_i}^{bi} \cdot \gamma_{MX_i}^{bi}}{\sum_k v_{MX_k} \cdot m_{MX_k}^{bi}} \quad (11)$$

The activity coefficient of the two electrolytes in a ternary solution $HNO_3/UO_2(NO_3)_2/H_2O$ is evaluated according to the following steps:

- water activity of the mixture is estimated by solving the Zdanovskii’s rule (1) according to an iterative procedure,
- the knowledge of the water activity enables us to estimate the couples of data $(C_H^{bi}, \gamma_H^{bi})$ and $(C_U^{bi}, \gamma_U^{bi})$ by interpolating binary data of nitric acid and uranyl nitrate.

1. Modelling of nitric acid extraction by DEHiBA

The experimental distribution ratios of nitric acid previously measured by Condamines [35] were complemented in our laboratory. These extraction data were obtained with a one molar solution of DEHiBA diluted in an aliphatic diluent (HTP). The nitric acid extraction could be well described by taking into account

the formation of the three organic complexes $(HNO_3)(DEHiBA)$, $(HNO_3)(DEHiBA)_2$ and $(HNO_3)_2(DEHiBA)$ as reported in Figure 4. Activity coefficients of the nitric acid were evaluated by interpolating binary data of Charrin [5] as mentioned previously. The solvate $(HNO_3)(DEHiBA)$ is predominant in the whole acidity range and the equilibrium constant linked to its extraction was estimated : $K_H = 0.112 \pm 0.04$. These results are consistent with those obtained previously by Condamines [35].

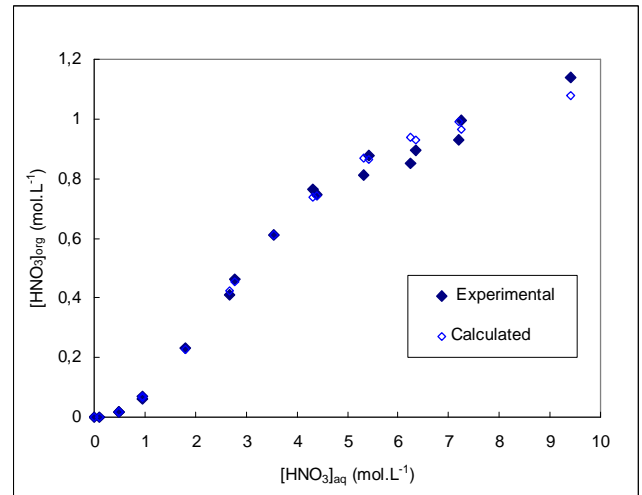


Figure 4: Modelling of the nitric acid extraction by DEHiBA 1M at 25°C

2. Modelling of the uranyl nitrate extraction by DEHiBA

The uranium extraction was measured from solutions containing various concentrations of nitric acid and uranyl nitrate. The acidity range was from 0.1 molar to 6 molar while the total uranium concentration range was from 2 to 120 grams per litre. The organic complexes formed between nitric acid and monoamide were unchanged and were taken into account to model the uranium extraction. The activity coefficients of nitric acid and uranyl acid were both evaluated according to the “simple solutions concept”. Thus, the water activity of the electrolytes mixture was evaluated by solving the Zdanovskii’s relation (1) while the activity coefficients were estimated using the Mikulin’s relation (11).

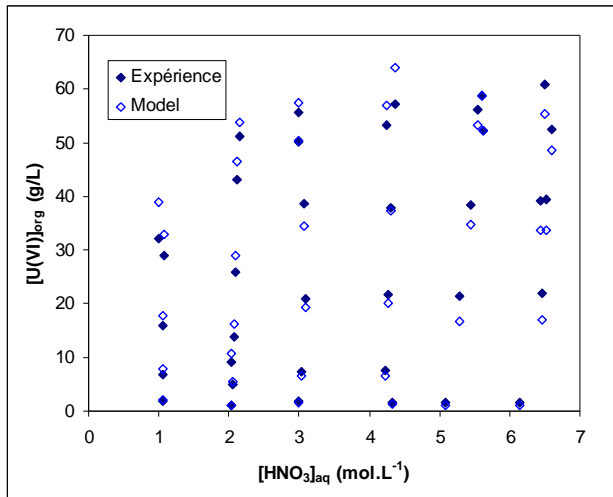


Figure 5: Modelling of the uranium (VI) extraction by DEHiBA 1M at 25°C from nitric acid solutions

The uranyl nitrate extraction is well modelled by considering the formation of a single complex: the disolvate $UO_2(NO_3)_2(DEHiBA)_2$. This speciation is consistent with previous experimental studies using the slope analysis [36, 37], the saturation technique [36] or the IR spectroscopy [36]: the same stoichiometry was found for the extracted uranyl complex from 1 to 4 mol.L⁻¹ of nitric acid in the aqueous solutions. The extraction equilibrium constant of U(VI) for 1M DEHiBA/HTP was calculated: $K_U = 1.51 \pm 0.13$. At HNO_3 2M and for trace concentrations of ²³³U, Pathak *et al.* [37] determined by the slope analysis method, an equilibrium constant of 0.87 ± 0.08 for the extraction of U(VI) by 1M DEHiBA/HTP but without taking into account the activity coefficients of the constituents in the aqueous phase.

3. Design of a counter-current validation test

The equilibrium constants optimized to represent the extraction of both nitric acid and uranium(VI) were integrated into the process simulation software PAREX developed by CEA [38] to design a flowsheet for a validation test. The flowsheet was calculated to recover more than 99.9% of uranium from the feed solution. This flowsheet, illustrated in Figure 6, was carried out in 2008 with a surrogate feed solution, in a counter-current test using laboratory scale mixer-settlers. The objectives were, on the one hand, to validate the extraction performance of DEHiBA in liquid-liquid discontinuous devices and, on the other hand to check the accuracy of the model.

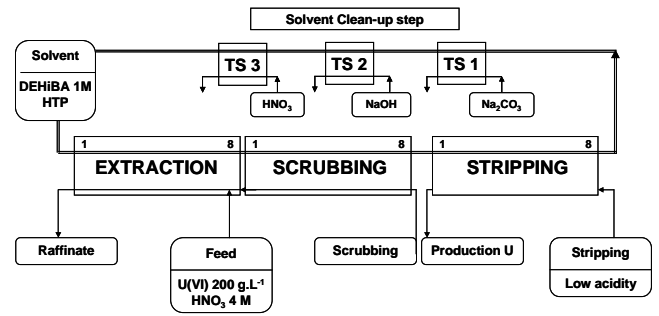


Figure 6: Flowsheet for the uranium extraction process

The uranium concentration remaining in the raffinate and in the solvent was too low to be measured by classical techniques (ICP-AES, potentiometry), Time-Resolved Laser Induced fluorescence (TRLIF) was used to determine the extraction and recovery yields of uranium at the end of this test. 1.2 mg/L of uranium was measured in the raffinate, which represents an extraction yield of 99.9992%, while 0.103 mg/L of uranium remained in the solvent, which corresponds to a recovery yield of 99.9997%. The uranium was quantitatively extracted and well stripped from the solvent, which confirms that DEHiBA is suitable for the selective separation of uranium.

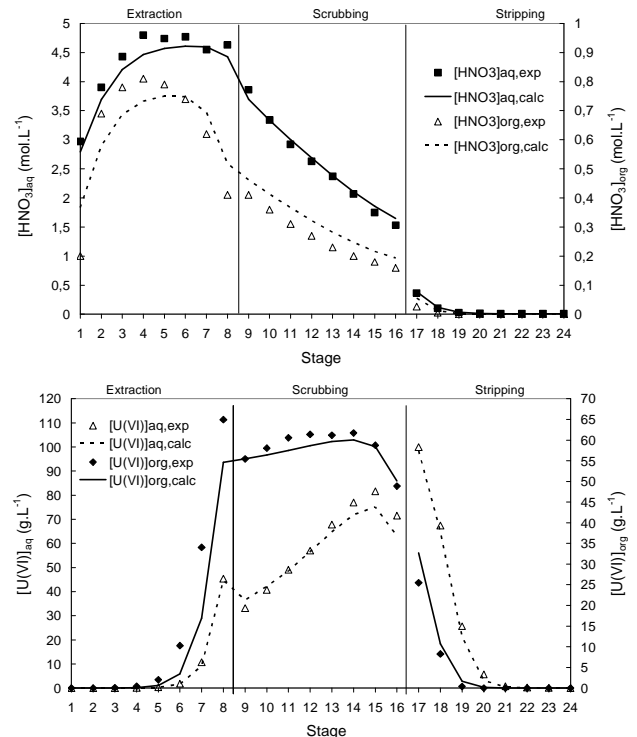


Figure 7 : Aqueous and organic concentration profiles of nitric acid and uranium

At the end of the test, the experimental profiles of uranium and nitric acid concentration in organic and aqueous phases were measured and compared to the calculated concentrations (Figure 7). The good agreement between experimental and calculated profiles confirms the validity of the model. Regarding the profiles of the nitric acid concentration, the model predicts the trends, however, the deviation of the calculated organic concentration from the

experimental data reaches 20% (while it is only about 5% in aqueous phase). This difference could be explained by a flooding or another problem occurred during the sampling or by larger analytical errors in organic phase. Overall, the values of distribution ratios of nitric acid calculated from the aqueous composition are consistent with the experimental results.

4. Design of the GANEX 1st cycle hot test

The model previously developed and validated to describe uranium (VI) and nitric acid extraction by DEHiBA was supplemented with modelling of the extraction of other actinides (Pu(III, IV), Np(V, VI) and Th(IV)) and some fission products such as Tc and Zr. After its implementation in the PAREX code, the flowsheet of a high active demonstration test for the selective uranium recovery from HLW was designed. Flow rates were optimized and the composition of the scrubbing solution was determined to achieve a recovery yield of uranium exceeding 99.99% with the highest decontamination factors towards the other FP and transuranic elements (Np and Pu in particular).

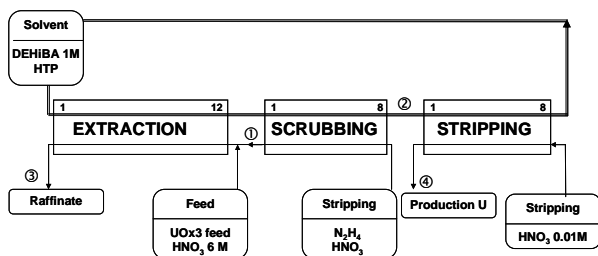


Figure 8: Flowsheet for the GANEX 1st cycle hot test

The uranium separation was performed in three sections of laboratory scale mixer-settlers corresponding to the extraction, scrubbing, and stripping steps. The device set-up consisted of 3 banks of mixer-settlers of 12, 8 and 8 stages, respectively. The experimental flowsheet is shown in Figure 8. Before introducing the genuine feed, a surrogate solution of uranium(VI)/HNO₃ (176 g.L⁻¹ at 6M HNO₃) has been used for ten hours to reach nitric acid and uranium equilibrium. The genuine solution was then treated and the test has ran for 58 hours at steady state to produce enough feed solution for the Ganex 2nd cycle test. The steady state was checked online with the help of a spectrophotometric monitor supplemented by laboratory analyses. Uranium (and plutonium) concentrations were monitored in four different flows: the aqueous phase coming back from the scrubbing section ①, the organic loaded solvent ②, the raffinate ③ and the uranium production ④. At the end of the experiment, the profiles of uranium concentrations were measured in both phases by X-ray Fluorescence after collecting an aliquot of the solution from each mixer-settler. The profiles of aqueous technetium concentrations were also determined in each section by ICP/QMS. Neptunium and technetium concentrations in the uranium product were measured by ICP/SFMS and ICP/QMS to determine accurately the

decontamination factors (DF). Gamma and alpha spectrometries were also used to estimate the α and $\beta\gamma$ decontamination factors of uranium and the remaining activity in the spent solvent.

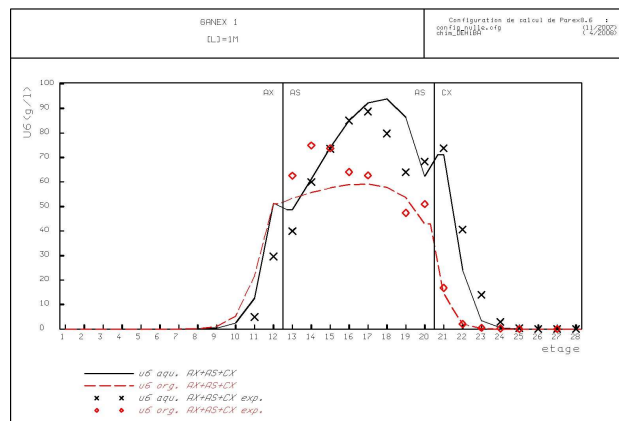


Figure 9: Experimental and calculated profiles of uranium and technetium concentrations in aqueous and organic phases for the three sections

Uranium concentration profiles in aqueous phase (and organic phase for uranium) obtained during the continuous hot test are shown in Figure 9 and compared with calculated data for the three sections (extraction, scrubbing, stripping). These predicted values reproduced quite well the experimental concentrations, which confirm the validity of the model for uranium extraction by DEHiBA (extraction constants, kinetics and speciation).

IV. Conclusion

Two examples involving concentrated mixtures of uranyl nitrate and nitric acid were used in this paper to illustrate the application of the “simple solutions” concept in order to estimate the deviation from ideality. The outstanding experimental behaviour of isopiestic solutions (solutions having the same water activity) pointed out by Zdanovskii, offers very convenient and powerful methods to overcome the difficulties derived from the use of concentrated solutions in hydrometallurgical applications. The assessment of the density is useful to quantify the variation of the aqueous volume and to evaluate the critical parameters such as number density of nuclides. This feature is implemented in simulation codes such as the CRISTAL code. In the same manner, the estimation of the aqueous activity coefficients has been implemented in our PAREX simulation code to master the effect of high concentration of electrolytes on the performances of solvent extraction processes such as PUREX or more innovative separation routes.

NOMENCLATURE

- a_w : Water activity
- C_i : Molarity of component i in the mixture (mol.L⁻¹)
- m_i : Molality of component i in the mixture (mol.kg⁻¹)

C_i^{bi} : Molarity of component i in the binary solution at the same a_w as the mixture (mol.L^{-1})
 m_i^{bi} : Molality of component i in the binary solution at the same a_w as the mixture (mol.kg^{-1})
 V : Mixture volume
 V_i^{bi} : Volume of the binary solution at the same a_w as the mixture
 ρ : Mixture density (g.cm^{-3})
 ρ_i^{bi} : Density of the binary solution at the same a_w as the mixture (g.cm^{-3})
 M_i : Molecular weight of component i (g.mol^{-1})
 $a_{M_pX_q}$: Activity of M_pX_q electrolyte
 $\gamma_{M_pX_q}$: Stoichiometric activity coefficient of M_pX_q electrolyte
 ν_{MX_i} : Number of ions solubilised by MX_i electrolyte
 M_{MX_i} and Γ_{MX_i} : Molality and activity coefficient of MX_i in the binary solution at the same a_w as the mixture

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