Determination of U(VI) and Pu(IV) Mass Transfer Constants with N,N-dialkylamides in Liquid-Liquid Extraction

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Abstract - In the frame of the development of Generation IV reactors, CEA is developing a liquid-liquid extraction process for the multirecycling of plutonium from the future spent nuclear fuels. Thermodynamic data have already been acquired for the modelling of the extraction equilibriums in this process, however, a full phenomenological model requires kinetic data too.
Thus, this paper summarizes the acquisition of mass transfer coefficients of uranium(VI) and plutonium(IV) between nitric acid and a monoamide-based solvent upon extraction with three different techniques using a constant interfacial area: the single drop technique. They are compared to results obtained with Nitsch cell and rotating membrane cell (RMC) methods.
The influence of temperature, nitric acidity, viscosity of the organic phase and, in the case of the moving drop technique, the drop size and the nature of the continuous phase (aqueous or organic) on the mass transfer coefficient of uranium and plutonium during the extraction step was studied.

Keywords: N,N-dialkylamides, uranium(VI), plutonium (IV), liquid-liquid extraction, single drop technique, Nitsch cell, Rotating membrane cell

1. Introduction

In the frame of the development of Generation IV reactors, CEA is developing a liquid-liquid extraction process for the multirecycling of plutonium from the future spent nuclear fuels based on the N,N-dialkylamides family well known for its high selectivity for hexavalent uranium (U(VI)) and tetravalent plutonium (Pu(IV)) versus fission products (Ban et al., 2012; Musikas and Zorz, 1992). Many thermodynamical data have already been acquired but the mass transfer kinetics of U(VI) and Pu(IV) with this solvent are therefore important parameters for the development of solvent extraction processes at a larger scale.

Because of the existence of many kinetic methods (Hanna and Noble, 1985), our study was focused on techniques using a constant interfacial area: the single drop technique, the Rotating Membrane Cell (also called RMC) and the Nitsch cell. The first part of our work consisted in measuring the extraction kinetics constants of U(VI) and Pu(IV) by N,N-dialkylamides performing each methods. The influence of temperature, nitric acidity, viscosity of the organic phase on the transfer of uranium and plutonium during the extraction step was studied. In addition, in the case of the single drop technique, the drop size and the nature of the continuous phase (aqueous or organic) were looked at too.

This paper focus on the single drop method but briefly describes the Nitsch cell and the RMC techniques. The results obtained on the extraction kinetics of U(VI) and Pu(IV) by N,N-dialkylamides by the single drop technique are developed and compared to the results obtained with the other techniques in the last part of the paper.

2. Materials and Method

2.1. Single drop technique

This method, involving a constant interfacial area (drops), is based on the travel of a liquid drop (organic or aqueous phase) through a continuous phase into a thermostated column. During the drop course (organic or aqueous phase), the mass transfer occurs and the analysis of the gradient of the solute concentration into the drop depending of its travel time leads to the determination of the global kinetic constant, K_g. A moving funnel allows the variation of the drop travel time then avoiding the end-effects (transfer occurring during the drop formation and drop coalescence in the funnel).

The interfacial transfer process can be controlled by different regimes: kinetic (process limited by the interfacial chemical reaction), diffusional, or mixed (when the limitation is due to chemical reaction and molecular diffusion). Extraction may take place in two possible configurations: the rising drop configuration (continuous aqueous phase-CAP) or the falling drop ones (continuous organic phase-COP).

Assuming that the transfer within the single drop method follows the double film theory and that the seconds Fick's law is respected, the mass transfer kinetic constant (K_g) could be determined from the slope of Eq.(1).

$$ln(1 - E) = -\frac{6K_g}{d}t + cst \tag{1}$$

where the drop diameter d was calculated from the number of drops and the injection flow, assuming the drops to be perfect spheres (no distortion of drops area was observed). The travel time t is assumed to be the interval from the drop breaks free to its coalescence in the funnel; the *cst* term is a constant value including the end-effects. E is the transfer efficiency of the element from one phase to the other. Depending on the transfer mode, the efficiency E is described by:

$$E_{drop \rightarrow continuous\ phase} = \frac{C_d^0 - C_d}{C_d^0} \ or \ E_{continuous\ phase \rightarrow drop} = \frac{C_d}{D.C_c} \tag{2}$$

with C_d the solute concentration in the drop, C_d^0 the concentration in the feed solution (initially in the drop), C_c the concentration in the continuous phase (supposed constant). D corresponds to the distribution ratio of the solute between the organic phase at thermodynamical equilibrium (C_{org}^{eq}) with the aqueous phase (C_{aq}^{eq}):

$$D = \frac{C_{org}^{eq}}{C_{aq}^{eq}} \tag{3}$$

The experiments were carried out as follows: An aqueous solution of 40 g.L^{-1} of uranyle ion was prepared by dissolution of $UO_2(NO_3)_2(H_2O)_5$ into 5 M HNO_3. A Pu(IV) (7.5 mg.L^{-1}, 10^5 Bq.L^{-1}) solution was prepared by diluting a Pu nitrate solution into 5 M nitric acid. N,N-dialkylamides are diluted in TPH and pre-equilibrated with 5 M HNO_3.

The actinides (U(VI) or Pu(IV)) were extracted from an aqueous nitric solution by the N,N-dialkylamides-based solvent for four different travel times obtained by using four column heights (50, 70, 100 and 130 cm). Each extraction experiment was performed twice. U(VI) concentration was measured in each aqueous and organic phase with UV-vis spectrophotometry (Helios Zeta, Thermo Scientific double-beam). $^{239+240}$Pu was analyzed in both phases by alpha spectrometry.

2.2. Nitsch cell

The used stirred cell is a scaled-down version of the Nitsch-type stirred cell, provided by KIT-INE (Weigl et al., 2006). The stirred cell was filled with both aqueous and organic phases (60 mL each), which are stirred independently by a paddle. In order to get a planar interface, the stirring speed of each phase is adapted to get the same apparent Reynolds number.

2.3. RMC technique

The technique consists of a membrane, containing one of the phases, that is glued on the base of a cylinder and that is rotated at a definite speed. The transfer, occurring in a transient regime, is assumed to be limited by the kinetics of the chemical reactions at the beginning of the transfer process (Simonin and Weill, 1998).

3. Extraction Kinetics with U(VI) and Pu(IV) - Single Drop Method

Experiments were conducted using both rising-drop (K_g^{org}) and falling-drop (K_g^{aq}) configuration. The drop size was modified using the hammered needle by applying frequencies from 0 to 2 Hz.

Fig.1: Influence of the drop size on the kinetics extraction of U(VI) *(orange)* and Pu(IV) *(blue)* depending on the column configuration (falling drop – *triangle* and rising drop – *dot*).

According to Fig.1, kinetics of uranium(VI) and plutonium(IV) extraction seems to be quite similar whatever the column configuration is. However, mass transfer from the continuous aqueous phase (CAP) to the organic drop seems to be slower than the transfer from the aqueous drop to the continuous organic phase (COP). Depending on the drop size (from 1.4 to 3.2 mm), the global mass transfer coefficients obtained with the rising-drop configuration are 7 to 10 times lower than those obtained in the falling-drop configuration. The transfer resistance seems to be located into the organic phase. Moreover, because the fluid circulation in a drop is supposed to increase with the drop size, promoting the outer diffusion, mass transfer is then supposed under diffusionnal or mixed control.

In order to evaluate the influence of the organic phase viscosity on the global mass-transfer coefficient, experiments of extraction of U(VI) at 40 g.L^{-1} in 5 M HNO$_3$ by a U(VI) loaded solvent (0; 40; 80; 100 gU.L^{-1}) were carried out in falling-drop configuration (COP). For each kinetics experiment, drop size was set to 2.3 mm diameter (Fig.2). The dynamic viscosities measured for different U(VI) organic concentrations are reported in Table 1.

Fig. 2: Influence of the U(VI) organic concentration on the U(VI) and Pu(IV) mass transfer constant (COP).

Table 1: Values of organic phase dynamic viscosity depending on the U(VI) concentration.

$[U]_{org}$ (g.L^{-1})	0	40	80	100
$\mu_{25°C}$ (mPa.s)	3.5	6.4	9.7	12.3

As shown on Fig.2, the higher the viscosity of the solvent, the lower U(VI) and Pu(IV) mass transfer constants are. The increase of the boundary layer of the organic phase at the drop interface with the organic viscosity could explain these results. Again it suggests that the resistance to the transfer is located into the organic phase and that kinetics extraction is under diffusionnal control.

4. Contribution of Nitsch Cell and RMC

Despite many experiments, Nitsch cell and RMC methods appeared only as complementary methods to the single drop technique:

The mass transfer coefficients of U(VI) extraction by the monoamide solvent obtained with the Nitsch cell are 10 times lower than the values determined by single drop despite a significant increase of the stirring speed. Nevertheless the results are in agreement with the single drop conclusion: the resistance of the U(VI) transfer is located in the monoamide-based solvent.

The rotating membrane cell gave a chemical constant value for U(VI) extraction on the same order of magnitude than the single drop one. A mixed kinetic regime might be supposed, but the results suggest still a high influence of diffusion.

5. Conclusion

The results obtained by the single drop technique showed that U(VI) and Pu(IV) mass transfer constants are quite similar. These coefficients are strongly influenced by the drop size and the monoamide-based solvent viscosity. The single drop method allowed the most complete study but the other methods brought some qualitative information to better understand the phenomena involved in the transfer of uranium and plutonium with this system. The global results point out that the resistance to the transfer is essentially located in the organic phase and the diffusion process would mainly control the kinetics. An attempt to estimate the chemical and the diffusionnal kinetic constants based on experimental results led also to the same conclusion.

These results lead to a better understanding of the this extraction system with this solvent and will help to simulate experimental profiles of uranium and plutonium concentrations measured in continuous tests performed in mixer-settlers or pulsed columns with this monoamide solvent.

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