Description of partition equilibria for uranyl nitrate, nitric acid and water extracted by tributyl phosphate in dodecane

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ABSTRACT

Experiments were carried out on the partitioning of uranyl nitrate in nitric acid solution extracted by 30 vol.% of tributyl phosphate (TBP) in dodecane at 25 °C. The model proposed by Naganawa and Tachimori (*Bull. Chem. Soc. Jap.* 70, 809, (1997)) for the case of aqueous solutions of nitric acid was used to additionally describe the extraction equilibria of uranyl nitrate. The treatment is based on the assumption of thermodynamic ideality for the organic solution composed of the diluent, the free extractant and the complexes. The stoichiometries of the metal complexes were determined one by one by a suitable procedure. The formation of 6 different complexes involving uranyl nitrate was found capable of representing the partition equilibria for the three extracted compounds: nitric acid, water and uranyl nitrate. This approach suggests the formation of 2:1 and 3:1 complexes for TBP and uranyl nitrate, respectively.

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1. Introduction

Nuclear reprocessing uses chemical procedures to separate the useful components, e.g., the remaining uranium and the newly-created plutonium, from the fission products and other radioactive waste in the spent fuel produced by nuclear reactors. Reprocessing serves multiple purposes. Originally used solely to extract plutonium for producing nuclear weapons, it is mainly used nowadays for the reduction of the volume and radiotoxicity of the waste, allowing separate management (destruction or storage) of nuclear waste components. Plutonium is worth being recovered because it can be recycled to produce a new fuel, like the so-called MOX (mixture of oxides) fuel for instance. The reprocessed uranium, which constitutes about 95% of the mass of the spent fuel material, can be reused as a fuel, but it is extracted mainly to decrease the amount of waste (the former use is profitable only when prices are high). The rest of the waste, composed of fission products and neutron capture products (minor actinides) (Nash et al., 2006), is extracted to decrease the radiotoxicity of the waste (Baron et al., 2007; Warin et al., 2009).

The extent of the benefits of reprocessing is determined by the efficiency of the separation process. Among the different actinide separation methods, solvent extraction (Rydberg et al., 2004) has several advantages at industrial scale, including the ability for continuous operation, high throughput and solvent recycling (Nash et al., 2006). So, it constitutes the basis of the PUREX (Plutonium–URanium EXtraction) process, which is the standard method for the recovery of uranium and plutonium.

The PUREX process can be roughly described as the extraction of plutonium and uranium into an organic phase composed of 30% tributyl phosphate (TBP) in odourless kerosene or dodecane from an aqueous solution containing nitric acid, the fission products remaining in aqueous phase. After this first separation stage, further processing leads to the separation of the heavier plutonium from the uranium. The process is based on the complexation of species by TBP.

A description of metal partitioning equilibria may have value for the modelling of extraction stages in the nuclear reprocessing industry. Such a model may be utilised for various purposes including real-time safety analysis in a plant (in particular to prevent criticality accidents), the implementation of pilot extractors, and the good working of an industrial process (for instance during its starting phase).

A number of models has been presented in the literature for the description of partitioning equilibria: for the extraction of acid and water (Alcock et al., 1956; Blaylock and Tedder, 1989; Chaiko and Vandegrift, 1988; Davis, 1962; Davis et al., 1970; Healy and McKay, 1956; Naganawa and Tachimori, 1997a; Rozen et al., 1971; Schaekers, 1986; Ziat et al., 2002), of acid and metal (uranyl nitrate) (Comor et al., 1989), and of metal in trace concentrations and water (Hesford and McKay, 1958).

On the other hand, models describing the extraction of all species (metal, acid and water) are very scarce in the literature. To our best knowledge, only Mokili and Poitrenaud proposed such a description

for the extraction of lanthanides by TBP (Mokili and Poitrenaud, 1996, 1997). However, the latter treatment gives a prominent role to the water on the deviations from ideality in organic phase.

In contrast, in the present study, all species in organic phase are treated on an equal footing and the organic phase is globally regarded as ideal. Moreover this latter classic assumption is used on the mole fraction scale, in which the diluent is included. This framework may be expected to be more suited to the description of this phase as compared to previous studies developed on molality or concentration scale for the solute species.

In the present work, the partitioning of uranyl nitrate, nitric acid and water extracted by 30 vol.% TBP in dodecane has been studied experimentally. This TBP content is that used in the PUREX process. The experimental work was aimed at measuring the concentrations of all species in organic phase, which was required for the subsequent development of the model. Indeed, previously published data on this system did not provide the amount of extracted water and/or density data that are needed in our present model on mole fraction scale. A quantitative model capable of describing the partition equilibria of all components has been developed. The approach is motivated by a previous successful work by Naganawa and Tachimori for modelling the extraction of nitric acid and water in a wide range of TBP concentrations (Naganawa and Tachimori, 1997a). The latter treatment involved the formation of 8 different complexes in organic phase and was expressed in terms of thermodynamic partition constant that were indeed independent of the TBP concentration. Thus, it was appealing to examine whether this purely chemical approach could also describe the extraction of metal from acid aqueous phases.

2. Materials and methods

The aqueous ternary $UO_2(NO_3)_2$/HNO_3/H_2O solutions were prepared using Prolabo Normapur hexahydrate uranium nitrate ($UO_2(NO_3)_2$, 6 H_2O), Prolabo nitric acid and deionised water. The organic phases were made from dry dodecane (Prolabo, 99% purity, without further purification, d = 0.7452 kg dm^{-3}) and purified pre-equilibrated tributyl phosphate (TBP) (Prolabo, 99% purity, d = 0.9721 kg dm^{-3}, water content = 0.854 mg g^{-1}). The TBP was purified by shaking it together with a 0.1 M NaOH solution, and then washing it twice with distilled water (d = 0.9760 kg dm^{-3}, water content = 66.6 mg g^{-1}).

Aqueous and organic solutions were equilibrated by vigorously shaking equal volumes for 20 min at 25 °C. After centrifugation and separation of the two phases, the densities, the concentrations of uranyl nitrate and nitric acid in each phase, and the concentration of water in organic phase, were measured at 25 °C.

The densities of aqueous and organic phases were measured using an Anton-Paar DMA 55 tuning-fork density transducer. The concentrations of uranyl nitrate and nitric acid in the phases were determined by spectrophotometric measurement (using a Hitachi U-3000 spectrophotometer) and acid–base titration, respectively. The concentration of water in organic phase was measured by coulometric Karl Fischer titration with a Metrohm KF 737 titrator.

3. Model

3.1. Partition equilibrium

We consider the extraction of uranyl nitrate, nitric acid and water by an organic phase composed of tributyl phosphate (TBP) diluted in dodecane. At equilibrium the organic phase extracts all the species composing the aqueous phase, viz. uranyl nitrate, nitric acid and water. Dodecane and TBP are considered to be insoluble in water (the solubility of TBP is on the order of 10^{-3} mol dm^{-3} in 0–3 mol dm^{-3} HNO$_3$ (Wright and Paviet-Hartmann, 2010)).

Extraction of the constituents of aqueous phase by TBP is supposed to lead to the formation of well defined complexes of the form

$$(TBP)_t \bullet (UO_2(NO_3)_2)_m \bullet (HNO_3)_a \bullet (H_2O)_h$$
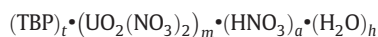
where t, m, a and h are the stoichiometric numbers of TBP, uranyl nitrate, nitric acid and water, respectively. To simplify the notations we will denote a complex by $T_tU_mA_aW_h$, with T standing for TBP, U for the metal salt (uranyl nitrate), A for nitric acid and W for water. This notation also includes the case of free TBP ($t = 1$, $m = a = h = 0$) and of free water ($t = m = a = 0$, $h = 1$). We will use the letter D for dodecane. Nitric acid and uranyl nitrate will be assumed to be present in organic phase only in the form of complexes with TBP.

As done before (Naganawa and Tachimori, 1997a), we admit that free water may be present in organic phase. Although the solubility of water in pure dodecane is low (ca. 2.5×10^{-3} mol dm^{-3} (Skurtvelt and Olsson, 1992)) the amount of free water in the systems studied here is not negligible as compared to the amount of extracted water (see Table 3) when the ionic solute concentration is high.

The partition equilibrium may then be expressed as

$$m\,U + a\,A + h\,W + t\,T \leftrightarrow T_tU_mA_aW_h \qquad (1)$$

in which T and the complex are in organic phase, and the other species are in aqueous phase.

The mass action law applied to the partition equilibrium (Eq. (1)) gives

$$K_{t,m,a,h} \equiv \frac{a_{t,m,a,h}}{(a_T)^t \left(a_{U,aq}\right)^m \left(a_{A,aq}\right)^a \left(a_{W,aq}\right)^h} \qquad (2)$$

where $K_{t,m,a,h}$ is the thermodynamic equilibrium constant for the formation of the $T_tU_mA_aW_h$ complex, $a_{t,m,a,h}$ and a_T are the activities of the complex and of T, respectively, and $a_{X,aq}$ is the activity of component X in aqueous phase.

The activities of the ionic compounds A ($= H^+ + NO_3^-$) and U ($= UO_2^{2+} + 2\,NO_3^-$) appearing in Eq. (8) are defined by

$$a_{A,aq} \equiv a_{H^+}\ a_{NO_3^-} = \gamma_A^2 m_A^2 \qquad (3)$$

and

$$a_{U,aq} \equiv a_{UO_2^{2+}}\ a_{NO_3^-}^2 = 4\gamma_U^3 m_U^3 \qquad (4)$$

in which γ_A and γ_U represent the stoichiometric activity coefficients of nitric acid and uranyl nitrate, respectively, and m_A and m_U are their molalities. The stoichiometric activity coefficients were computed as explained in Section 4.

3.2. Thermodynamic description of organic phase

In this work we make the classic assumption that deviations from ideality in organic phase originate only from association phenomena. In the present case, nonideality is assumed to be due to the formation of complexes with TBP. Besides, the system of the chemical species composing the organic phase (complexes + free TBP + free water + dodecane) is regarded as ideal. This approximation was proposed a long time ago for the description of associating nonelectrolyte solutions. The latter were called physically ideal by Dolezalek (1908) (Prausnitz et al., 1999) and semi-ideal by Scatchard (1921).

Then, we may write that the activity of every component of organic phase is equal to its true mole fraction (Prausnitz et al., 1999), which reads

$$a_Y = \zeta_Y \qquad (5)$$