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Modelling of nitric and nitrous acid chemistry for solvent extraction purposes

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Abstract

Nitric acid plays an integral role in the reprocessing of irradiated fuel. It is well known that nitric acid degrades; its often yellow hue signifies the presence of decomposition products. The decomposition of nitric acid is accelerated by temperature and radiolysis; therefore it is an important consideration in the reprocessing of nuclear fuels.

Thermal and radiolytic reactions of nitric acid result in the formation of redox active nitrogen species, of which nitrous acid is of particular concern, largely due to its redox reactions with plutonium and neptunium. Such reactions are important to understand as plutonium and neptunium can exist in a number of oxidation states; the oxidation state has a direct effect on the species extractability. The effect of nitrous acid is exacerbated as it catalyzes its own production and its reactions with actinides are typically autocatalytic; thus even micromolar quantities can have a large effect. A full understanding of solvent extraction requires us to understand actinide valence states which in turn require us to understand what nitrogen species are present and their concentrations.

As a first step in the overall objective of enhancing process models, the kinetic data for nitric acid decomposition reactions has been investigated in order to produce an initial dynamic model of decomposition under aqueous conditions. The identification of a set of kinetic reactions suitable for modelling has been the primary focus of this work. A model of nitric acid thermal decomposition will help develop a better understanding of nitric acid decomposition chemistry and enable better prediction of the oxidation states of species in solution. It is intended to later extend the model to include radiolytic reactions and then further to incorporate an organic phase in order to have a model which covers all decomposition routes for nitric acid within a nuclear fuel reprocessing scheme. The model will be used as a sub model for process models relating to nuclear fuel reprocessing to allow the nitric acid decomposition to be included and the effect of this on operations to be predicted. This is particularly relevant for models of maloperations where different fault scenarios can be investigated and the results of these predicted, as for example unusually high acidity could increase the yields of redox active species significantly altering actinide oxidation states.

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1. Introduction

Nitric acid (HNO_3) is integral to the reprocessing of irradiated fuel and as such understanding its behavior is important. Nitric acid undergoes thermal and radiolytic degradation, the products of which include nitrous acid (HNO_2) and nitrogen oxide species (NO_x). These species are of interest as they affect the valence state of actinide species. An example of why the production of nitrous acid is of particular concern for the solvent extraction process is its oxidation Pu(III), equation (1). Once formed, nitrous acid effectively catalyzes its own production as shown in equations (3) and (4), whereby NO is a product from equation (1).[1]

$$Pu(III) + HNO_2 + H^+ \rightarrow Pu(IV) + NO + H_2O \qquad (1)$$

$$NpO_2^{2+} + HNO_2 \rightarrow NpO_2^+ + NO_2^\bullet + H^+ \qquad (2)$$

$$HNO_3 + HNO_2 \rightleftharpoons 2NO_2^\bullet + H_2O \qquad (3)$$

$$NO + NO_2^\bullet + H_2O \rightleftharpoons 2HNO_2 \qquad (4)$$

A full understanding of solvent extraction requires us to understand actinide valence states which in turn require us to understand what nitrogen oxide species are present in nitric acid solutions and their concentrations. Developing a better understanding of nitric acid decomposition chemistry will result in an improved ability to support plant operations particularly for maloperations. This is achieved through capturing knowledge from available literature with a focus on thermal and radiolytic degradation of nitric acid, and an emphasis on reactions that generate and remove NO_x species and on quantifying HNO_3/NO_3^- and HNO_2/NO_2^- species.

Herein we describe the compilation of a set of kinetic data for nitric acid decomposition. This data set will be used in an initial dynamic model of thermal nitric acid decomposition under aqueous conditions. It is intended that this model will be updated to incorporate actinide redox chemistry, radiolytic reactions and later an organic phase so as to cover all decomposition routes of nitric acid within the nuclear fuel reprocessing scheme.

2. Nitric acid decomposition data set

2.1. Considerations for the model

Before compiling the kinetic data set for use in the model careful consideration is required to avoid potential error traps. One such trap is that the literature describes many non-elementary reactions for nitric acid and NO_x chemistry; as such it must be ensured that reactions are not repeated within the model. This was achieved by identifying non-elementary reactions and deducing their mechanism. This article does not go into the detail of this, but reports the final data set.

Once a set of reactions with available kinetic data were identified the most appropriate rate constant were selected for the relevant conditions. Rate constants in the literature for aqueous phase nitric acid and NO_x reactions are sporadic; suitable values that have been sourced have been included alongside the equations. It should be highlighted that the reactions with water do not have water included in the rate equations as at low concentrations of nitric acid water is in large excess. However, at very high nitric acid concentrations the concentration of water will affect the rate of these reactions. Therefore, the model will likely breakdown at very high nitric acid concentrations. These very high concentrations are out of the expected range of use for the model and expected concentrations, except in a very extreme maloperation which is unlikely. The rate constants reported here are those that will be utilized in the thermal aqueous model.

So as not to over-complicate the model, the number of species has been reduced where possible, as such N_xO_y species were excluded and non-elementary reactions were used instead. Caution was taken to ensure that reactions were not duplicated in this approach. Finally, most of the relevant data in the literature were measured in the temperature range of $25 \pm 3°C$, therefore the initial model will describe such conditions. Temperature dependence has been noted where available as it is desirable to include this in future versions.

2.2. Dissociation of nitric acid

$$HNO_3 \rightleftharpoons H^+ + NO_3^- \qquad (5)$$

Before considering the decomposition of nitric acid, one must first consider the dissociation of nitric acid (5), as this affects the reactions that it undergoes. The dissociation of nitric acid in aqueous solutions at various concentrations has been measured by ^{1}H NMR,[2-6] X-ray photoelectron,[7] Raman[8-10] and IR[11] spectroscopy and calculated from activity coefficients[12] at 25°C, shown in Fig. 1 (a). The data from Davis and de Bruin[12] was from fitting the activity coefficient for un-dissociated acid vs. stoichiometric nitric acid concentration using the Setchenov approximation together with dissociation data from a number of