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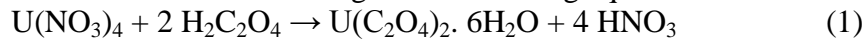
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Thermodynamic study of uranium oxalate precipitation: solubility and supersaturation ratio determination

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Oxalic precipitation is usually applied to process radioactive wastes or to recover actinides from a multicomponent solution. The driving force of precipitation reactions is given by supersaturation, which characterizes the deviation from the equilibrium state. Precipitation mechanisms, such as nucleation, crystal growth or agglomeration, are governed by supersaturation, which is therefore a crucial parameter to determine for process control. This work focuses on the description of a thermodynamic study of uranium (IV) oxalate precipitation in order, on the one hand, to develop a solubility model and, on the other hand, to estimate supersaturation ratio.

Uranium (IV) oxalate can be precipitated by mixing an uranium (IV)-nitric acid solution and an oxalic acid solution according to the following equilibrium:



The supersaturation ratio (S) is defined using the reagent activities (a_i) as follows:

$$S = \sqrt[3]{\frac{a_{\text{U}^{4+}} \times a_{\text{C}_2\text{O}_4^{2-}}^2}{a_{\text{U}^{4+},eq} \times a_{\text{C}_2\text{O}_4^{2-},eq}^2}} \quad (2)$$

where eq denotes the equilibrium state.

As uranium (IV) ions can be oxidized by nitrous acid HNO_2 , present in small quantities in nitric acid media due to the dynamic equilibrium of this solution, hydrazine nitrate is added to stabilize the uranium (IV) ions for several months.

As very few information is available in the literature dealing with uranium oxalate [1,2], an experimental study was performed in order to determine solubilities over a wide range of conditions. The data acquisitions were carried out by dissolution of uranium oxalate powder (Fig1) in aqueous solutions with different nitric acid, oxalic acid and hydrazine nitrate concentrations at controlled temperature of 25°C and protected from light. Experimental results are of the same order of magnitude as the values of the literature (see Fig2) in spite of experimental differences between the studies (duration of the experiment, analytical methods...).

The mathematical treatment of experimental results allowed a thermodynamic model for both solubility and supersaturation ratio of uranium oxalate to be developed. The comparison between the model and the experimental data points out a good agreement as shown in the figure 3.

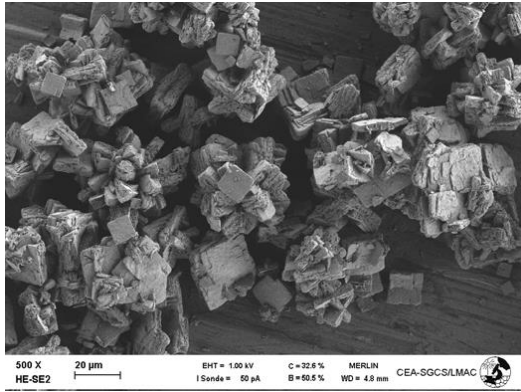


Fig1: Uranium (IV) oxalate crystals (SEM)

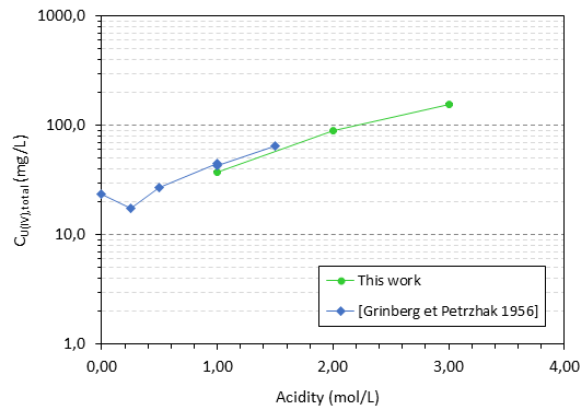


Fig2: Comparison this work / literature

The thermodynamic model was then applied to compare two different approaches to determine the supersaturation ratio described in the literature: either from the free ion concentration and the ionic activity coefficient (eq 1) or from the total concentration of species using the mean stoichiometric activity coefficients (eq 3):

$$S = \sqrt[3]{\frac{a_{U(IV)} \times a_{Ox}^2}{a_{U(IV),eq} \times a_{Ox,eq}^2}} \quad (3)$$

The comparison leads to the very interesting conclusion that both approaches are equivalent as they result in the same supersaturation values as shown in figure 4.

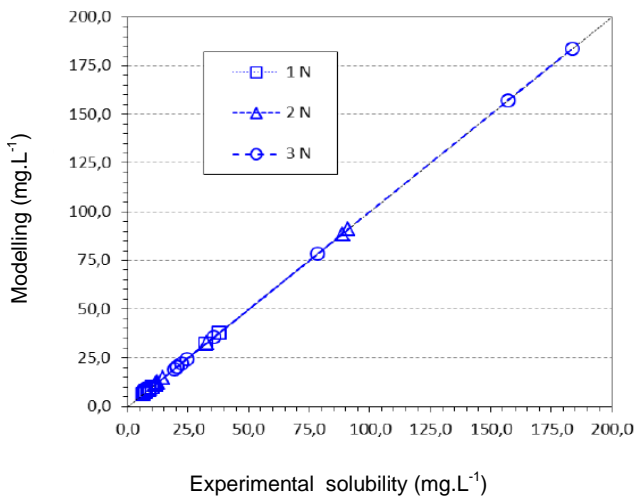


Fig3: Comparison experimental/modelling

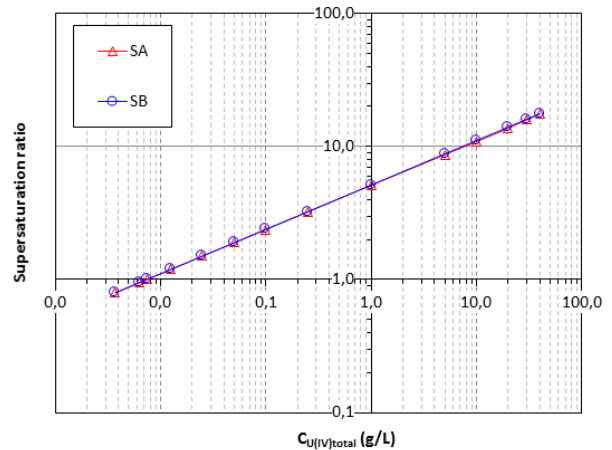


Fig 4: comparison equations (2) / (3)

[1] Grinberg, A.A., Petezhak, G.I., 1956. A Study of the Oxalate Compounds of Tetravalent Uranium. Trudy Radiyevogo Instituta Khimiya i Gokhimiya, 7, 18-80.

[2] Grinberg, A.A., Petrzhak, G.I., 1963. Supplementary data on the solubility of the oxalate of quadrivalent uranium. Radiochemistry, 5, 319-329.