Applied thermodynamics in nuclear industry modelling of precipitation processes

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DE LA RECHERCHE À L'INDUSTRIE

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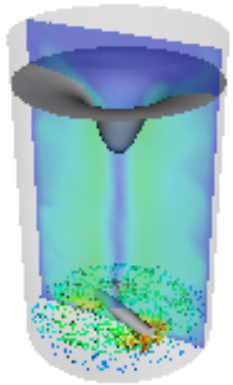

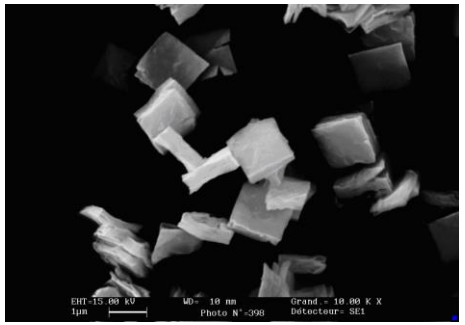

Applied thermodynamics in nuclear industry: modelling of precipitation processes

Taking account for ideality deviation in neodymium oxalate and uranium peroxide precipitation

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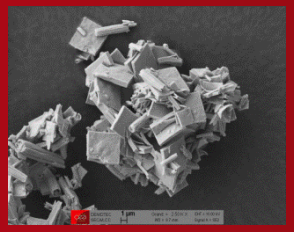
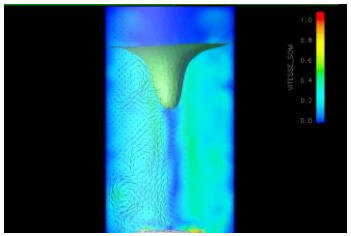


PRECIPITATION PROCESS MODELLING

Precipitation Modelling :

Coupling Chemistry/Turbulence

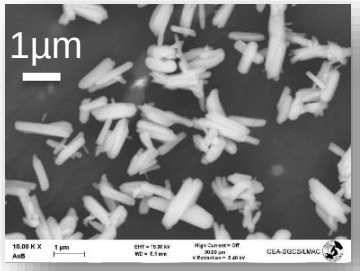


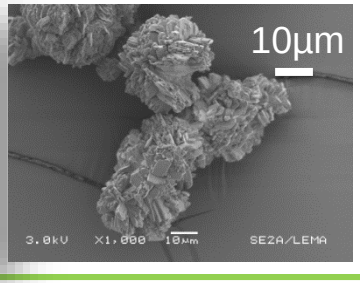
Population balance

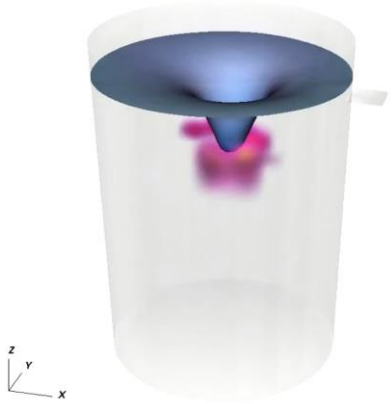
CFD simulation

$$\frac{1}{V}\frac{\partial V\varphi(L,t)}{\partial t}+\frac{\partial G\varphi(L,t)}{\partial L}+\frac{Q_o\varphi\ (L,t)-Q_i\varphi_i(L,t)}{V}=R_N\ \delta(L)$$

Kinetics + **Thermodynamics**







3D LES

Calculation of Supersaturation

➢ Objective:

- Calculation of the driving force = supersaturation S during the precipitation process

$$\nu_+ M^{z+} + \nu_- X^{z-} \xrightarrow{H_2O} \underline{M_{\nu+}X_{\nu-}.xH_2O} \qquad S = \left(\frac{a_{M^{z+}}^{\nu_+} \times a_{X^{z-}}^{\nu_-}}{a_{M^{z+},eq}^{\nu_+} \times a_{X^{z-},eq}^{\nu_-}} \right)^{\frac{1}{\nu_+ + \nu_-}}$$

- In concentrated solutions involving salts and ions of high valence

➢ Coefficient activity models:

- **Physico-chemical approaches**
  Pitzer equations

➡ **Inconvenient ☹ ⇨ Heavy implementation + many parameters to be adjusted**

- **Empirical approaches**
  Bromley method or
  SIT specific interaction theory

➡ **Good compromise ☺: Easy-to-use / accuracy for process modelling and CFD simulations**

Applications

➢ **2 examples of applications in nuclear industry:**

Actinide / lanthanide oxalate precipitation

very low solubility ⇒ widely used in the Ln and An separation, analytical chemistry and treatment of high-level liquid wastes - in nitric acid medium

Uranium peroxide precipitation

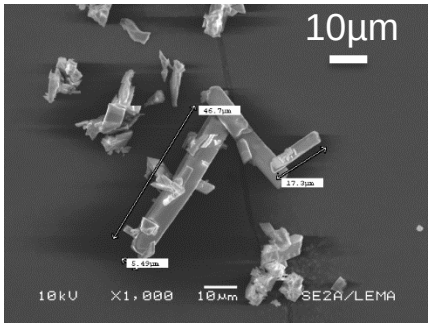
From uranium ore
U < 1%

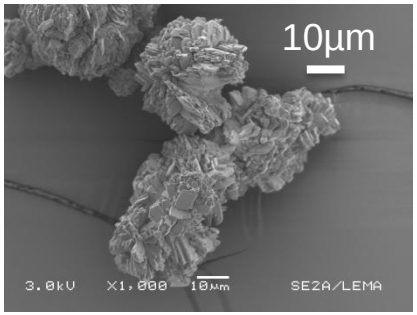
Uranium ore processing

Crushing grinding → Leaching → U extraction → **Precipitation**

Purification, concentration and sharping step

to yellow cake
U ~ 75 %





- 2 -
Neodymium oxalate precipitation
The Bromley method

Bromley model

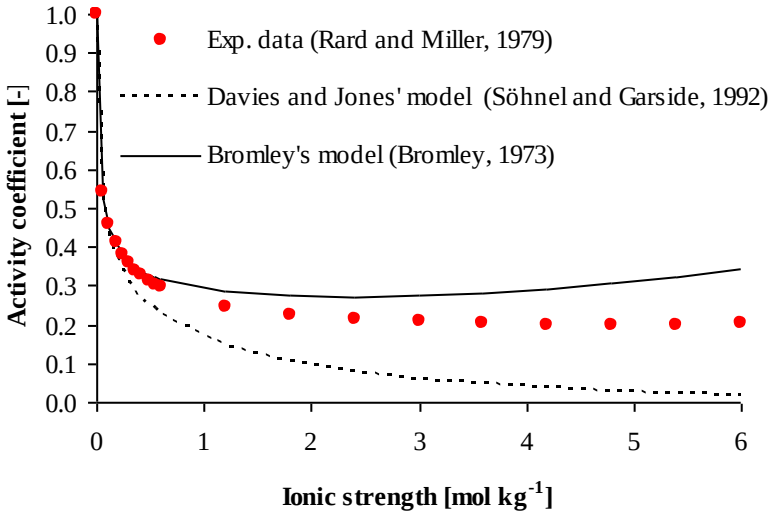
Bromley method for multicomponent systems

- Based on the contributions B_{M1X1} of every electrolytes present in solution

$$B_{M_1X_1} = B_+ + B_- + \delta_+\delta_-$$

Neodymium individual contributions

- Tabulated by Bromley in 1973
- After ⇒ New experimental binary data published later for neodymium nitrate and chloride



- ✓ The Bromley model not in good agreement
- ✓ Determination of new values for neodymium contributions (B_+,δ_+) using tow salts:

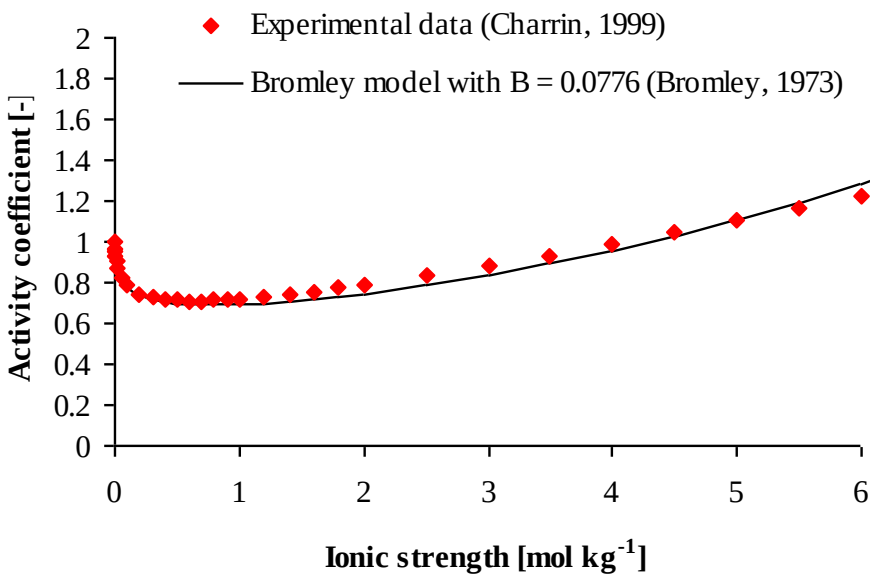
  Neodymium nitrate + Neodymium chloride

$$B_{Nd(NO_3)_3} = B_{Nd^{3+}} + B_{NO_3^-} + \delta_{Nd^{3+}}\delta_{NO_3^-}$$
$$B_{NdCl_3} = B_{Nd^{3+}} + B_{Cl^-} + \delta_{Nd^{3+}}\delta_{Cl^-}$$

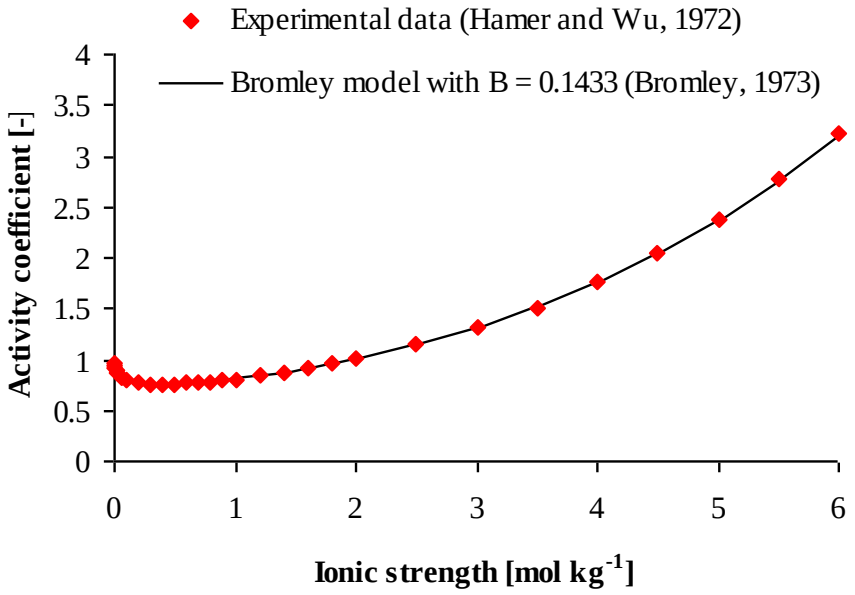
New contributions of Nd^{3+} in the Bromley model

1st STEP: Validation of the Bromley individual contributions for NO_3^- and Cl^- from experimental data of HNO_3 and HCl

HNO_3



HCl



Very good agreement between exp. data and the Bromley model combined with the contributions of HNO_3 and HCl

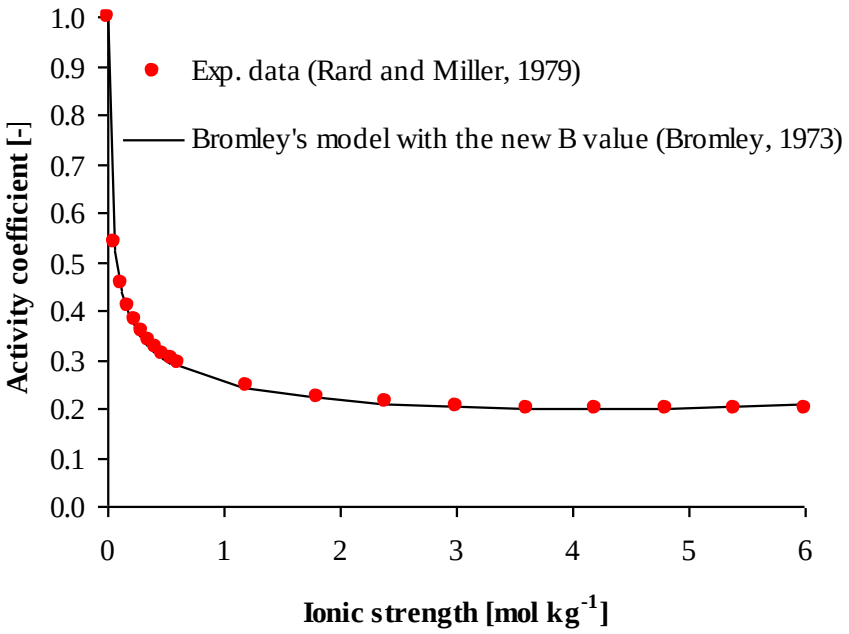
[1] Rard J.A. and Miller D.G, 1979. J. Chem. Eng. Data 24, 348-353

[2] Spedding et al., 1976. J. chem. Eng. Data 21, 341-360.

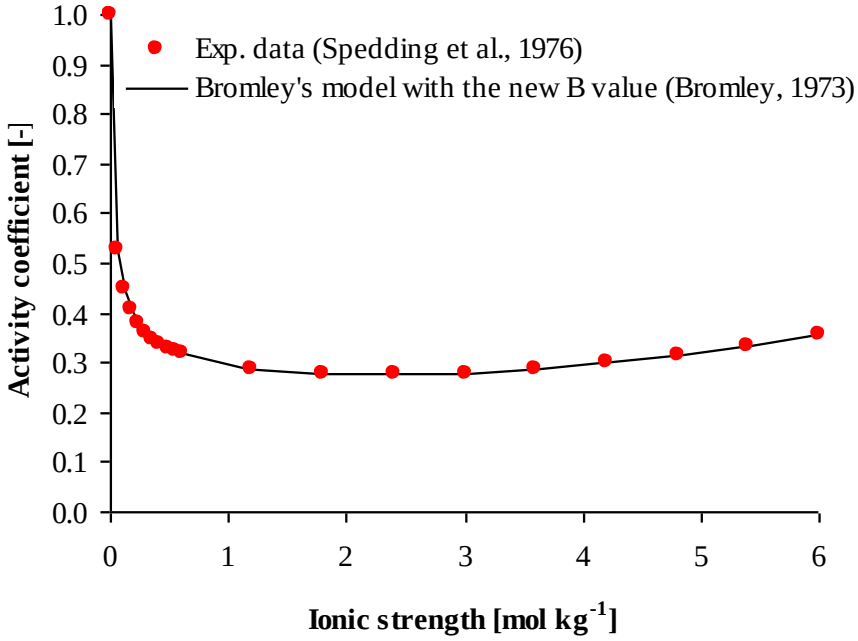
New contributions of Nd^{3+} in the Bromley model

2nd STEP: Determination of the salt contributions and adjustment of the Bromley contributions for Nd^{3+}

$Nd(NO_3)_3$ => $B_{Nd(NO_3)_3} = 0.0511$



$NdCl_3$=> $B_{NdCl_3} = 0.0855$



Very good agreement between exp. data and the Bromley model with the new contributions of $Nd(NO_3)_3$ et $NdCl_3$

$B_{Nd^{3+}} = 0.0321$ and $\delta_{Nd^{3+}} = 0.163$

$B_{Nd^{3+}} = 0.035$ and $\delta_{Nd^{3+}} = 0.27$
Bromley's values

Lalleman, Bertrand, Plasari, Sorel, Moisy, Chemical Engineering Science 77 (2012) 189-195

Application of the Bromley model to ternary mixtures

- **These new contributions ⇒ application to ternary solutions**

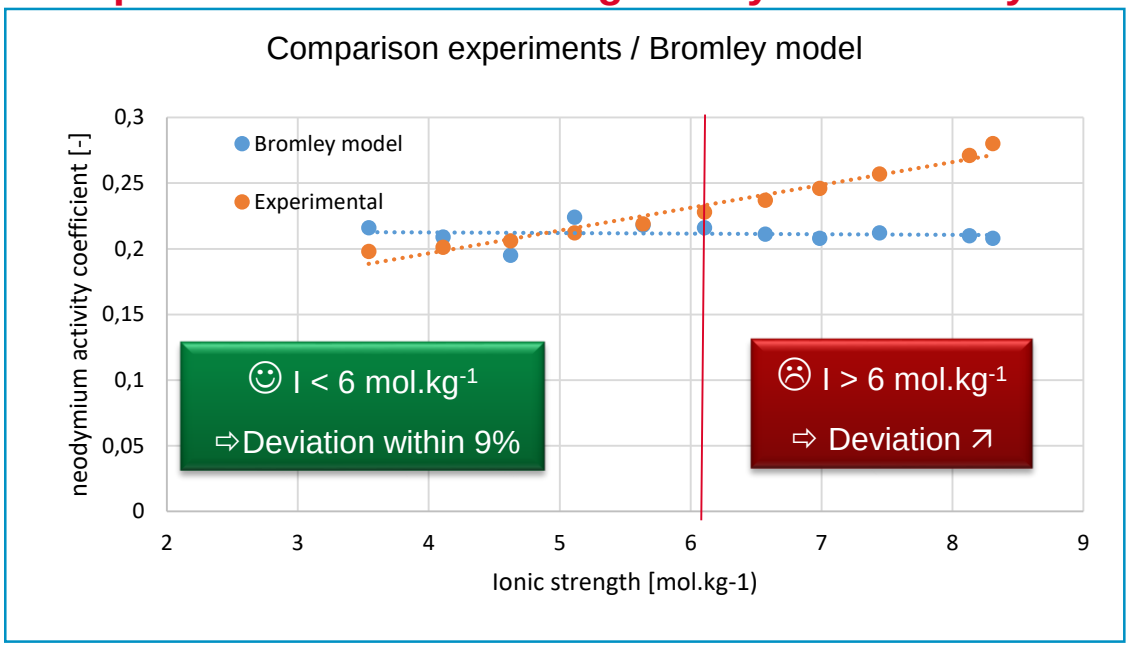
  $Nd(NO_3)_3/HNO_3/H_2O$

- **Measurements of water activity a_W in ternary mixtures**
  - Using the concept of simple solutions and Mikulin equation*:

    a_W ⇒ activity coefficients $\gamma_{Nd(NO3)}^{mixture}$

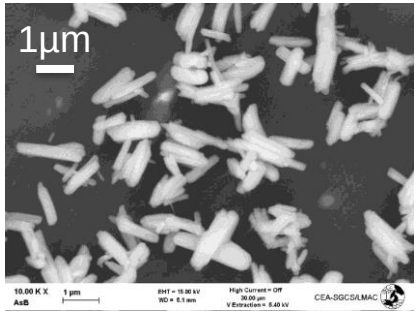
Variable-impedance hygrometer AW Center™ (Novasina)

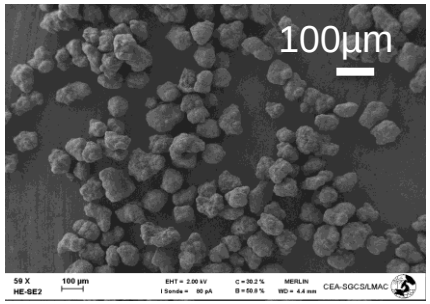
- **Comparison with the values given by the Bromley method**



* Charrin et al., 1999. Radiochim. Acta 86, 143-149.

* Kappenstein et al., 2000. Phys. Chem. Chem. Phys. 2, 2725-2730





- 3 -
Uranium Peroxide precipitation
SIT

Specific Interaction Theory SIT

Precipitation in sulphuric media

$$UO_2^{2+} + O_2^{2-} + 4H_2O \leftrightarrow UO_2(O_2) \cdot 4H_2O$$

UO_2SO_4 / H_2SO_4 / Na_2SO_4 / H_2O_2 / H_2O

- Bromley method not adapted: sulphuric acid partially dissociated
- + no data for hydrogen peroxide

$$S = \sqrt{\frac{a_{UO_2^{2+}} a_{O_2^{2-}}}{a_{UO_2^{2+},eq} a_{O_2^{2-},eq}}}$$

Specific Interaction Theory* **

- Based on specific interaction coefficients between ions of opposite charge

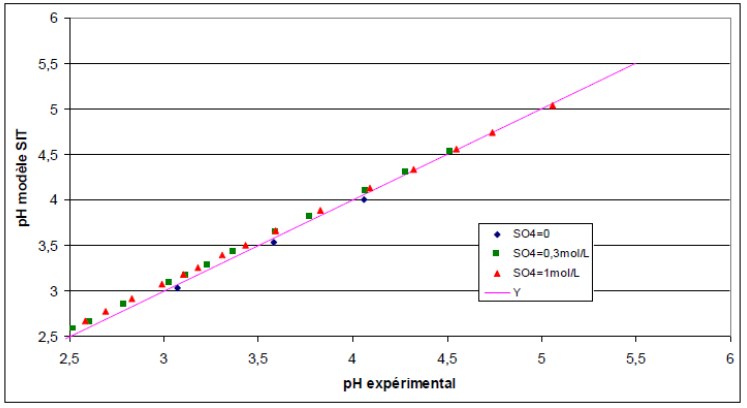
$$\log\gamma_i = -z_i^2 \frac{a\sqrt{I}}{1+b_{i,j}\sqrt{I}} + \sum_j \varepsilon(i,j) m_j$$

← Specific interaction coefficient

1st step: Validation of the specific interaction coefficients of ions: SO_4^{2-}, HSO_4^- and H^+

- Comparison between experimental pH and pH calculated using SIT in ternary systems H_2SO_4 - Na_2SO_4 - H_2O

Very good agreement between experimental pH and SIT



*T. Vercouter, B. Amekraz, C. Moulin, E. Giffaut and P. Vitorge, Inorg. Chem., 2005, 44, 7570–7581Bromley L.A., 1973. AIChE J. 19, 313-320

**R. M. Cigala, F. Crea, C. De Stefano, G. Lando, D. Milea and S. Sammartano, Geochim. Cosmochim. Acta, 2012, 87, 1–20

Determination of specific interaction coefficients

➢ 2nd step: determination of the specific interaction coefficients of other ions

- from experimental data of uranium peroxide solubility (ICP-AES and ICP-MS)

- And by application of the SIT hypothesis:
  - Commutative function $\varepsilon(i,j) = \varepsilon(j,i)$
  - Independent from I
  - $\varepsilon(i,j) = 0$ for ions of same charge
  - For unknown coefficients ⇨ analogies between ions of same charge

➡ **Determination of a set of values for SI coefficients:**

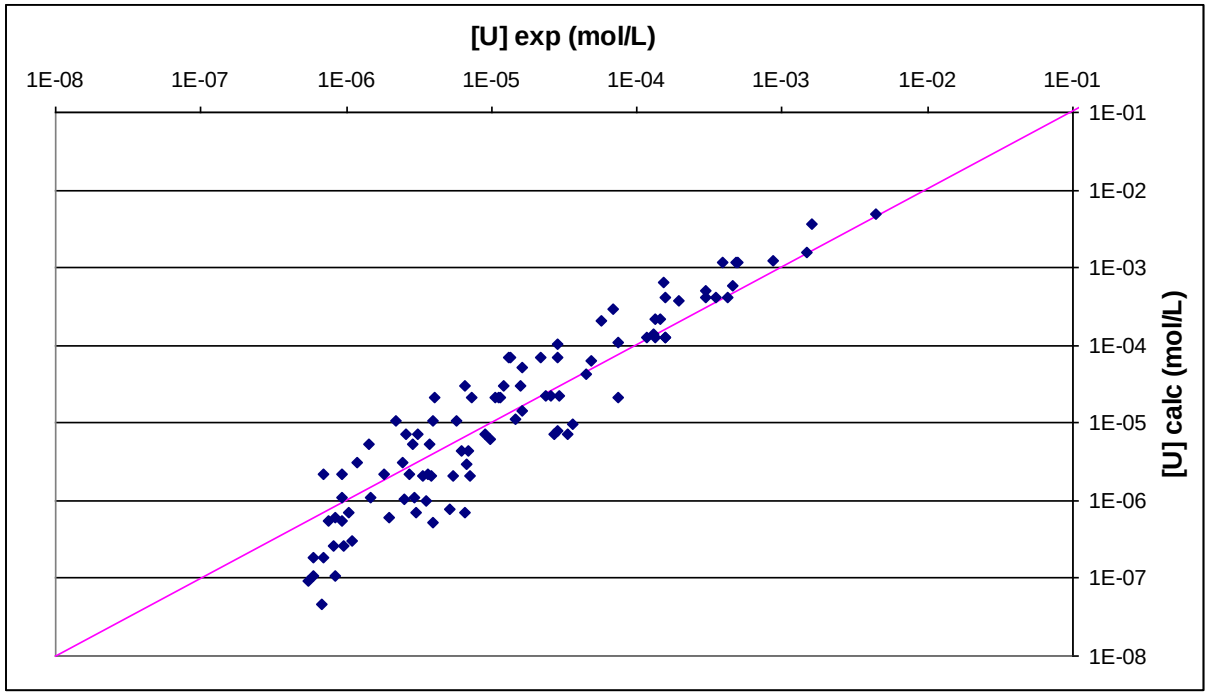
- **blue:** from the literature
- **green**: by analogy
- **red:** optimised values from experimental data

	ε (kg.mol^{-1})		
	UO_2^{2+}	Na^+	H^+
SO_4^{2-}	0,12	-0,12 ± 0,06 → **-0,18**	0 → **0,046**
HSO_4^-	0,46 ± 0,03 → 0,46	-0,01 ± 0,02 → **-0,03**	-0,01 ± 0,02 → -0,01
$UO_2(SO_4)_2^{2-}$	0,12	-0,12 ± 0,06 → **-0,18**	-0,12 ± 0,06 → -0,12
$UO_2(SO_4)_3^{4-}$	0,24	**-0,06**	-0,24

* Bromley L.A., 1973. AIChE J. 19, 313-320

Determination of specific interaction coefficients

- **Comparison between experimental and calculated solubilities over a wide range of operating conditions**



Good agreement
higher deviations at low sulphate concentrations ⇨ very low solubilities ⇨ high analytical uncertainties

Conclusion and outlooks

- **For precipitation process modelling ⇒ development of thermodynamic models to calculate the supersaturation taking into account the nonideality of the solutions**
- **On the basis of simple empirical methods**
- **Advantage ⇒ easy to use and accurate**
- **Application ⇒ Experiments**
  - New individual contributions of the neodymium ion for the Bromley model
  - New specific interaction coefficients for SIT
- **Comparison between experiments and models ⇒ a good agreement**

These methods can be applied to many other systems provided
- the binary data of 2 salts are known for the Bromley model
- solubility measurements can be performed for SIT

Scientific team

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Thank you for your attention !