Electronic Supplementary Material (ESI) for Dalton Transactions.
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Thermodynamic description of Tc(IV) solubility and hydrolysis in dilute to concentrated NaCl, $MgCl_2$ and $CaCl_2$ solutions

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Supplementary Information

Specific ion interaction theory (SIT)

The SIT approach is based on the extended Debye-Hückel law, and accounts for the influence of electrostatic, non-specific long-range, binary interactions between oppositely charged ions to calculate activity coefficients. SIT defines the activity coefficient of an ion *j*:

$$\log \gamma_j = -z_j^2 D + \sum_k \varepsilon(j,k)\, m_k \qquad \text{(A1)}$$

where z_j is the charge of the ion *j*, *D* is the Debye-Hückel term ($D = A\sqrt{I_m}/1 + Ba_j\sqrt{I_m}$), $\varepsilon(j,k)$ is the specific ion interaction coefficient of the ion *j* with the counter-ion *k* of the background electrolyte and m_k is the molality of the ion *k*.

The validity of SIT is considered to be limited to $I \leq 3.5$ M[1]. It is to note that recent experimental studies providing a thermodynamic description of actinide and lanthanide systems have demonstrated the good performance of SIT in concentrated $MgCl_2$ and $CaCl_2$ solutions with $I \leq 13.5$ M[2-4], although this observation cannot be generalized to other systems.

Pitzer model

The Pitzer model describes the effect of ionic strength with short-range binary interactions, interactions between ions of the same charge, between charged ions and neutral species as well as ternary interactions[5]. This results in a more realistic modelling of mean activity coefficients especially at medium and high ionic strengths, at the cost of requiring a significantly large number of parameters for the calculation of activity coefficients.

In mixed electrolytes with cations c, c′ and anions a, a′, the individual activity coefficients for a cation M and an anion X are described by equations (A2) and (A3), respectively:

$$\ln \gamma_M = z_M^2 F + \sum_a m_a \left(2\, B_{Ma} + Z\, C_{Ma}\right) + \sum_c m_c \left(2\, \Phi_{Mc} + \sum_a m_a \psi_{Mca}\right)$$

$$+ \sum_{a<}\sum_{a'} m_a m_{a'} \psi_{Maa'} + z_M \sum_{c<}\sum_a m_c m_a C_{ca} + 2\sum_n m_n\, \lambda_{nM} \qquad \text{(A2)}$$

$$\ln \gamma_X = z_X^2 F + \sum_c m_c \left(2\, B_{cX} + Z\, C_{cX}\right) + \sum_a m_a \left(2\, \Phi_{Xa} + \sum_c m_c \psi_{cXa}\right)$$

$$+ \sum_{c<}\sum_{c'} m_c m_{c'} \psi_{cc'X} + |z_X| \sum_{c<}\sum_a m_c m_a C_{ca} + 2\sum_n m_n\, \lambda_{nX} \qquad \text{(A3)}$$

where $Z = \sum_i m_i |z_i|$, and F includes the Debye-Hückel term and the ionic strength dependence specific to the salt. The Pitzer model defines binary parameters $\beta^{(0)}_{MX}$, $\beta^{(1)}_{MX}$, $\beta^{(2)}_{MX}$ and $C^{(\varphi)}_{MX}$ specific to the interacting ions. $\theta_{aa'}$ (or $\theta_{cc'}$) and $\Psi_{aa'c}$ (or $\Psi_{acc'}$) are the mixing parameters in the case of ternary and higher electrolyte systems and their contribution is expected to be very small except for mixing of non-identical charged species. The interactions between the ions and the neutrally charged species are defined with λ_{nM} (or λ_{nX}). The formulism of the terms used in the Pitzer equations are given elsewhere[5].

Comparison of Tc(IV) solubility data generated in this study and reported in Hess et al. (2004)

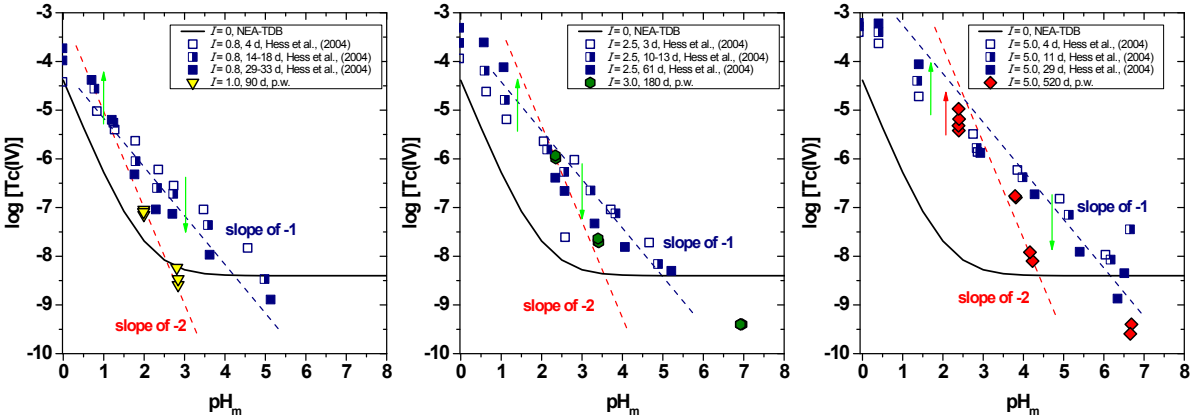

Figure A1. Experimental solubility data of Tc(IV) determined in the present work and reported in Hess *et al.* (2004) for dilute to concentrated HCl–NaCl systems. Solid lines correspond to overall solubility curve of $TcO_2 \cdot 1.6H_2O(s)$ calculated for $I = 0$ with the current NEA–TDB thermodynamic selection. Dashed lines indicate slopes of –2 and –1 in the solubility diagram.

Linear SIT-regression plots of the solubility reactions $TcO_2 \cdot 0.6H_2O(s) + n\ Ca^{2+} + 3.4\ H_2O(l) \Leftrightarrow Ca_nTcO(OH)_5^{(2n-3)} + 3\ H^+$ with $n = 0 - 4$

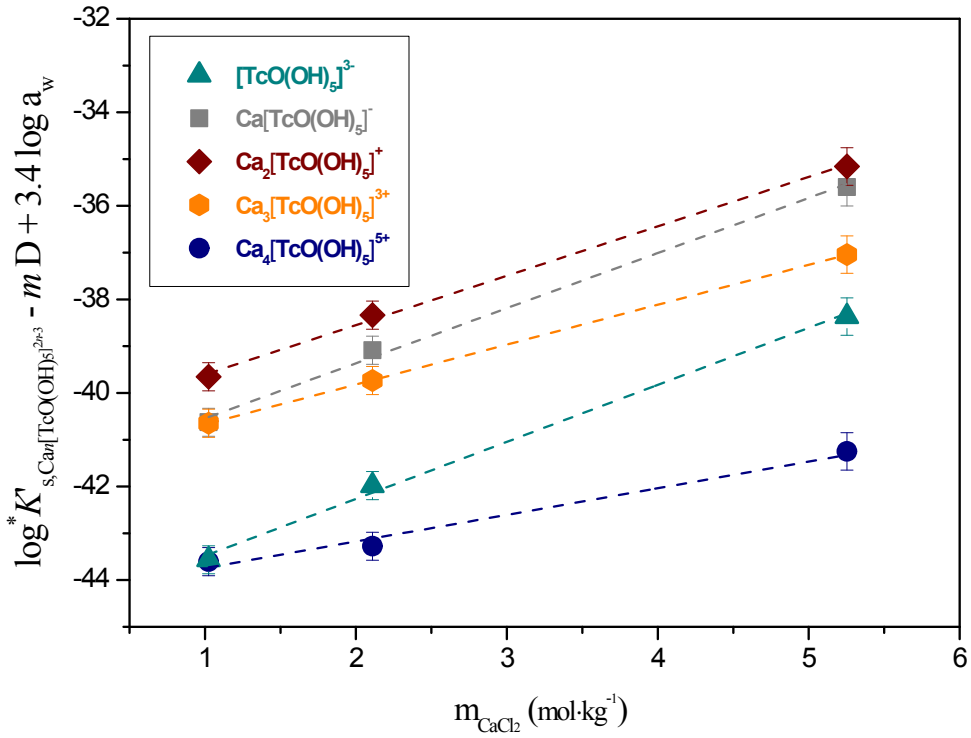

Figure A2. SIT-plot for the solubility reactions $TcO_2 \cdot 0.6H_2O(s) + n\ Ca^{2+} + 3.4\ H_2O(l) \Leftrightarrow Ca_nTcO(OH)_5^{(2n-3)} + 3\ H^+$ with $n = 0 - 4$ considering the conditional equilibrium constants $log^* K'_{s,Ca_nTcO(OH)_5^{(2n-3)}}$ determined in dilute to concentrated $CaCl_2$ solutions.

Comparison of the plots for conditional equilibrium constants for $Ca_nTcO(OH)_5^{(2n-3)}$ (with n = 0 – 4) *vs.* m_{CaCl2}

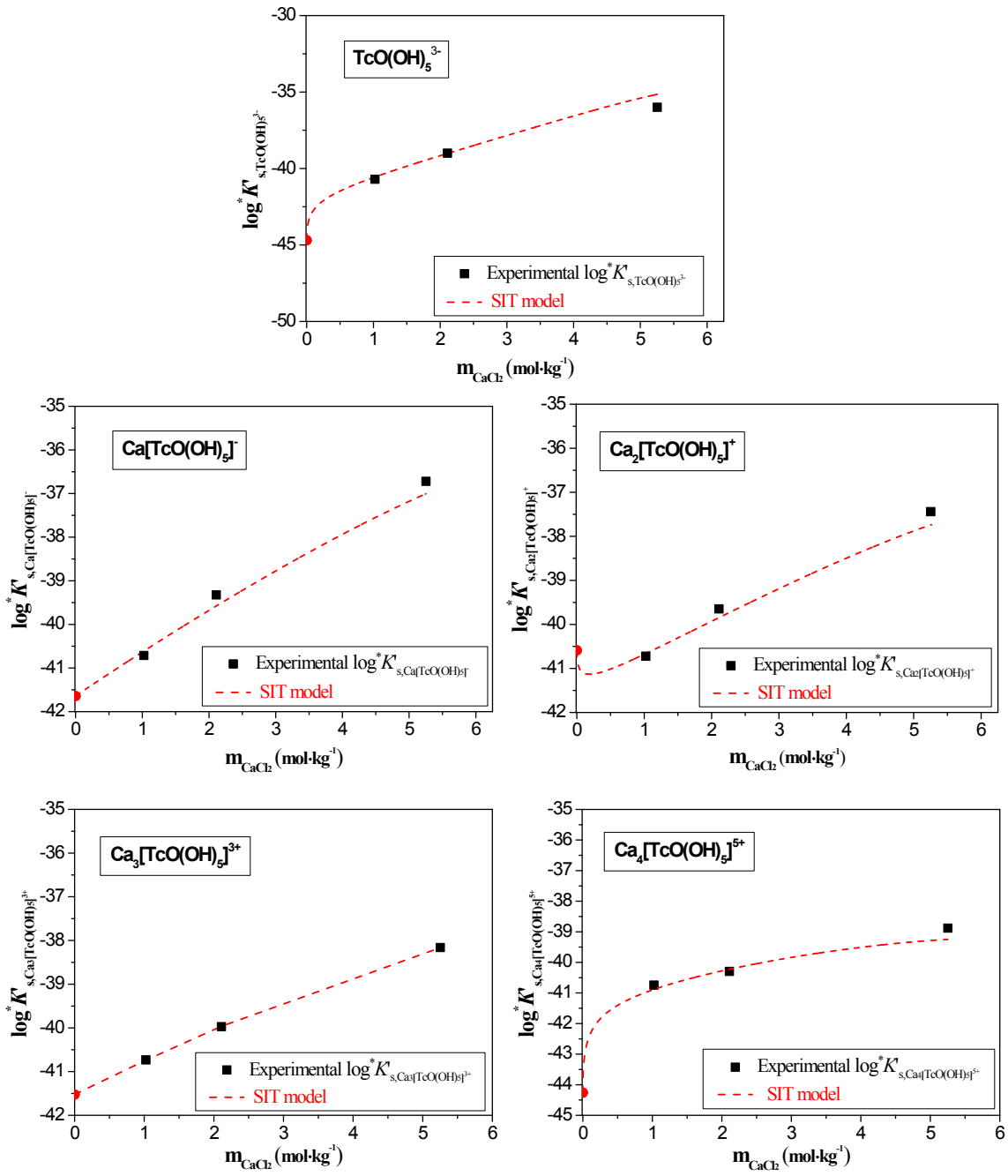

Figure A3. Conditional equilibrium constants for $Ca_nTcO(OH)_5^{(2n-3)}$ (with n = 0 – 4) as a function of $CaCl_2$ molality; experimental values (symbols) and calculated functions based on the SIT (dashed line).

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