Supporting information

Demonstration of equation

The distribution ratio of Pa^{V+} when [NTA] = 0 is defined as (equation S.1):

$$D_0 = \frac{[Pa(TTA)]_{org}}{[PaO(OH)^{2+}] + [PaO(OH)_2^+]} \qquad \text{S.1}$$

In presence of ligand, the distribution ratio is defined as (equation S.2):

$$D = \frac{[Pa]_{org}}{[Pa]_{aq}} = \frac{[Pa(TTA)]_{org}}{[PaO(OH)^{2+}] + [PaO(OH)_2^+] + [Pa(NTA)] + [Pa(NTA)_2]} \qquad \text{S.2}$$

The ratio $\frac{D_0}{D}$ is written according to equation S.3:

$$\frac{D_0}{D} = 1 + \frac{[Pa(NTA)] + [Pa(NTA)_2]}{[PaO(OH)^{2+}] + [PaO(OH)_2^+]} \qquad \text{S.3}$$

According to equation 7, $[PaO(OH)_2^+]$ can be expressed as (equation S.4):

$$[PaO(OH)_2^+] = \frac{K_2 . [PaO(OH)^{2+}]}{[H^+]} \qquad \text{S.4}$$

Inserting equation S.4 into equation S.3 and rearranging:

$$\frac{D_0}{D} = 1 + (\frac{[H^+]}{[H^+] + K_2})(\frac{([Pa(NTA)] + [Pa(NTA)_2])}{[PaO(OH)^{2+}]}) \qquad \text{S.5}$$

According to equation 6, species $Pa(NTA)$ and $Pa(NTA)_2$ can be written according to the following equations S.6 and S.7:

$$Pa(NTA) = \beta_1^{cond} = \frac{[PaNTA]}{[Pa][NTA]} \qquad \text{S.6}$$

$$Pa(NTA)_2 = \beta_2^{cond} = \frac{[Pa(NTA)_2]}{[Pa][NTA]^2} \qquad \text{S.7}$$

Inserting equations S.6 and S.7 into equation S.5 and rearranging:

$$\frac{D_0}{D} = 1 + \left(\frac{[H^+]}{[H^+] + K_2}\right)(\beta_1^{cond})[NTA] + \beta_2^{cond}[NTA]^2$$

Determination of acidity constant K_{a_i} of NTA

Thakur et al. determined the values of the acidity constants for different ionic strength (0.304; 0.511; 1.03; 2.18; 3.44; 4.92; 6.60 molal) in $(Na,H)ClO_4$ medium at 25°C.[21] The pK_a values are listed in Table S. 1.

Table S. 1 : Values of the acidity constants and their uncertainties extracted from the work of Thakur et al. [21]

Ionic strength (m)	pKa_2	pKa_3	pKa_4
0.304	1.85 ± 0.07	2.75 ± 0.01	9.44 ± 0.06
0.511	1.84 ± 0.05	2.66 ± 0.09	9.35 ± 0.02
1.03	1.82 ± 0.06	2.61 ± 0.06	9.28 ± 0.08
2.18	1.94 ± 0.05	2.53 ± 0.08	9.12 ± 0.03
3.44	2.03 ± 0.05	2.64 ± 0.07	9.33 ± 0.04
4.92	2.09 ± 0.05	2.69 ± 0.08	9.41 ± 0.02
6.60	2.14 ± 0.05	2.71 ± 0.08	9.56 ± 0.06

From these values, the $pKa_i + \Delta z_i^2.D - \varepsilon(H^+,ClO_4^-).I_{(m)}$ plots as function of the ionic strength have been made taking into account the parameters of the specific interaction theory (SIT)(Figure S. 1 to Figure S. 3), with:

$\Delta z_i^2 = cz_c^2 + dz_c^2 - az_c^2 - bz_c^2$ (for a reaction aA + bB ⇌ cC + dD)

$I_{(m)}$: ionic strength in molal unit

D : coefficient of Debye-Hückel : $D = \frac{A\sqrt{I_{(m)}}}{1 + B.a.\sqrt{I_{(m)}}}$ with A the Debye Huckel's constant (A= 5091) [41] and Ba an empirical parameter ($1.5\ kg^{1/2}.mol^{1/2}\ at\ 25°C$) [42].

$\varepsilon_{i,j}$: specific interaction coefficients representing the interaction between the ions i and j.

$\varepsilon(H^+,ClO_4^-) = 0.14$

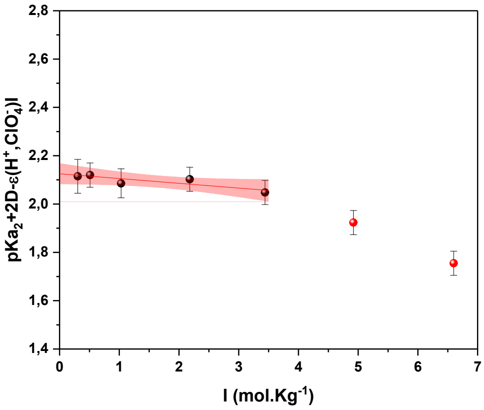

Figure S. 1 : Variation of $pKa_2 + 2.D - \varepsilon(H^+,ClO_4^-).I$ as a function of the ionic strength at 25°C.

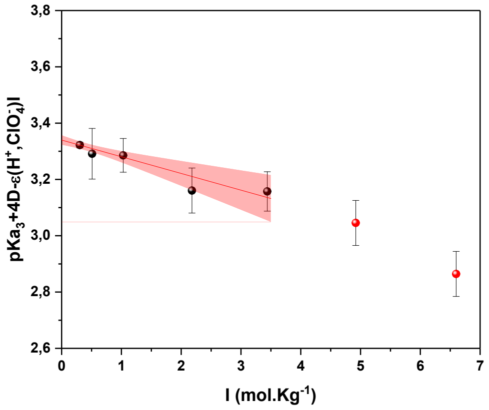

Figure S. 2 : Variation of $pKa_3 + 2.D - \varepsilon\left(H^+,ClO_4^-\right).I$ as a function of the ionic strength at 25°C.

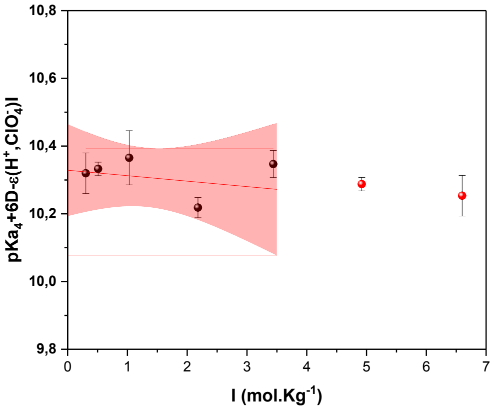

Figure S. 3 : Variation of $pKa_4 + 2.D - \varepsilon\left(H^+,ClO_4^-\right).I$ as a function of the ionic strength at 25°C.

Linear regressions of $pKa_i + \Delta z_i^2.D - \varepsilon\left(H^+,ClO_4^-\right).I_{(m)}$ as a function of the ionic strength were plotted to I = 3.5 m, molality corresponding to the validity limit of the SIT model.

These regressions made it possible to determine the values of pKa in our experimental conditions (1.051 molal in $(Na,H)ClO_4$ that is 1.0 molar $(Na,H)ClO_4$).

Specific interaction coefficients were calculated at 1 M $(Na,H)ClO_4$ at 25°C for each species and are grouped in Table S. 2.

Table S. 2: Specific interaction coefficients for each species at 1 M $(Na,H)ClO_4$ at 25°C.

$\varepsilon\left(Na^+,H_3NTA\right)$	0
$\varepsilon\left(Na^+,H_2NTA^-\right)$	0.02 ± 0.01
$\varepsilon\left(Na^+,HNTA^{2-}\right)$	0.08 ± 0.05
$\varepsilon\left(Na^+,NTA^{3-}\right)$	0.10 ± 0.26

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42 Allard, B. Banwart, A. Bruno, J. Ephrain, J.H. Graueur, R. Grenthe, I. Hadermann, J. In *Modelling in aquatic chemistry*, Grenthe I.; Puigdomenech I. OECD publication, Paris, 1997.