Solubility of NaNpO$_2$CO$_3$xH$_2$O(s) in NaClO$_4$ solution [91KIM/KLE, 94NEC/RUN]

The dissolution equilibrium of NaNpO$_2$CO$_3$xH$_2$O(s) can be written as

$$NaNpO_2CO_3\,xH_2O(s) \;+\; 2\,H^+ \;<=>\; Na^+ \;+\; NpO_2^+ \;+\; CO_2(g) \;+\; (x+1)\,H_2O$$
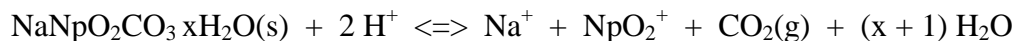
This formulation corresponds directly to the experimental data. It is independent of carbonic acid dissociation constants or carbonate activity coefficients, on which there is still ongoing discussion within the NEA-TDB project.

The H$^+$ concentration is obtained from the measured pH$_{(obs)}$ (the experimental relations between log [H$^+$] and pH$_{(obs)}$ are given in [91KIM/KLE, 94NEC/RUN]), the NpO$_2^+$ concentration is measured, Na$^+$ is given by the NaClO$_4$ concentration and pCO$_2$ = 10$^{-3.52}$ bar in the solubility experiments discussed.

The following equilibrium constants log K$_s$ for the reaction above can be derived directly from the experimental data:

> 0.1 M NaClO$_4$: log K$_s$ = 7.28 (a$_w$ = 0.997)
> 1.0 M NaClO$_4$: log K$_s$ = 7.37 (a$_w$ = 0.966)
> 3.0 M NaClO$_4$: log K$_s$ = 7.54 (a$_w$ = 0.884)
> 5.0 M NaClO$_4$: log K$_s$ = 7.82 (a$_w$ = 0.777)

If we apply the SIT extrapolation to these constants

$$\log K^\circ_s \;=\; \log K_s(I) \;+\; (x+1)\log a_{H2O} \;-\; 0\,D \;+\; \Delta\varepsilon\,I$$

and use the interaction coefficients for H$^+$ and Na$^+$ from the NEA-TDB, we obtain log K$^\circ_s$ = 7.28 (corresponding to log K$^\circ_{sp}$ = - 10.88) and

> $\Delta\varepsilon$ = -0.06 ± 0.02 and ε(NpO$_2^+$/ClO$_4^-$) = 0.21 ± 0.05
> (if we assume an unhydrated solid with x = 0)

or

> $\Delta\varepsilon$ = -0.01 ± 0.01 and ε(NpO$_2^+$/ClO$_4^-$) = 0.26 ± 0.04
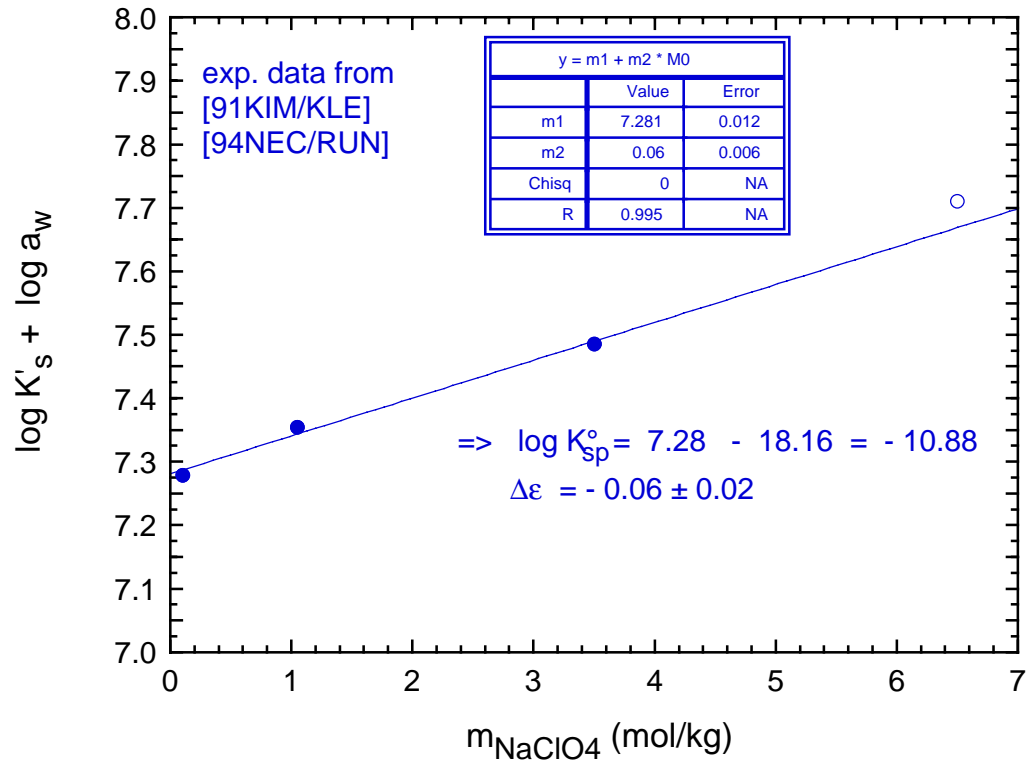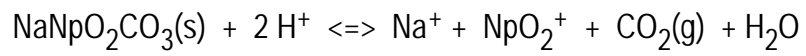> (if we assume the hydrated solid with x = 3.5)

These values are in good agreement with the SIT coefficient selected in the NEA-TDB (0.25 ± 0.05), i.e. the experimental data could, vice versa, be interpreted with a fixed value of $\Delta\varepsilon$ taken from the NEA-TDB and then all values of log K$_s$ in 0.1 to 3.5 and even in 6.5 m NaClO$_4$ would lead to a consistent value at I = 0.

The values for $\varepsilon(NpO_2^+/ClO_4^-)$ evaluated here from our Np(V) carbonate solubilities agree also with those from our solvent extraction study in [95NEC/FAN] (0.20 ± 0.03) and from our study on the solubility of $NpO_2OH(s)$ [92NEC/KIM] (0.19 ± 0.04).
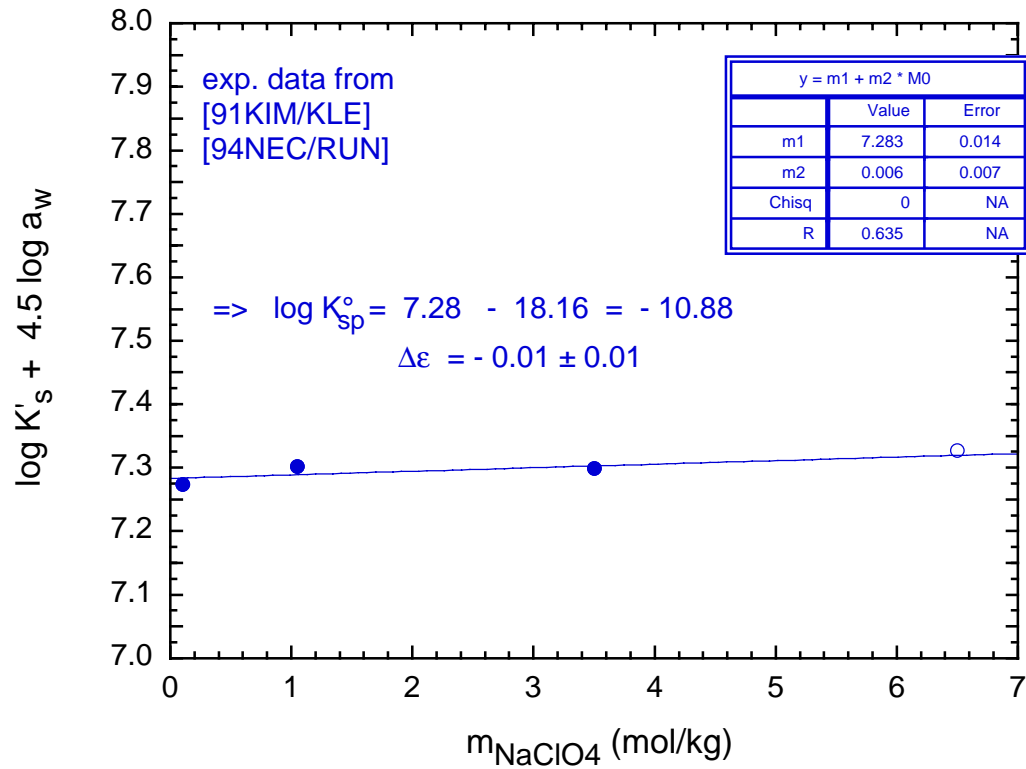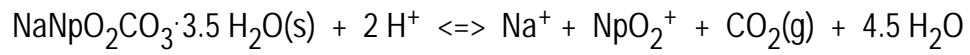
The application of the SIT extrapolation is illustrated in the Figures on the next pages. Formulating the dissolution reaction in this way (excluding the uncertainties from experimental carbonate dissociation constants) the scattering of our experimental data is very small (< 0.05 log units). This demonstrates that the solid phase must have been the same in these experiments.

We hope that these considerations will help to convince you that

1) our results are self-consistent and
2) reasonable SIT coefficients for the NpO_2^+ ion can be derived from the solubility experiments in [91KIM/KLE, 94NEC/RUN], but not those given in the NEA-TDB review (Table A.24, p.842). We would appreciate very much, if this table could be changed in the final version.

$$NaNpO_2CO_3(s) + 2 H^+ <=> Na^+ + NpO_2^+ + CO_2(g) + H_2O$$

exp. data from
[91KIM/KLE]
[94NEC/RUN]

y = m1 + m2 * M0		
	Value	Error
m1	7.281	0.012
m2	0.06	0.006
Chisq	0	NA
R	0.995	NA

$=>$ log K°_{sp} = 7.28 - 18.16 = - 10.88

$\Delta\varepsilon$ = - 0.06 ± 0.02

y-axis: log K'_s + log a_w

x-axis: m_{NaClO4} (mol/kg)

$\varepsilon(NpO_2^+/ClO_4^-) = \Delta\varepsilon - \varepsilon(Na^+/ClO_4^-) + 2 \varepsilon(H^+/ClO_4^-)$
$= (- 0.06 ± 0.02) - (0.01 ± 0.01) + 2 (0.14 ± 0.02) = 0.21 ± 0.05$

$$NaNpO_2CO_3 \cdot 3.5\, H_2O(s) + 2\, H^+ <=> Na^+ + NpO_2^+ + CO_2(g) + 4.5\, H_2O$$

exp. data from
[91KIM/KLE]
[94NEC/RUN]

y = m1 + m2 * M0	Value	Error
m1	7.283	0.014
m2	0.006	0.007
Chisq	0	NA
R	0.635	NA

=> $\log K_{sp}^° = 7.28 - 18.16 = -10.88$

$\Delta\varepsilon = -0.01 \pm 0.01$

y-axis: $\log K'_s + 4.5 \log a_w$

x-axis: m_{NaClO4} (mol/kg)

$\varepsilon(NpO_2^+/ClO_4^-) = \Delta\varepsilon - \varepsilon(Na^+/ClO_4^-) + 2\,\varepsilon(H^+/ClO_4^-)$
$= (-0.01 \pm 0.01) - (0.01 \pm 0.01) + 2(0.14 \pm 0.02) = 0.26 \pm 0.04$