Phase equilibria and thermodynamic properties of the nickel(II) methanesulfonate – methanesulfonic acid – water system

Femke Derison[a], Xu Jia[b], Luc Van Meervelt[b], Koen Binnemans[a] and Rayco Lommelen[a*],

[a] KU Leuven, Department of Chemistry, Solvomet Group, Celestijnenlaan 200F, box 2404, B-3001 Leuven, Belgium.

[b] KU Leuven, Department of Chemistry, Biomolecular Architecture, Celestijnenlaan 200F, box 2404, B-3001 Leuven, Belgium.

* Corresponding author: rayco.lommelen@kuleuven.be

Supplementary information (SI)

Powder X-ray Diffraction

Powder X-ray diffraction was performed to confirm the crystalline phase and purity of $Ni(CH_3SO_3)_2 \cdot 2H_2O$. The diffractogram is shown in Figure S1.

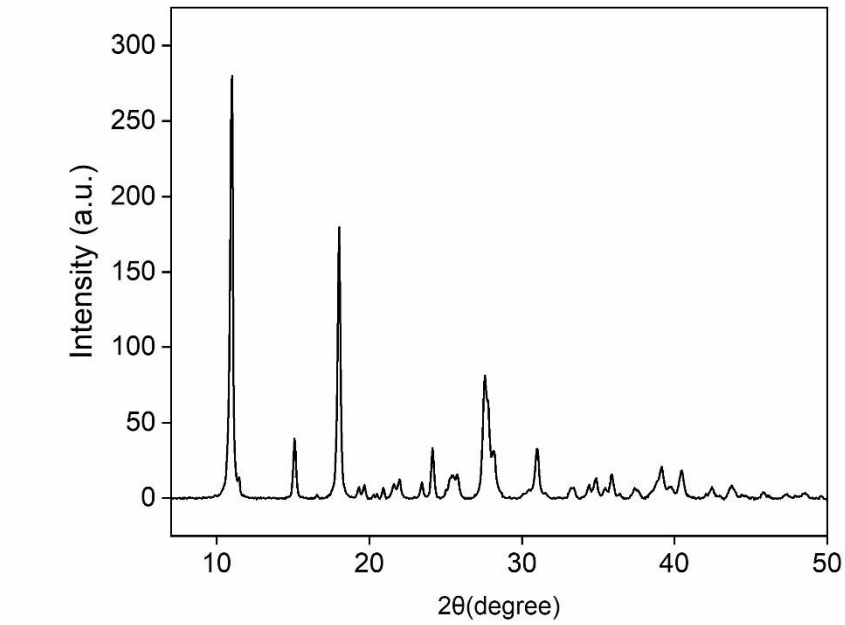

Figure S1: Powder XRD diffractogram of $Ni(CH_3SO_3)_2 \cdot 2H_2O$

Hydrate characterization

TGA graphs of the solids present in the saturation samples are shown in Figures S2-6. The mass loss percentages indicated in the graphs correspond to the loss of hydrate water molecules from the crystal structure and can be compared to theoretical values shown in Table S1. At 25 °C, correspondence between measured and theoretical values could indicate the presence of the dodecahydrate in the samples up until 10 wt% MSA. From 30 wt% MSA onwards, a deviation was present resulting in inconclusive results. For clarity, the sample codes used for the saturation experiments follow the format SXX.YY, where S denotes saturation, XX indicates the temperature in °C, and YY represents the initial MSA concentration in wt%.

Table S1: Theoretical mass loss of hydrate water percentages for the different hydrates.

Hydrate	Mass loss of hydrate water (%)
$Ni(CH_3SO_3)_2 \cdot 2H_2O$	12.65
$Ni(CH_3SO_3)_2 \cdot 3H_2O$	23.07
$Ni(CH_3SO_3)_2 \cdot 4H_2O$	22.45
$Ni(CH_3SO_3)_2 \cdot 6H_2O$	30.28
$Ni(CH_3SO_3)_2 \cdot 12H_2O$	46.48

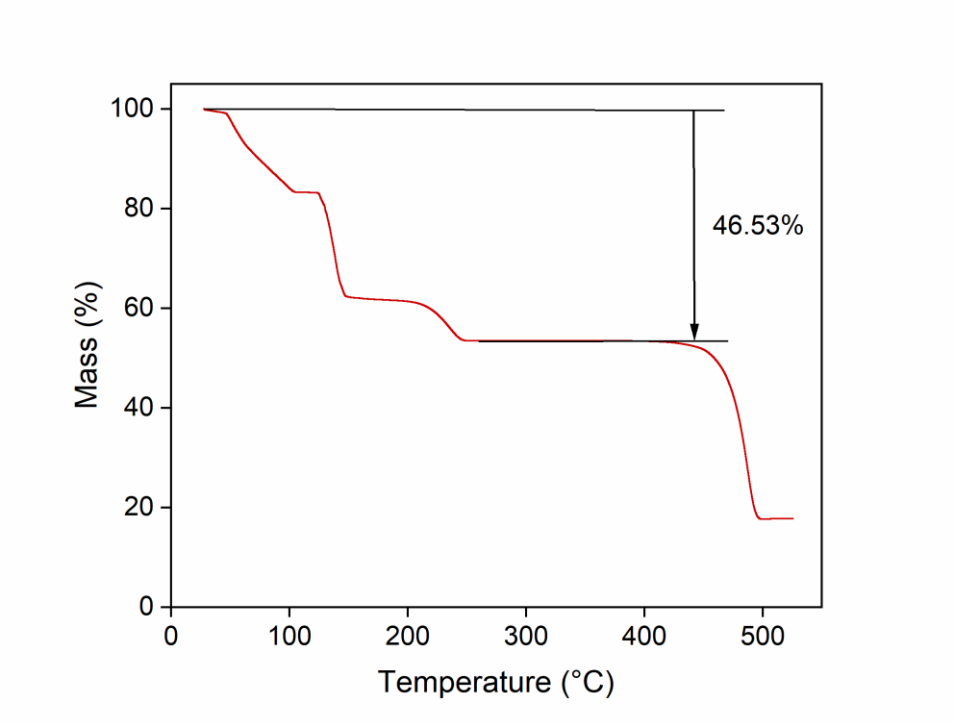

Figure S2: Thermogravimetric curve for S25.0 solubility sample during heating with a heating rate of 5 °C/min in nitrogen atmosphere at 60.0 mL min^{-1} flow rate.

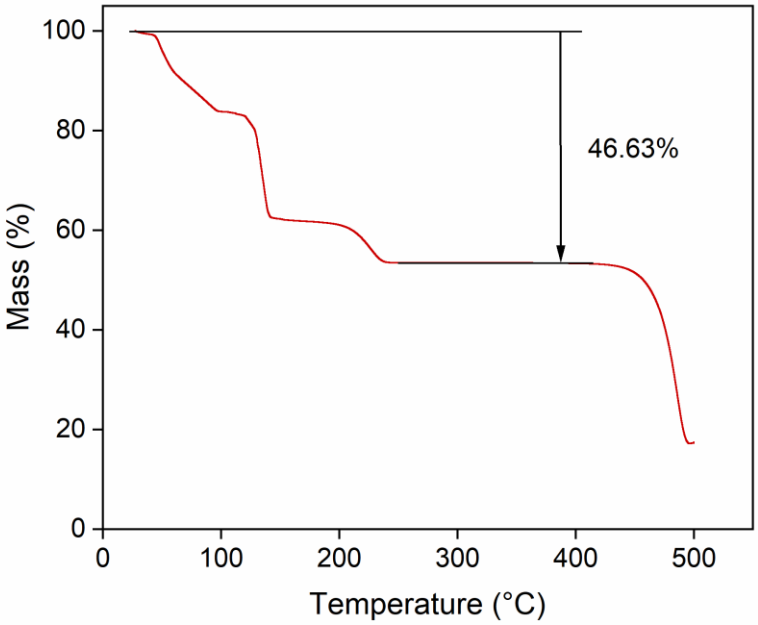

Figure S3: Thermogravimetric curve for S25.10 solubility sample during heating with a heating rate of 5 °C/min in nitrogen atmosphere at 60.0 mL min^{-1} flow rate.

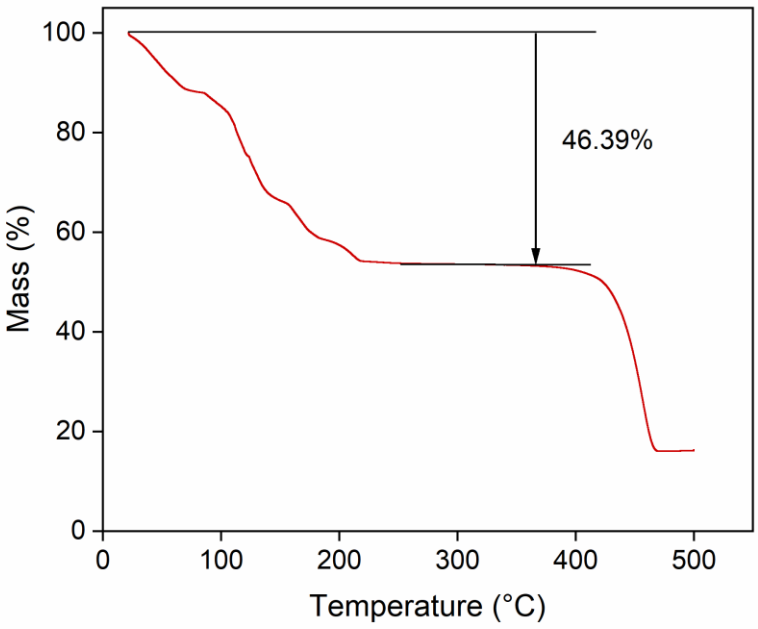

Figure S4: Thermogravimetric curve for S25.30 solubility sample during heating with a heating rate of 5 °C/min in nitrogen atmosphere at 60.0 mL min^{-1} flow rate.

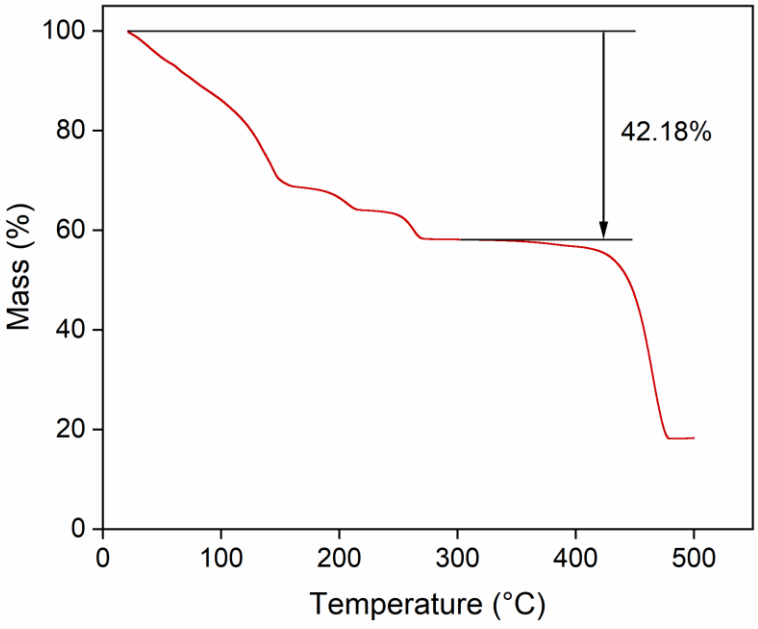

Figure S5: Thermogravimetric curve for S25.50 solubility sample during heating with a heating rate of 5 °C/min in nitrogen atmosphere at 60.0 mL min^{-1} flow rate.

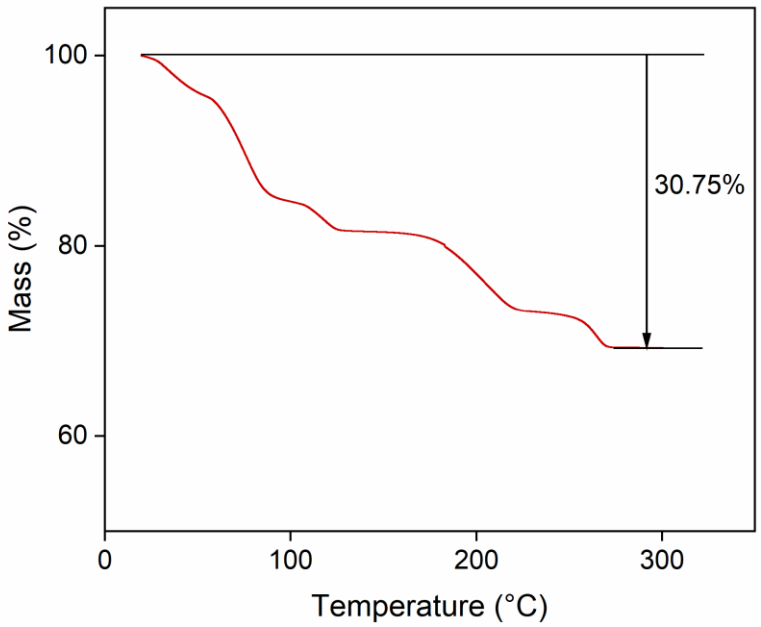

Figure S6: Thermogravimetric curve for S70.10 solubility sample during heating with a heating rate of 5 °C/min in nitrogen atmosphere at 60.0 mL min^{-1} flow rate.

Single-Crystal X-ray crystallography

X-ray intensity data were collected at 293(2) K on an Agilent SuperNova diffractometer with Eos CCD detector using MoKα radiation. The images were interpreted and integrated with CrysAlisPRO[1] and the implemented absorption correction was applied. The structure was solved using Olex2 1.5[2] with the ShelXT[3] structure solution program using Intrinsic Phasing and refined with the ShelXL[4] refinement package using full-matrix least-squares minimization on F^2. Non-hydrogen atoms were refined anisotropically and hydrogen atoms in the riding mode with isotropic temperature factors fixed at 1.5 times U_{eq} of the parent atoms. Crystal data, data collection parameters and refinement statistics are summarized in Table S2. The molecular structure of $Ni(CH_3SO_3)_2 \cdot 12H_2O$ is shown in Figure S7.

Table S2: Crystal data, data collection parameters and refinement statistics.

Empirical formula	$C_2H_{30}NiO_{18}S_2$
Formula weight	465.09
Temperature/K	293 ± 2
Crystal system	trigonal
Space group	R-3
a/Å	9.2073(4)
b/Å	9.2073(4)
c/Å	21.4213(8)
α/°	90
β/°	90
γ/°	120
Volume/Å^3	1572.68(15)
Z	3
ρ_{calc}g/cm^3	1.473
μ/mm^{-1}	1.194
F(000)	738.0
Crystal size/mm^3	0.6 × 0.45 × 0.4
Radiation	Mo Kα (λ = 0.71073 Å)
2Θ range for data collection/°	8.854 to 52.708
Index ranges	-11 ≤ h ≤ 10, -11 ≤ k ≤ 6, -26 ≤ l ≤ 26
Reflections collected	2293
Independent reflections	712 [R_{int} = 0.0311, R_{sigma} = 0.0294]
Data/restraints/parameters	712/1/44
Goodness-of-fit on F^2	1.095
Final R indexes [I>=2σ (I)]	R_1 = 0.0259, wR_2 = 0.0613
Final R indexes [all data]	R_1 = 0.0299, wR_2 = 0.0635
Largest diff. peak/hole / e Å^{-3}	0.19/-0.27

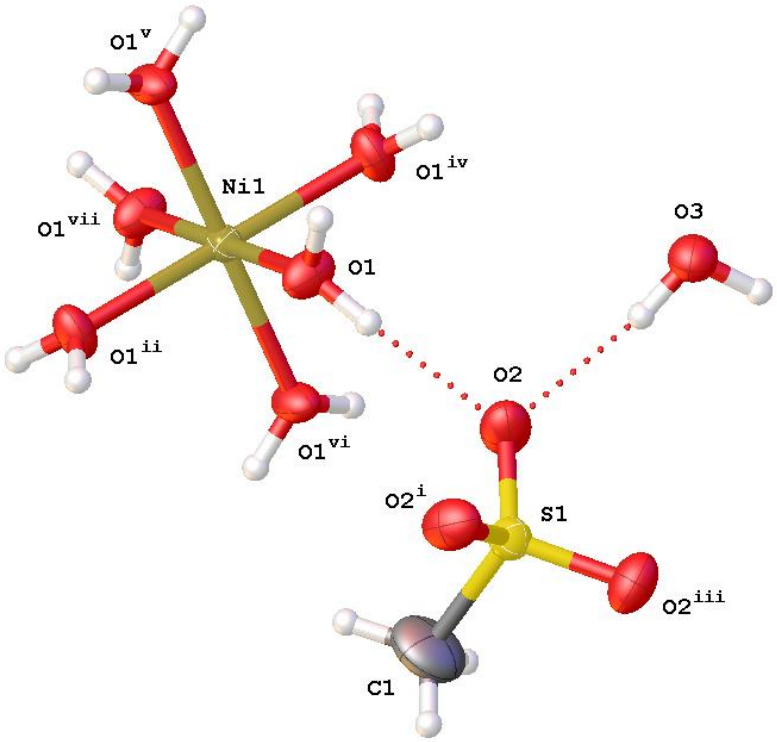

Figure S7. Molecular structure of $Ni(MSA)_2 \cdot 12H_2O$ showing the atom numbering scheme and thermal ellipsoids at 30% probability level. Symmetry codes: (i) 1-y, 1+x-y, z; (ii) 1/3+y, 2/3-x+y, 2/3-z; (iii) y-x, 1-x, z; (iv) 1-y,x-y,z; (v) 1+y-x, 1-x, z; (vi) 1/3-y+x, -1/3+x, 2/3-z; (vii) 4/3-x, 2/3-y, 2/3-z.

1. CrysAlis PRO (2012). Agilent Technologies UK Ltd, Yarnton, Oxfordshire, England.
2. Dolomanov, O. V., Bourhis, L. J., Gildea, R. J., Howard, J. A. K. & Puschmann, H. OLEX2: a complete structure solution, refinement and analysis program. *J. Appl. Cryst*. **42**, 339–341 (2009).
3. Sheldrick, G. M. SHELXT - Integrated space-group and crystal-structure determination. *Acta Cryst*. **A71**, 3–8 (2015).
4. Sheldrick, G. M. Crystal structure refinement with SHELXL. *Acta Cryst*. **C71**, 3–8 (2015).

Performance of general OLI-MSE database for MSA-water system

The performance of the data related to the MSA-water system in the general OLI-MSE database version 12.0 was validated against experimental data from the literature (Figure S8). There is a reasonable agreement between the experimental and calculated data points for the acid dissociation data at 25 °C,[1,2] the solution density data from 20 to 35 °C,[3] and the water activity data at 25 °C.[4]

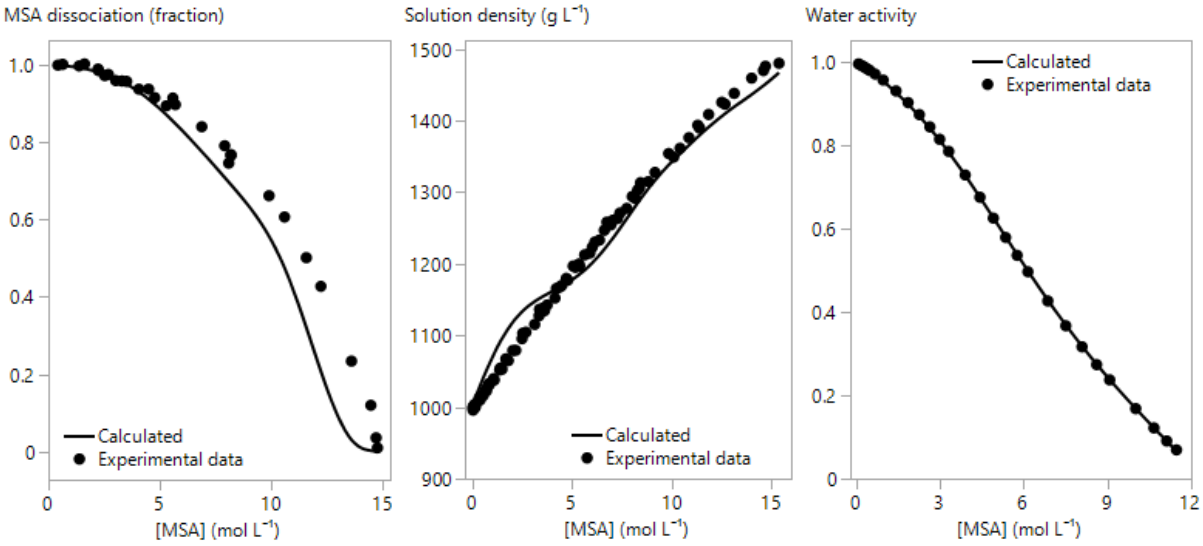

Figure S8. Validation plots for the MSA-water chemistry present in the general OLI-MSE database.

1. A. K. Covington and R. Thompson, *J Solution Chem*, **1974**, 3, 603–617.
2. A. K. Covington and T. H. Lilley, Trans. Faraday Soc., **1967**, 63, 1749–1753. doi: 10.1007/BF00650404
3. T. T. Teng and F. Lenzi, J. Chem. Eng. Data, **1975**, 20, 432–434. doi: 10.1021/je60067a008
4. 1 A. K. Covington, R. A. Robinson and R. Thompson, J. Chem. Eng. Data, **1973**, 18, 422–423.

Overview of experimental setup, conditions and results

A full overview of experimental details of the isothermal solubility method is shown in Tabel S3. All inflows are given together with the corresponding results and findings from the analysis.

Table S3: Overview of saturation samples conditions, inflows and results at equilibrium.

Inflows				Equilibrium					
Amount $Ni(CH_3SO_3)_2.2H_2O$ (g)	Amount MSA (g)	Amount H_2O (g)	T(°C)	$[Ni(II)]_{aq}$ (mol L^{-1})	$[MSA]_{aq}$ (wt%)	Water activity	Density (g mL^{-1})	Water content (mol L^{-1})	Hydrate of solid
6.15	0	4.98	25	2.388	0	0.7331	1.362263	41.40	$Ni(CH_3SO_3)_2 \cdot 12H_2O$
13.1	0	9.997225	25	2.296	0	0.7469	1.37629	N.A.[a]	$Ni(CH_3SO_3)_2 \cdot 12H_2O$
8.02	0	6.998058	25	2.361	0	0.7453	1.37392	N.A.[a]	$Ni(CH_3SO_3)_2 \cdot 12H_2O$
6.24	0.518948	4.671052	25	1.905	8.317	0.6284	1.39863	38.62	$Ni(CH_3SO_3)_2 \cdot 12H_2O$
6.52	0.6	5.399101	25	1.989	8.078	0.6496	1.37453	N.A.[a]	$Ni(CH_3SO_3)_2 \cdot 12H_2O$
7.36	0.8	7.198802	25	2.347	7.462	0.6879	1.36172	N.A.[a]	$Ni(CH_3SO_3)_2 \cdot 12H_2O$
4.41	1.692	3.948	25	1.958	23.80	0.4927	1.404283	33.84	-[b]
5.409	1.8	4.198835	25	1.690	20.83	0.4447	1.41409	N.A.[a]	-[b]
5.26	1.8	4.198835	25	2.007	20.83	0.4948	1.40683	N.A.[a]	-[b]
2.747	3.0204	3.004566	25	1.054	38.38	0.3532	1.37244	N.A.[a]	-[b]
2.502	3.0204	3.004566	25	1.162	39.18	0.3597	1.37504	N.A.[a]	-[b]
2.7	3.092679	3.077321	25	1.151	43.12	0.349067	1.370427	28.61	-[b]
0.47	3.4825	1.503583	25	0.105	66.19	0.1482	1.35817	N.A.[a]	-[b]
0.45	3.4825	1.503583	25	0.115	66.19	0.1542	1.35818	N.A.[a]	-[b]
0.33	3.978	1.003721	25	0.054	79.44	0.0558	1.40146	N.A.[a]	-[b]
0.33	3.978	1.003721	25	0.011	79.44	0.0559	1.40274	N.A.[a]	-[b]
0.2	4.332	0.75829	25	0.012	85.03	0.0307	1.42957	N.A.[a]	$Ni(CH_3SO_3)_2 \cdot 2H_2O$
0.16	4.332	0.75829	25	0.0086	85.03	0.0311	1.42944	N.A.[a]	$Ni(CH_3SO_3)_2 \cdot 2H_2O$
0.15	4.503	0.562344	25	0.0063	88.80	0.02	1.44044	N.A.[a]	$Ni(CH_3SO_3)_2 \cdot 2H_2O$
0.17	4.503	0.562344	25	0.0067	88.80	0.0204	1.44571	N.A.[a]	$Ni(CH_3SO_3)_2 \cdot 2H_2O$
0.48	4.728071	2.041929	25	0.0063	71.59	0.1195	1.36552	20.15	-[b]
0.13	4.7555	0.255929	25	0.0061	94.27	0.0113	1.46963	N.A.[a]	$Ni(CH_3SO_3)_2 \cdot 2H_2O$
0.12	4.7555	0.255929	25	0.0062	94.27	0.0105	1.46982	N.A.[a]	$Ni(CH_3SO_3)_2 \cdot 2H_2O$

Table S3 continued

Inflows				Equilibrium					
Amount $Ni(CH_3SO_3)_2.2H_2O$ (g)	Amount MSA (g)	Amount H_2O (g)	T(°C)	$[Ni(II)]_{aq}$ (mol L^{-1})	$[MSA]_{aq}$ (wt%)	Water activity	Density (g mL^{-1})	Water content (mol L^{-1})	Hydrate of solid
0.2	5.001	0	25	0.0070	94.60	N.A.[a]	1.47519	N.A.[a]	$Ni(CH_3SO_3)_2 \cdot (0\text{-}2)H_2O$ [b]
0.22	5.001	0	25	0.021	94.60	N.A.[a]	1.47757	N.A.[a]	$Ni(CH_3SO_3)_2 \cdot (0\text{-}2)H_2O$ [b]
0.37	5.605291	1.414709	25	0.020	81.92	0.04315	1.412063	13.48	-[b]
0.78	6.076118	1.063882	25	0.023	85.74	0.028833	1.426077	11.01	$Ni(CH_3SO_3)_2 \cdot 2H_2O$
0.17	6.47159	0.80841	25	0.0088	89.78	0.017667	1.449967	7.939	$Ni(CH_3SO_3)_2 \cdot 2H_2O$
0.13	6.974544	0.375456	25	0.0092	94.45	0.011167	1.468287	4.131	$Ni(CH_3SO_3)_2 \cdot 2H_2O$
0.29	7.37	0	25	0.010	95.48	N.A.[a]	1.474443	3.756	$Ni(CH_3SO_3)_2 \cdot (0\text{-}2)H_2O$ [b]
12.64	0	4.98	50	3.843	0	N.A.[a]	N.A.[a]	N.A.[a]	$Ni(CH_3SO_3)_2 \cdot 6H_2O$
10.35	0.519948	4.680052	50	3.476	3.818	N.A.[a]	N.A.[a]	N.A.[a]	-[b]
7.5	1.695	3.955	50	2.699	14.51	N.A.[a]	N.A.[a]	N.A.[a]	-[b]
3.53	3.087667	3.072333	50	1.536	32.69	N.A.[a]	N.A.[a]	N.A.[a]	-[b]
1.12	5.565367	1.404633	50	0.028	79.08	N.A.[a]	N.A.[a]	N.A.[a]	$Ni(CH_3SO_3)_2 \cdot 2H_2O$
0.42	6.373805	0.796195	50	0.016	88.73	N.A.[a]	N.A.[a]	N.A.[a]	$Ni(CH_3SO_3)_2 \cdot 2H_2O$
0.27	6.917609	0.372391	50	0.032	94.04	N.A.[a]	N.A.[a]	N.A.[a]	$Ni(CH_3SO_3)_2 \cdot (0\text{-}2)H_2O$ [b]
0.27	7.33	0	50	0.027	94.34	N.A.[a]	N.A.[a]	N.A.[a]	$Ni(CH_3SO_3)_2 \cdot (0\text{-}2)H_2O$ [b]
13.21	0	4.99	70	4.029	0	N.A.[a]	N.A.[a]	N.A.[a]	$Ni(CH_3SO_3)_2 \cdot 6H_2O$
11.24	0.418958	3.771042	70	3.532	3.516	N.A.[a]	N.A.[a]	N.A.[a]	-[b]
7.75	1.683	3.927	70	2.636	13.40	N.A.[a]	N.A.[a]	N.A.[a]	-[b]
4.03	3.057592	3.042408	70	1.464	30.29	N.A.[a]	N.A.[a]	N.A.[a]	-[b]
1.53	5.517459	1.392541	70	0.054	78.45	N.A.[a]	N.A.[a]	N.A.[a]	$Ni(CH_3SO_3)_2 \cdot 2H_2O$
0.51	6.356026	0.793974	70	0.030	88.73	N.A.[a]	N.A.[a]	N.A.[a]	$Ni(CH_3SO_3)_2 \cdot 2H_2O$
0.41	6.927098	0.372902	70	0.063	93.91	N.A.[a]	N.A.[a]	N.A.[a]	$Ni(CH_3SO_3)_2 \cdot (0\text{-}2)H_2O$ [b]
0.45	7.30	0	70	0.022	90.19	N.A.[a]	N.A.[a]	N.A.[a]	$Ni(CH_3SO_3)_2 \cdot (0\text{-}2)H_2O$ [b]

[a] This was not measured.

[b] Hydrate speciation could not be confirmed & was uncertain.