MSA-based circular hydrometallurgy for sustainable, cost-effective production of NMC cathode materials (CICERO)

D2.1

Public report on the solubility & dissolution enthalpies of MSA salts as a function of T

Public

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Executive Summary

$Me(MSA)_2$ salts (Me = Ni, Co, Mn) were synthesized as their dihydrates and dissolution enthalpies were determined. Furthermore, the solubility of these salts in pure water, 30 wt% MSA and 50 wt% MSA aqueous solution were measured. The dissolution of the $Me(MSA)_2$ salts is exothermic and the dissolution enthalpies calculated follow the order Mn < Co < Ni. Solubilities were significantly affected by the amount of MSA present in solution, showing a strong decrease from pure water to 50 wt% MSA solution.

Content:

Introduction

The project “MSA-based circular hydrometallurgy for sustainable, cost-effective production of NMC cathode materials – CICERO” aims to develop a sustainable, cost-effective refining model for Ni, Co and Mn, and the downstream conversion into NMC cathode materials by using a circular hydrometallurgical Ni, Co & Mn processing / refining scheme. Within the scope of the project, CICERO develops suitable, novel metallurgical unit processes based on the environmental friendly, green, REACH-compliant and affordable acid methanesulfonic acid (MSA) rather than H_2SO_4 for a more a sustainable, cost-effective refining model for Ni, Co and Mn. In this regard, processes for advanced MSA leaching and solution purification, the conversion to battery-grade MSA salts, and the synthesis of NMC cathode materials in MSA media, with sound reagent regeneration & iron recovery in line with the Twelve Principles of Circular Hydrometallurgy will be developed and supported by advanced thermodynamic & kinetic modelling for solid-liquid & liquid-liquid equilibria relevant for Ni/Co/Mn processing/refining in MSA media.

As a prerequisite, the determination of solubility and dissolution enthalpies of MSA salts as a function of temperature is required. The solubility of MSA salts in water is significantly higher than those of their sulphate counterparts. Very recently, some phase equilibria data were reported by Belova et al. for the $Ni(MSA)_2$, $Co(MSA)_2$ and $Mn(MSA)_2$ – water systems (J. Chem. Thermodynamics 182 (2023) 107049) up to 50 °C. They concluded, that although the MSA-salts were regarded as highly soluble at room temperature, low-temperature hydrates were present for all of the salts which decrease their solubilities, especially at slightly lower temperatures. However, no data at temperatures higher than 50 °C have been reported so far. Therefore, also solubility data for the salts at temperatures up to 80 °C will be provided. Furthermore, dissolution enthalpies in water will be measured via calorimetry.

Experimental details

Synthesis of the MSA salts of Ni, Co and Mn

Synthesis of the Ni(II), Co(II) and Mn(II)-methanesulfonate salts was done based on the diploma thesis of T. Trella (September 2010).

$Mn(MSA)_2$:

Briefly, in a 500 ml round bottom flask equipped with stirrer and reflux condenser, 29 g of manganese(II) oxide was suspended in 300 ml of DI water. Then, 73.8 g of methanesulfonic acid (95% of the calculated amount needed for the synthesis of $Mn(MSA)_2$) was added and the suspension stirred for 48 h at 90 °C. The resulting reddish solution was filtered to remove insoluble residues. The pale purple solution was evaporated to dryness using a rotary evaporator (~50 mbar, 60 °C) giving a light purple solid, which was washed with 25 ml of isopropanol and dried. Yield: 92.1 g. Thermogravimetric (TG) measurements of the obtained solid showed mass loss between 155 °C and 195 °C of approximately 13.3 wt%, which corresponds well to the loss of 2 molecules of crystal water from the compound $Mn(MSA)_2 \cdot 2H_2O$.

$Co(MSA)_2$:

The synthesis was done according to the synthesis of $Mn(MSA)_2$ using 54.7 g of cobalt(II) carbonate monohydrate and 73.1 g of methanesulfonic acid. Yield was 97.6 g of a violet solid. TG measurements of the obtained solid showed mass loss between 148 °C and 210 °C of approximately 13 wt%, which corresponds well to the loss of 2 molecules of crystal water from the compound $Co(MSA)_2 \cdot 2H_2O$.

$Ni(MSA)_2$:

The synthesis was done according to the synthesis of $Mn(MSA)_2$ using 40.9 g of nickel(II) hydroxide and 80.3 g of methanesulfonic acid. Yield was 113.8 g of a green solid. TG measurements of the obtained solid showed mass loss between 195 °C and 260 °C of approximately 13.3 wt%, which corresponds well to the loss of 2 molecules of crystal water from the compound $Ni(MSA)_2 \cdot 2H_2O$.

Solubility measurements

Solubility of the $Me(MSA)_2$ salts was determined using a Crystalline™ PV (particle viewer) from Technobis Crystallization Systems B.V..

The Crystalline™ is a laboratory setup with 8 parallel reactors which can be individually cooled and heated from -25 °C to 145 °C. Light transmission measurements are possible for the detection of events such as dissolution, crystallization or phase separation. The Crystalline™ PV used is supplied with 2 particle visualization modules, comprising 8 parallel visualization probes.

The Crystalline™ is based on a small volume parallel crystallizer. It combines turbidity measurements with independent real time particle visualization. With high quality digital visualization probes, monitoring of what is happening in the reaction vial is possible. The through the vial visualization does not interfere with the process and there are no moving parts or cumbersome insertion probes, which could act as nucleation surface. The visualization probes are controlled separately from each other and can be synchronized with the turbidity measurements and temperature profile of each independent reactor.

Turbidity measurements:

Each reactor possesses real time turbidity analytics. Both the detector and light source (LED) are located outside the reaction vial. The turbidity measurement can be tuned to clear solutions. A schematic drawing is shown in Figure 1.

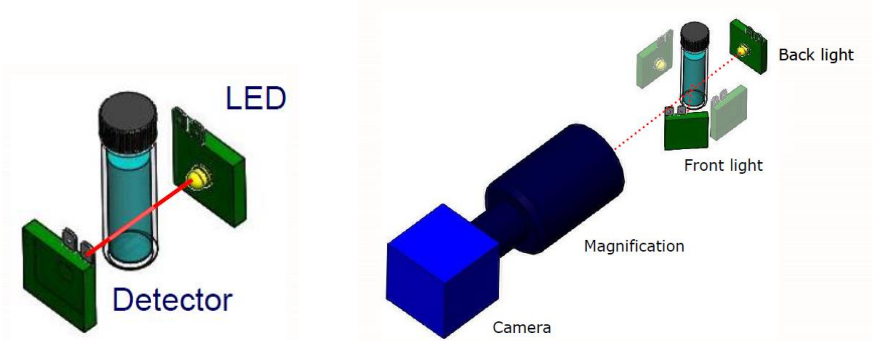

Figure 1: Turbidity measurement(left) and particle visualization (right)

Particle visualization module

The assembly of the visualization probes, with respect to the reaction vessel, can be seen in Figure 1. The wavelength of the LED is 460 nm with a band width between 400–520 nm. In order to obtain sharp images of the moving particles in the reactor the optical system (Camera's and LED's) are triggered by a microprocessor. To ensure consistent high quality images for image analysis, the backlight LED intensity is automatically optimized during the experiment. Magnification is done, using a telecentric lens to avoid distortion of particles in the field of view. This is done in order to obtain reliable particle analysis information. Particle analysis (Size and Shape) is carried out during the experiment.

Measurement protocol:

The measurement was done by mixing a dedicated amount of salt in a dedicated amount of solvent, heating the solution until complete dissolution occurred to prepare a homogenous starting solution. Quick cooling to e.g. -15 °C gave a homogenous dispersion, which was then continuously heated until complete dissolution occurs.

$Mn(MSA)_2$ in 30% MSA (30 w% solids)

Exemplary transmissivity curve with two cycles (= Double determination of the solubility temperature)

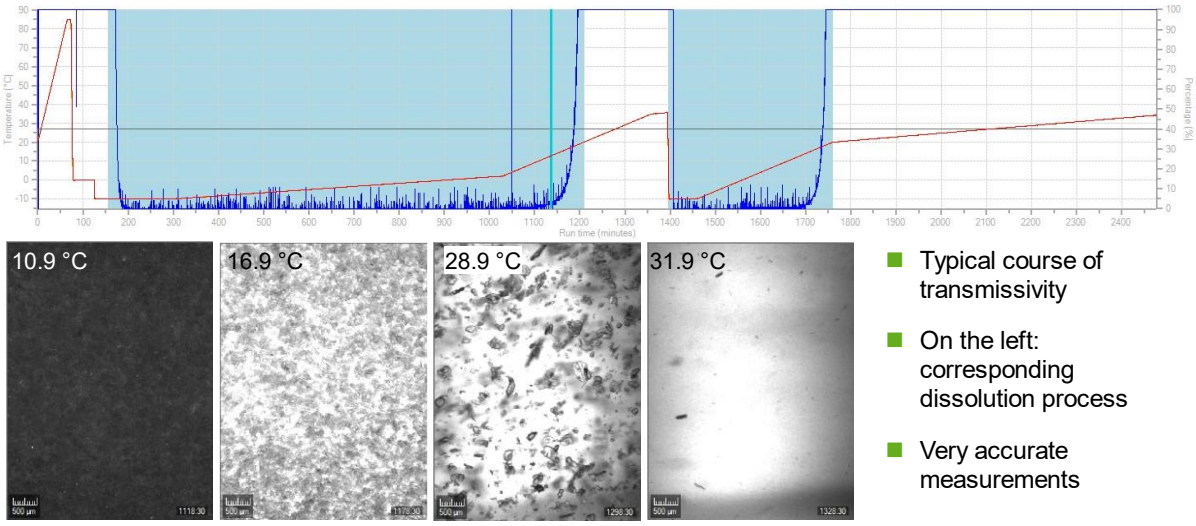

Figure 2: Exemplary transmissivity curve for the solubility measurements of $Mn(MSA)_2$ salts

In a typical experiment, a dedicated amount of salt was put into one reaction vessel (typically around 3–4 g) and a respective amount of water was added (2–3 ml). The amounts were chosen that insoluble material was present at the starting temperature (e.g. -10 °C or room temperature). The suspension was put into the Crystalline™, heated to ~85 °C to allow complete dissolution, cooled down to ~-15 °C to start the heating process. The dispersion was slowly heated (heating rate 1 °C/min) until complete dissolution occurred. Turbidity measurement was done continuously and visual inspection was done every 1 °C by taking pictures of the reaction vessel. Upon heating, within the course of dissolution, the transmissivity increases until a value of 100%, indicating complete dissolution. At the same time, visual inspection shows the disappearance of particles in the reaction vessel. An exemplary transmissivity curve is shown in Figure 2. For this sample, the solubility of $Mn(MSA)_2$ was determined to be 29.9 wt% at 31.9 °C, giving a solubility of ~425 g of $Mn(MSA)_2$/kg solvent (30% MSA in water) at 31.9 °C. Typically, the solubility was determined twice, giving very similar results.

In some cases, the solution was too strongly colored (e.g. by using high amounts of $Co(MSA)_2$), so particles could not be visualized. In that case, only transmissivity was taken to determine the solubility (100% transmissivity = complete dissolution).

Dissolution enthalpy

Dissolution enthalpy was determined using a reaction calorimeter Mettler-Toledo RC1mx with a glass reactor type AP01-0.5L.

Briefly, the reactor was charged with 150.0 g of DI-water at 23 °C and the Cp-value was determined at 23 °C. Then, 64.3 g of the respective $Me(MSA)_2$ (as dihydrate, determined by TG measurements, see above) salt was added in portions of 21.43 g (representing 12.5wt%, 22.2wt% and 30 wt% salt in solution). After each addition, the reaction mixture was stirred until the solid is completely dissolved and no further temperature change is observed. Finally, the Cp-value of the final mixture was determined at 23 – 20 °C.

Results and Discussion

Solubility of $Me(MSA)_2$ salts in water

The solubility of the prepared $Me(MSA)_2 \cdot 2H_2O$ salts was determined according to the procedure above and reported as masses of pure $Me(MSA)_2$ salts (without included crystal water).

The solubility of $Ni(MSA)_2$, $Co(MSA)_2$ and $Mn(MSA)_2$ in water was already investigated by Belova et al. in 2023 up to temperatures of 50 °C. (Table 3 appendix, J. Chem. Thermodynamics 182 (2023) 107049).

For $Ni(MSA)_2$, the solubility slightly increases from 326 g/kg solvent (0 °C) up to 735 g/kg solvent at 25 °C. At 30 °C a steeper increase takes place with up to 1309 g/kg at 35 °C. Then solubility levels out with a maximum determined solubility of 1546 g/kg solvent at 85 °C.

The solubility curves for $Co(MSA)_2$ and $Mn(MSA)_2$ were found to be very similar, starting at ~350 g/kg solvent ($Mn(MSA)_2$) to 390 g/kg solvent ($Co(MSA)_2$) and steadily increase to ~1050g/kg solvent at 25 °C (both $Co(MSA)_2$ and $Mn(MSA)_2$). At higher temperatures, the solubility was determined to be 1220 g/kg at 59 °C for $Co(MSA)_2$, whereas $Mn(MSA)_2$ is dissolved with 1190 g/kg at 82.4 °C.

Figure 3 and Figure 4 and Table *3* (appendix) summarize the reported results of Belova et al. as well as the data generated using the method above. The newly generated data fit well to those reported by Belova et al.

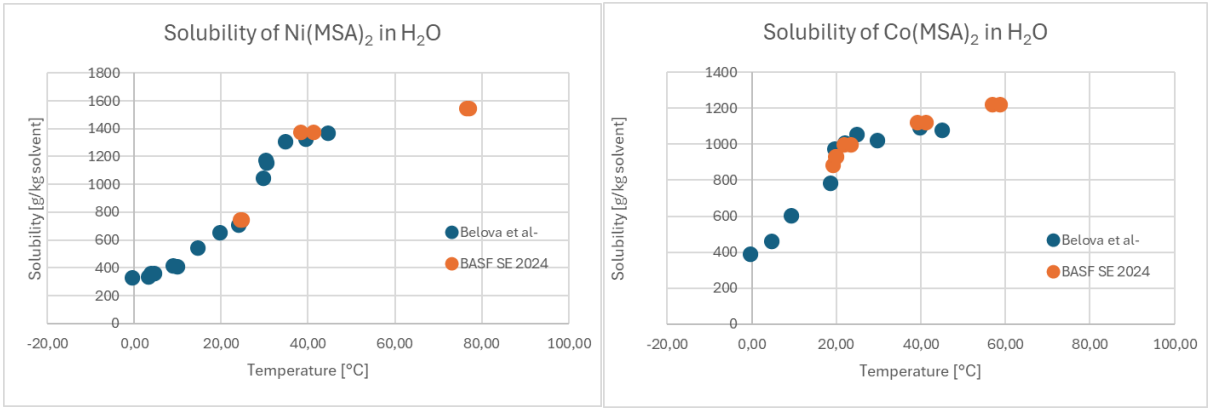

Figure 3: Solubility data for $Ni(MSA)_2$ and $Co(MSA)_2$ with data from Belova et al. and measured data.

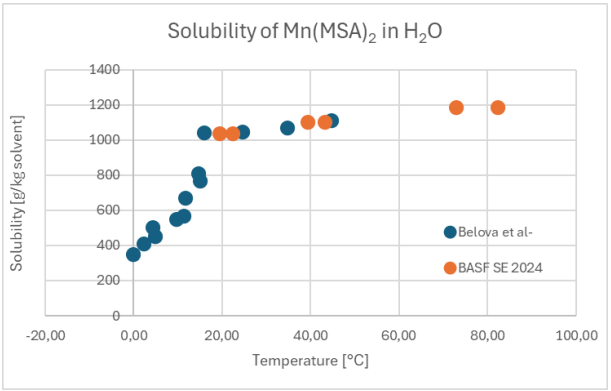

Figure 4: Solubility data for $Mn(MSA)_2$ with data from Belova et al. and measured data.

Solubility of $Me(MSA)_2$ salts in 30 wt% MSA and 50 wt% MSA

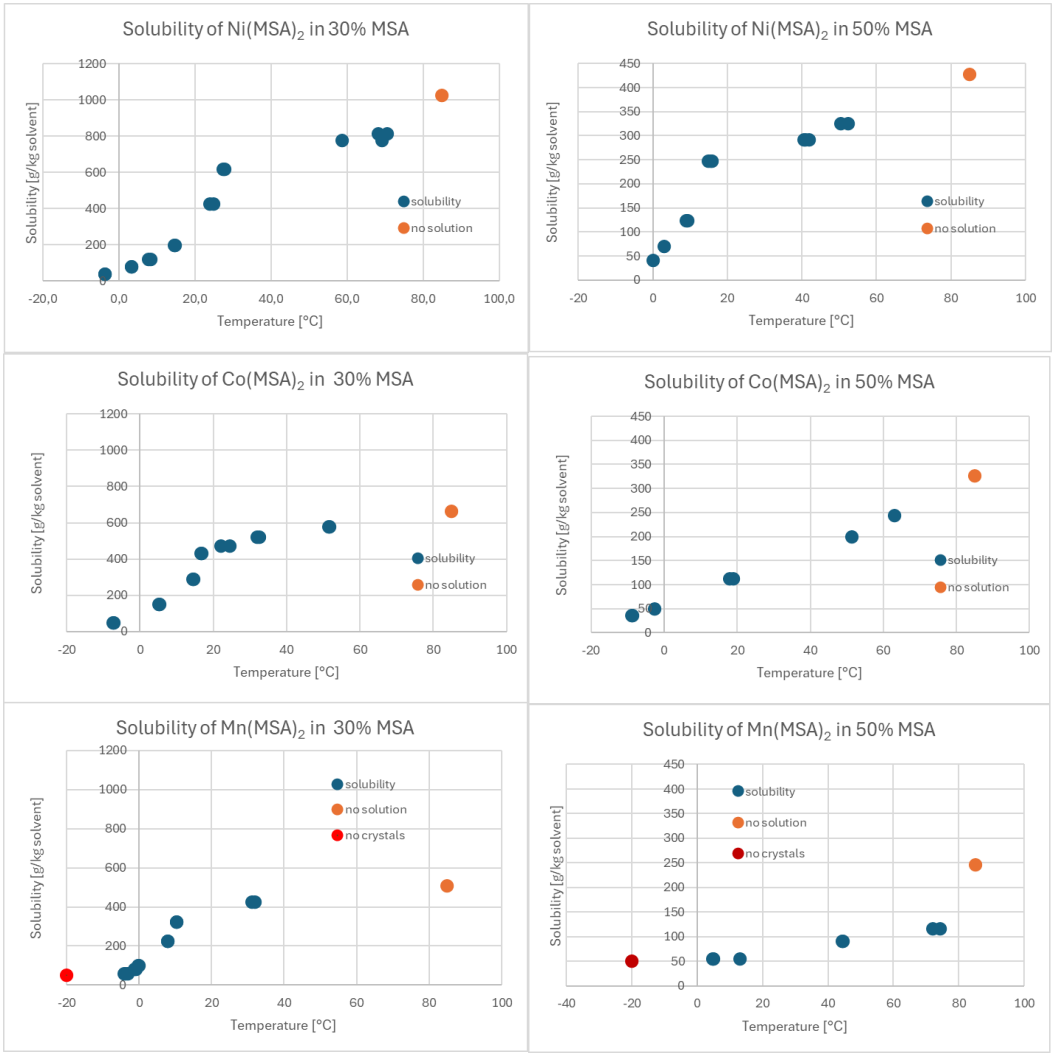

Figure 5: Solubility data for $Me(MSA)_2$ (Me = Ni, Co, Mn) in 30 wt% MSA (left) and 50 wt% MSA (right).

The solubilities of the different salts were also determined in 30 wt% MSA and 50 wt% MSA solutions.

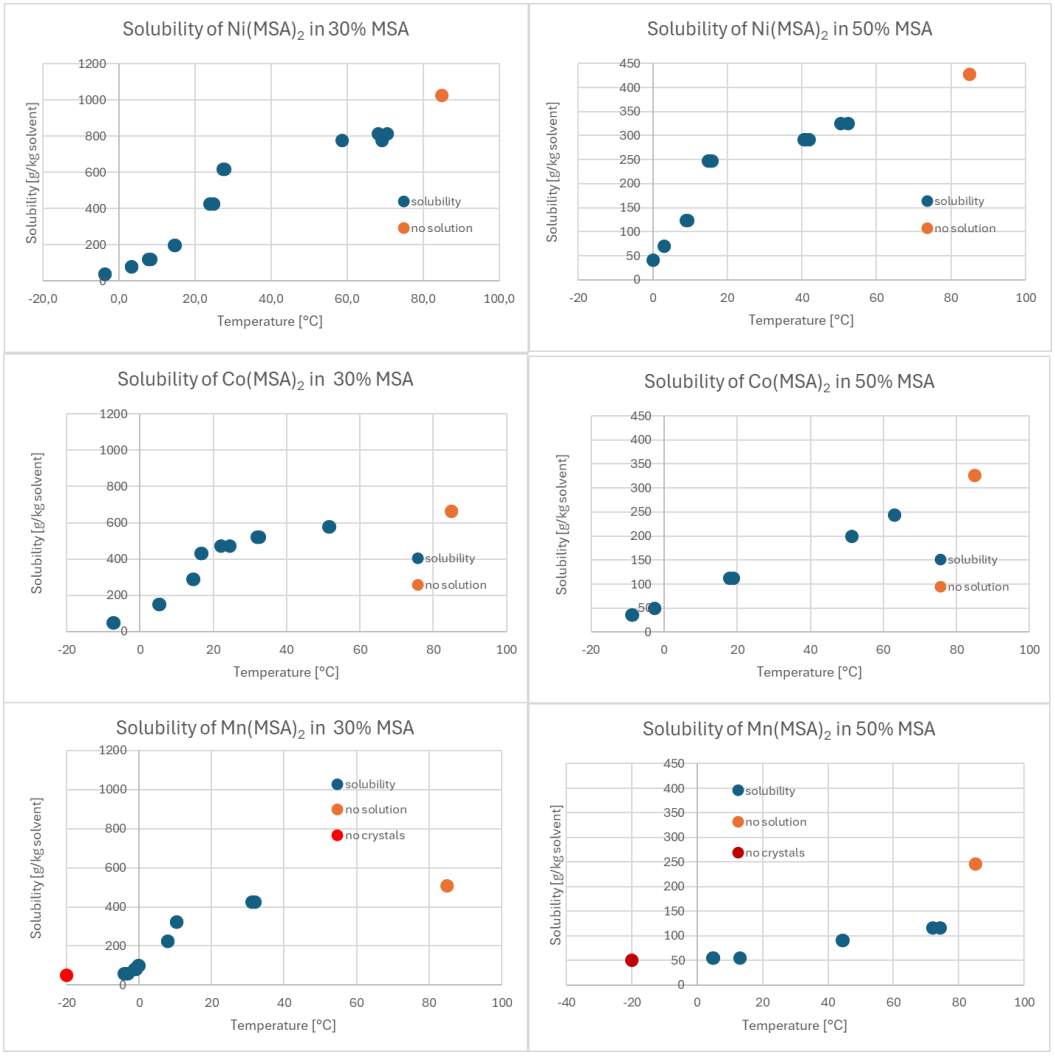

Figure 5, Table 4 and Table 5 (appendix) show the respective solubilities. Due to the measurement method, in some cases no solutions (high temperatures) or no crystals (low temperatures) were observed, indicating too high (at high temperatures) or too low concentrations (at low temperatures). The respective measurement points are indicated in the graphs below as orange (high temperatures) or red (low temperatures) dots.

As expected, the solubility decreases with increasing MSA amount in the solute. At 50 wt%, the solubility is only about 20% of the solubility in water for $Ni(MSA)_2$ and $Co(MSA)_2$, whereas for $Mn(MSA)_2$ only about 10% can be dissolved in 50 wt% MSA solution compared to pure water. Figure 6 gives an overview of the obtained data.

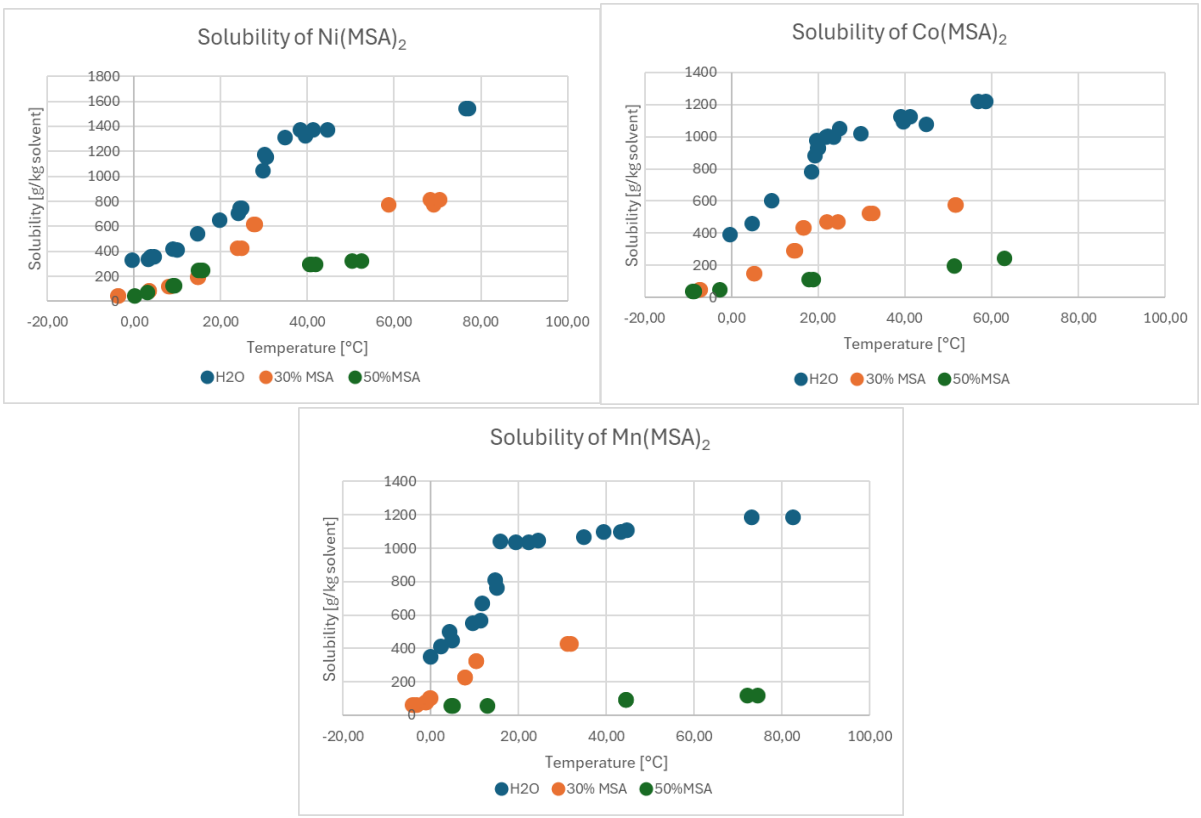

Figure 6: Solubility data of $Me(MSA)_2$ salts (Me = Ni, Co, Mn) in H2O, 30 wt% MSA and 50 wt% MSA.

Dissolution enthalpy

The dissolution enthalpies (for $Me(MSA)_2 \cdot 2H_2O$ salts) determined according to the procedure described above are summarized in Table 1. Table 2 contains relevant heat capacities measured. The dissolution of all $Me(MSA)_2$ salts (Me = Ni, Co, Mn) are exothermic with expected decrease in enthalpy with increasing concentration. In this series, the dissolution enthalpy of the MSA salts follow the order Mn < Co < Ni.

*Table 1: Measured dissolution enthalpies of $Me(MSA)_2$ * $2H_2O$ salts (Me = Ni, Co, Mn)*

Step	Enthalpy a) [kJ/step] b)	ΔTad [K] c)	Concentration (m/m)	Enthalpy [kJ/kg]
1. Addition Mn(MSA)2·2H₂O in 20 sec + 20 min stirring at 23 °C	-1.2	2	12.5	-56.1
2. Addition Mn(MSA)2·2H₂O in 20 sec + 20 min stirring at 23 °C	-0.9	1	22.2	-49.1
3. Addition Mn(MSA)2·2H₂O in 20 sec + 20 min stirring at 23 °C	-0.7	1	30	-43.6
1. Addition Co(MSA)2·2H₂O in 20 sec + 20 min stirring at 23 °C	-1.9	3	12.5	-88.8
2. Addition Co(MSA)2·2H₂O in 20 sec + 20 min stirring at 23 °C	-1.6	3	22.2	-81.3
3. Addition Co(MSA)2·2H₂O in 20 sec + 20 min stirring at 23 °C	-1.4	2	30	-76.3
1. Addition Ni(MSA)2·2H₂O in 20 sec + 20 min stirring at 23 °C	-2.4	4	12.5	-112.1

2. Addition Ni(MSA)2·2H₂O in 20 sec + 20 min stirring at 23 °C	-2	3	22.2	-102.8
3. Addition Ni(MSA)2·2H₂O in 20 sec + 20 min stirring at 23 °C	-1.8	3	30	-96.6

a) negative values: exothermal; b) batch size; c) calculated according to $\Delta T_{ad} = \Delta H/m*Cp$, m = mass of batch

Table 2: Heat capacities Cp (experimental data)

Compound / Mixture / Temperature	Heat capacity Cp [kJ/kg*K]	Source
Water at 20 °C	4.182	VDI – Atlas
Water at 23 °C	4.18	KIN_2024_028, 029, 030
After 1. Addition Mn(MSA)2·2H₂O at 23 °C	3.825	KIN_2024_028
After 2. Addition Mn(MSA)2·2H₂O at 23 °C	3.475	
Final mixture at 23–20 °C	3.165	
After 1. Addition Co(MSA)2·2H₂O at 23 °C	3.72	KIN_2024_029
After 2. Addition Co(MSA)2·2H₂O at 23 °C	3.285	
Final mixture at 23–20 °C	3.05	
After 1. Addition Ni(MSA)2·2H₂O at 23 °C	3.645	KIN_2024_030
After 2. Addition Ni(MSA)2·2H₂O at 23 °C	3.33	
Final mixture at 23–20 °C	2.965	

Conclusion

Within the CICERO project, $Me(MSA)_2$ salts of nickel(II), cobalt(II) and manganese(II) have been successfully synthesized from nickel(II) hydroxide, cobalt(II) carbonate monohydrate and manganese(II) oxide by a simple acid-base reaction with MSA. The respective isolated MSA-salts were found to be dihydrates, as TG measurements revealed. The solubility of these salts was investigated in pure water as well as in 30 wt% and 50 wt% MSA aqueous solutions from -20 °C up to 80 °C. The solubility data provided were referred to the pure salts (not the dihydrates). The experimental data for the solubilities in pure water fit well to the reported data by Belova et all. and extend them to temperatures higher than 50 °C. As expected, the solubility data determined for all 3 salts investigated is significant lower in 30 wt% MSA as well as 50 wt% MSA, being 15–20%, in 50 wt% MSA, compared to the solubility in pure water.

Furthermore, dissolution enthalpies of the three salts were determined for the dissolution of 12.5 wt%, 22.2 wt% as well as 30 wt% in water together with the respective heat capacities. The dissolution is exothermic and the enthalpies calculated follow the order Mn < Co < Ni.

The provided values can be used for advanced thermodynamic & kinetic modelling for solid-liquid & liquid-liquid equilibria relevant for Ni/Co/Mn processing/refining in MSA media

Acknowledgments

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Appendix:

Table 3: Solubility data for $Me(MSA)_2$ (Me = Ni, Co, Mn) in water taken from Belova et al. and measured data

Temperature [°C]	Ni(MSA)2 [g/kg]	source
-0,48	326	Belova et al-
3,20	333	
4,66	356	
3,94	356	
9,91	410	
8,98	416	
14,69	542	
19,65	651	
24,07	705	
24,62	735	
29,78	1043	
30,51	1156	
30,23	1172	
34,75	1309	
39,51	1326	
44,67	1370	
24,4	745	BASF SE 2024
24,9	745	
41,3	1372	
38,4	1372	
76,5	1546	
77,2	1546	

Temperature [°C]	Co(MSA)2 [g/kg]	source
-0,25	389	Belova et al
4,70	460	
9,37	601	
18,55	781	
19,65	975	
22,12	1005	
24,87	1052	
29,82	1021	
39,73	1091	
44,95	1078	
19,2	885	BASF SE 2024
19,9	931	
20	931	
21,8	999	
23,5	999	
39,1	1123	
41,3	1123	
56,9	1221	
58,7	1221	

Temperature [°C]	Mn(MSA)2 [g/kg]	source
-0,11	350	Belova et al
2,40	410	
4,92	450	
4,31	502	
9,63	550	
11,33	567	
11,73	670	
15,04	765	
14,74	809	
15,94	1042	
24,55	1046	
34,79	1067	
44,71	1108	
19,4	1035	BASF SE 202
22,4	1035	
39,4	1100	
43,3	1100	
73	1185	
82,4	1185	

Table 4: solubility data for $Me(MSA)_2$ (Me = Ni, Co, Mn) in 30 wt% MSA; measured data

Temperature [°C]	Ni(MSA)2 [g/kg]	remark
-3,7	39	
-3,6	39	
3,4	81	
3,4	81	
7,9	121	
8,4	121	
14,7	195	
14,9	195	
23,9	424	
24,9	424	
27,5	617	
27,9	617	
58,8	775	
68,3	813	
69,2	775	
70,5	813	
85,0	1025	no solution

Temperature [°C]	Co(MSA)2 [g/kg]	remark
-7,4	50	
-7,1	50	
5,1	149	
5,4	149	
14,4	289	
14,7	289	
16,6	432	
16,8	432	
22	473	
24,5	473	
31,9	521	
32,5	521	
51,5	578	
51,8	578	
85,0	662	no solution

Temperature [°C]	Mn(MSA)2 [g/kg]	remark
-20,0	50	no crystals
-4,1	59	
-3,7	59	
-3,2	59	
-1,2	79	
-0,9	79	
-0,2	100	
-0,1	100	
7,8	225	
7,9	225	
10,4	322	
10,4	322	
31,1	426	
31,9	426	
85,0	452	no solution
85,0	509	no solution
85,0	667	no solution

Table 5: solubility data for $Me(MSA)_2$ (Me = Ni, Co, Mn) in 50 wt% MSA; measured data

Temperature [°C]	Ni(MSA)2 [g/kg]	remark
0,1	41	
3,1	70	
8,9	124	
9,4	124	
14,9	247	
15,4	247	
15,8	247	
40,5	292	
41	292	
41,9	292	
50,4	325	
52,4	325	
85,0	428	no solution

Temperature [°C]	Co(MSA)2 [g/kg]	remark
-8,9	36	
-8,6	36	
-2,6	49	
17,9	113	
18,9	113	
51,4	199	
63	243	
85,0	327	no solution

Temperature [°C]	Mn(MSA)2 [g/kg]	remark
-20,0	50	solution
4,7	54	
5	54	
13	54	
44,4	91	
44,5	91	
72	116	
74,4	116	
85,0	246	no solution