

Supplementary information

Synthesis of calcium carbonate in trace water environment

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Experimental section

Crushed anhydrous CaCl_2 (Sigma-Aldrich, granular, $\geq 93.0\%$) and anhydrous $(\text{NH}_4)_2\text{CO}_3$ (Acros organics, for analysis ACS) were put in a desiccator with P_2O_5 for several days in order to dry them completely. After this, they were stored in a closed desiccator with P_2O_5 until usage.

0.1 M solutions of CaCl_2 and $(\text{NH}_4)_2\text{CO}_3$ in absolute ethanol (sigma Aldrich, $\geq 98.0\%$) were prepared stirring the previously dried salts overnight. The solutions were filtered with 0.2 μm filters before use. Then, both solutions were injected with syringe pumps (rate 7.5 mL/h, era pump system inc.) in a volume of alcohol to reach the desired concentration, as reported in Table S1.

After 3 hours from the end of addition, the solutions were centrifuged at 4500 g for 10 minutes (ALC PK121). It was possible to separate the sample prepared using 10 mM salts in 1-PropOH only after 5 days (highlighted in patterned grey in Table S1). The samples were not washed with any solvent since the synthesis produced a very small amount of powder that would be almost totally lost with further processing. It was possible to separate a precipitate only from the samples highlighted in grey. After the centrifugation, the precipitate was collected and dried at 60 °C.

Characterization

Fourier transform infrared (FTIR) spectra of samples in KBr pellet were collected at room temperature by using a FT-IR Bruker Alpha System spectrometer working in the range of wavenumbers 4000–400 cm^{-1} at a resolution of 1 cm^{-1} with 64 scans.

High resolution X-ray powder diffraction (HRPXRD) measurements were collected with a dedicated high-resolution powder diffraction synchrotron beamline (ID22 at the European Synchrotron Radiation Facility (ESRF), Grenoble, France) using as wavelength 0.039 nm.

X-ray powder diffraction (XRPD) measurements reported in Figure SI 4 were carried out using a PanAnalytical X'Pert Pro diffractometer equipped with X'Celerator detector with Cu $\text{K}\alpha$ radiation (range 20°-60°, step size 0.05°, time per step 120 s).

Scanning electron microscopy (SEM) images were collected with a Phenom G2 Pure microscope (FEI) for uncoated samples (reported in figure SI 3) and a Hitachi FEG 6400 microscope for samples after coating with 5 nm of gold (Figure 2).

Thermogravimetric analysis (TGA) was performed using an SDT Q600 instrument (TA Instruments).

Dynamic light scattering (DLS) was performed using a Malvern Zetasizer Nano ZS.

Analytical Ultracentrifugation (AUC) measurements were performed on an Optima XL-I analytical ultracentrifuge (Beckman-Coulter, Palo Alto, CA, United States) using Rayleigh Interference optics and 12 mm double-sector titanium centerpieces (Nanolytics, Potsdam, Germany). Samples were investigated at 25 °C and 5 000 rpm, 16 000 rpm and 60 000 rpm. 320 μl of the prepared salt solutions were used for the measurements. 350 μl of the corresponding organic solvent was used as reference solution.

The sedimentation velocity experiments at 5 000 rpm and 16 000 rpm were evaluated with the $l_s\text{-}g^*(s)$ model using the SEDFIT software version 14.4d by Peter Schuck (<http://www.analyticalultracentrifugation.com/default.htm>). The measurement data at 60 000 rpm were evaluated with numerical fitting of the Lamm equation using a noninteracting species model yielding sedimentation and diffusion coefficient s resp. D as well as species concentration in fringe units using the same SEDFIT software.

Table S11. Volumes of reagents used to obtain each sample

Solvent Conc.	MeOH	EtOH	1-PropOH	1-BuOH
33 mM	5 mL CaCl ₂ in EtOH 5 mL (NH ₄) ₂ CO ₃ in EtOH 5 mL MeOH	5 mL CaCl ₂ in EtOH 5 mL (NH ₄) ₂ CO ₃ in EtOH 5 mL EtOH	5 mL CaCl ₂ in EtOH 5 mL (NH ₄) ₂ CO ₃ in EtOH 5 mL 1-PropOH	5 mL CaCl ₂ in EtOH 5 mL (NH ₄) ₂ CO ₃ in EtOH 5 mL 1-BuOH
20 mM	5 mL CaCl ₂ in EtOH 5 mL (NH ₄) ₂ CO ₃ in EtOH 15 mL MeOH	5 mL CaCl ₂ in EtOH 5 mL (NH ₄) ₂ CO ₃ in EtOH 15 mL EtOH	5 mL CaCl ₂ in EtOH 5 mL (NH ₄) ₂ CO ₃ in EtOH 15 mL 1-PropOH	5 mL CaCl ₂ in EtOH 5 mL (NH ₄) ₂ CO ₃ in EtOH 15 mL 1-BuOH
10 mM	5 mL CaCl ₂ in EtOH 5 mL (NH ₄) ₂ CO ₃ in EtOH 40 mL MeOH	5 mL CaCl ₂ in EtOH 5 mL (NH ₄) ₂ CO ₃ in EtOH 40 mL EtOH	5 mL CaCl ₂ in EtOH 5 mL (NH ₄) ₂ CO ₃ in EtOH 40 mL 1-PropOH	5 mL CaCl ₂ in EtOH 5 mL (NH ₄) ₂ CO ₃ in EtOH 40 mL 1-BuOH
5 mM	2.5 mL CaCl ₂ in EtOH 2.5 mL (NH ₄) ₂ CO ₃ in EtOH 45 mL MeOH	2.5 mL CaCl ₂ in EtOH 2.5 mL (NH ₄) ₂ CO ₃ in EtOH 45 mL EtOH	2.5 mL CaCl ₂ in EtOH 2.5 mL (NH ₄) ₂ CO ₃ in EtOH 45 mL 1-PropOH	2.5 mL CaCl ₂ in EtOH 2.5 mL (NH ₄) ₂ CO ₃ in EtOH 45 mL 1-BuOH

Table S12. Unit cell parameters of calcite and vaterite obtained by the Rietveld analysis of the diffraction patterns of the samples investigated by synchrotron high resolution powder X-ray diffraction (see Fig. S1). The weight fraction of the detected mineral phases is also reported. The samples coded with heated were heated for 2 hours at 300 °C and then analysed at room temperature.

Sample	Calcite			Vaterite			NH ₄ Cl
	a,b (Å)	c (Å)	Weight fraction (wt%)	a,b (Å)	c (Å)	Weight fraction (wt%)	Weight fraction (wt%)
MeOH_33	4.986(1)	17.101(2)	35	4.1285(5)	8.4778(8)	65	
MeOH_33 heated	4.985(2)	17.087(4)	39	4.1287(8)	8.474(1)	61	
EtOH_33	4.9879(5)	17.0999(9)	6	4.1290(3)	8.4742(4)	80	14
EtOH_33 heated	4.9906(8)	17.075(2)	7	4.1294(3)	8.4713(4)	93	
PropOH_33	4.9849(3)	17.1040(3)	0.1	4.1260(6)	8.495(1)	74.9	25
PropOH_33 heated	5.00(5)	17.0(1)	0.7	4.1274(5)	8.479(1)	99.3	
BuOH_33	4.987(1)	17.097(2)	3	4.1291(3)	8.4808(6)	84	13
BuOH_33 heated	4.990(1)	17.078(2)	5	4.12966(2)	8.4707(4)	95	

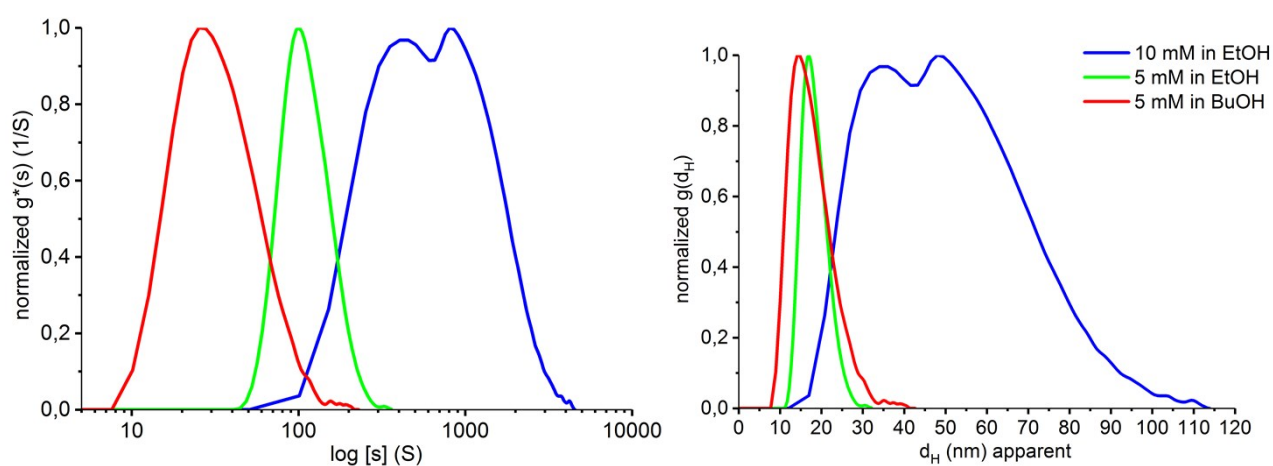


Figure S11. Sedimentation coefficient distribution of different salt concentrations in organic solvents from AUC and the corresponding particle size distribution calculated on basis of a density of ACC = 1.48 g/ml and using the densities and viscosities of the pure solvents.

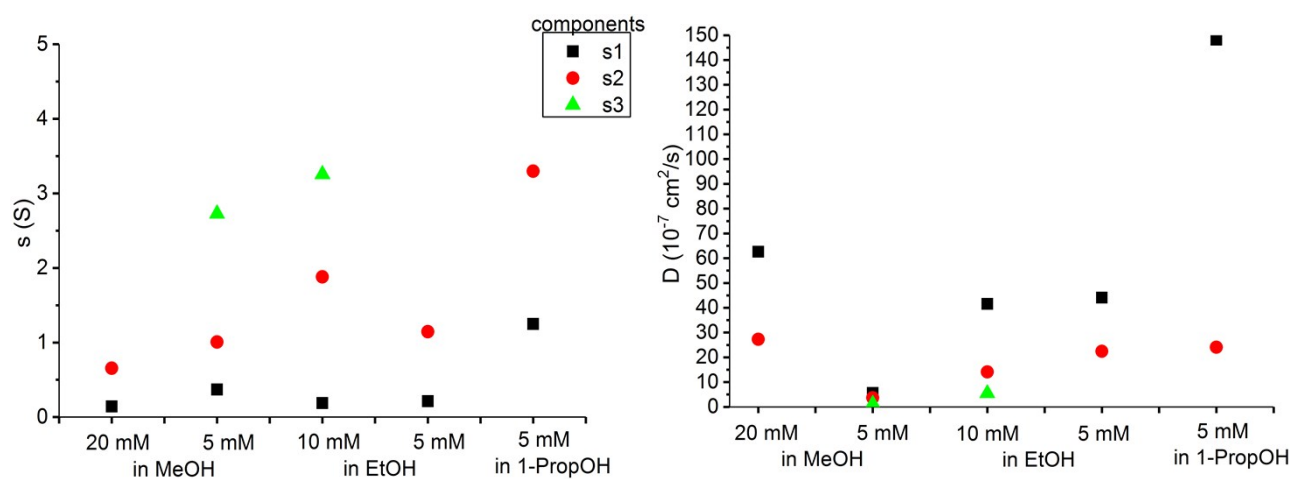


Figure S12. Sedimentation coefficients (left) and diffusion coefficients (right) of different CaCO_3 concentrations in organic solvents from AUC Non-Interacting Discrete Species Model. Up to three independent species are detected and marked with colours (black = species 1, red = species 2 and green = species 3)

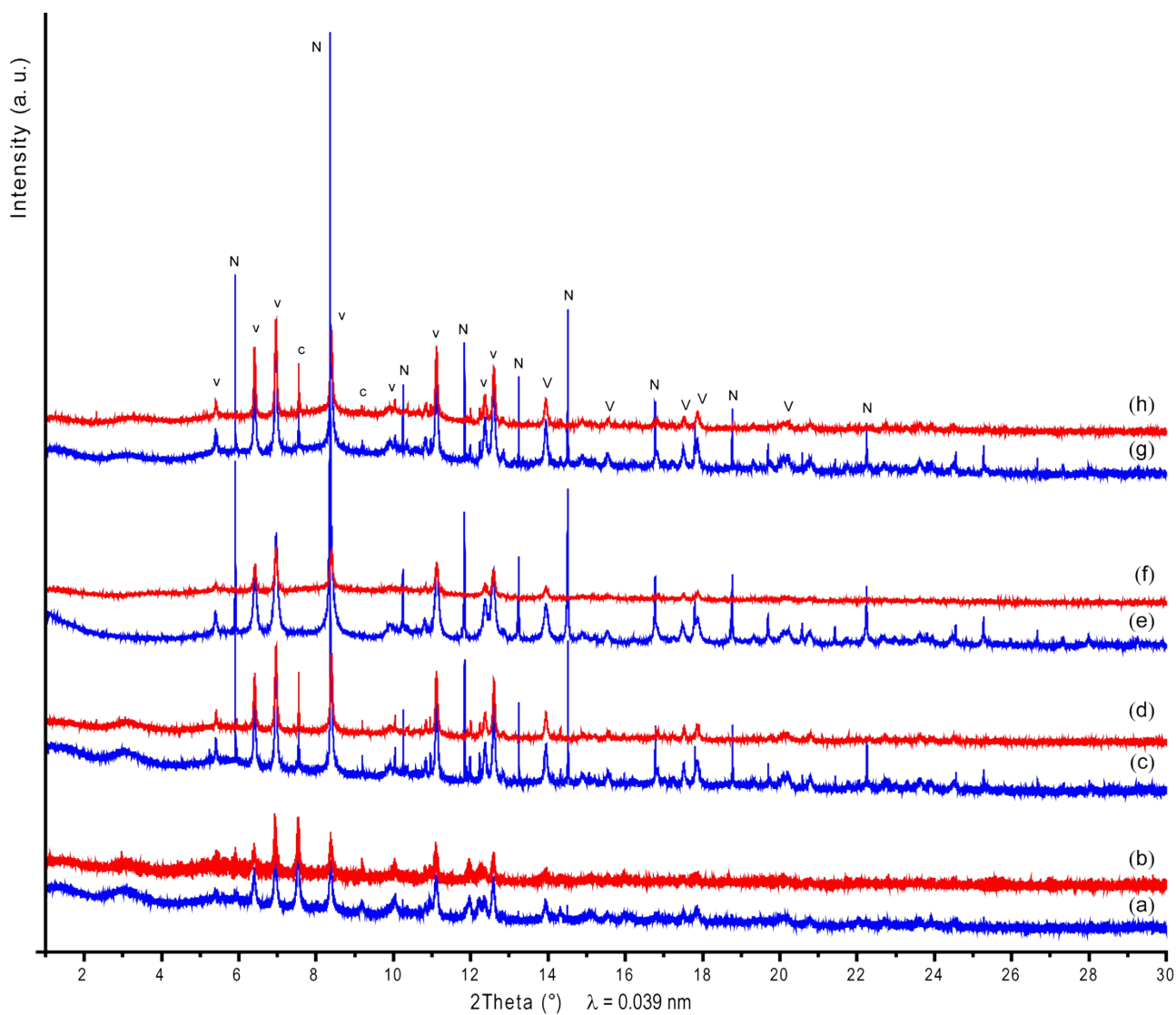


Figure S13. High resolution powder X-ray powder patterns of samples obtained using MeOH and 33 mM salts (a) before and (b) after heating at 300 °C, EtOH and 33 mM salts (c) before and (d) after heating at 300 °C, PropOH and 33 mM salts (e) before and (f) after heating at 300 °C and BuOH and 33 mM salts (g) before and (h) after heating at 300 °C. Peaks marked with N correspond to NH₄Cl, the ones marked with V correspond to vaterite and the ones marked with C correspond to calcite.

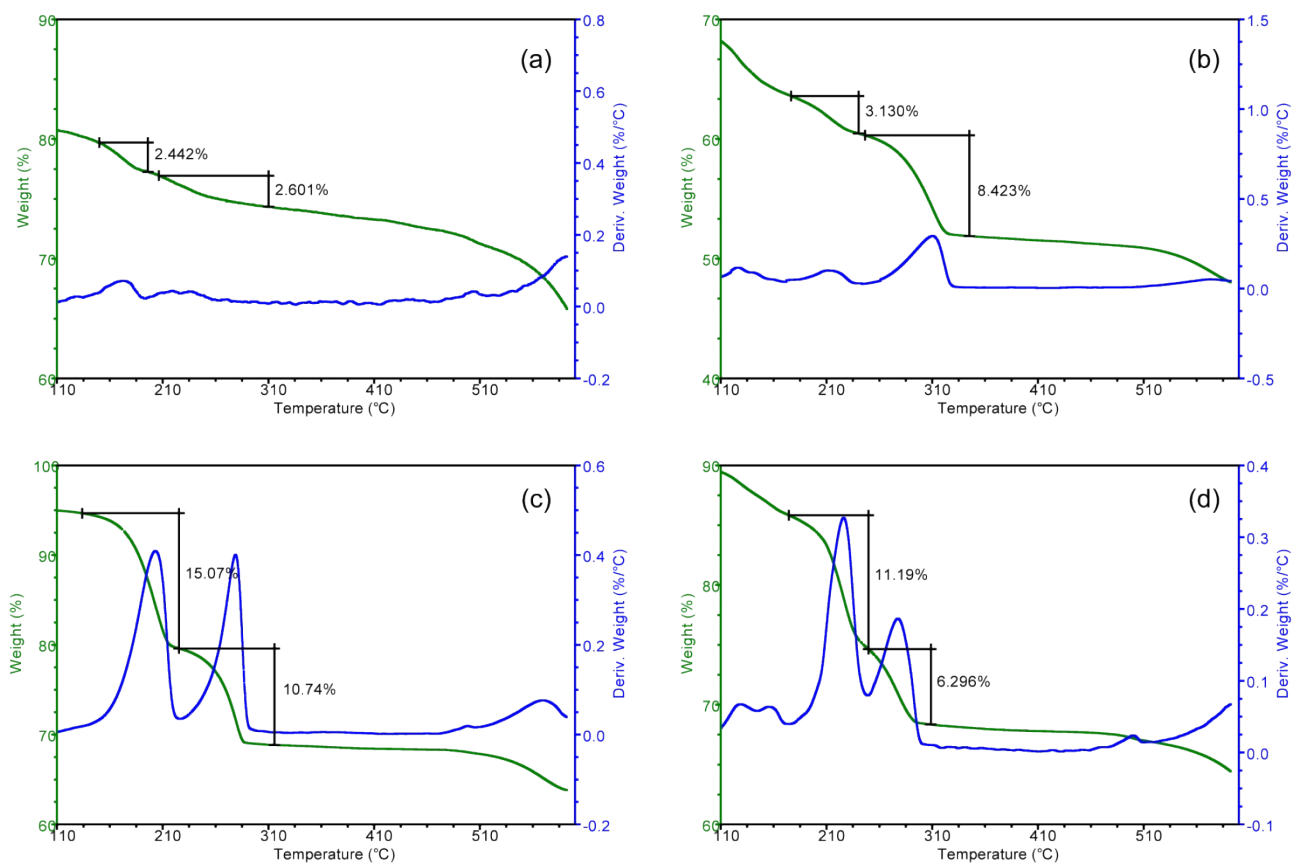


Figure S14. TGA profiles of samples obtained using (a) MeOH and 33 mM salts, (b) EtOH and 33 mM salts, (c) PropOH and 33 mM salts and (d) BuOH and 33 mM salts. The weight lost at about 200 °C is associated to a water lost, while that at about 280 °C to the sublimation of NH_4Cl .

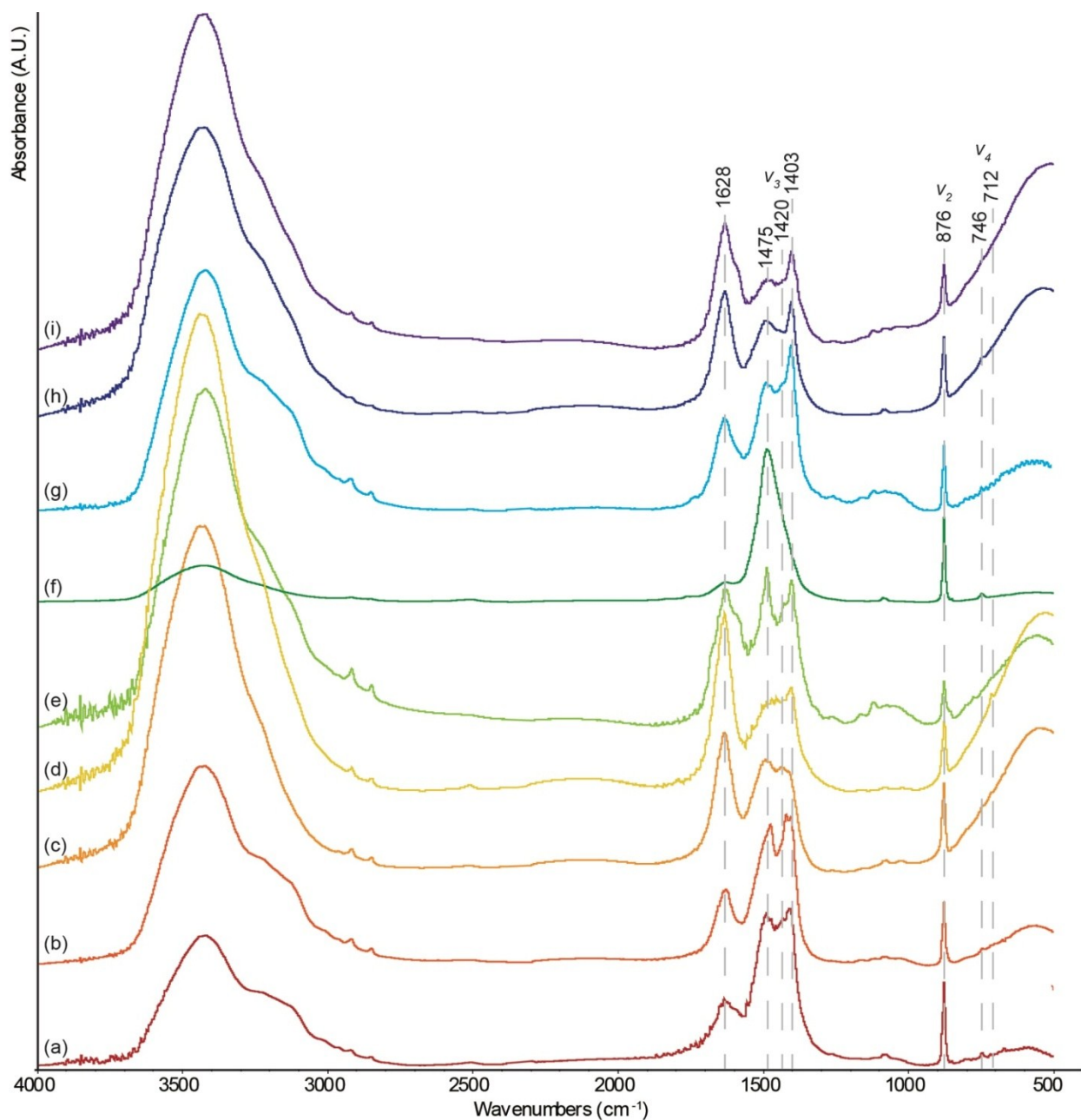


Figure S15. FTIR spectra of samples obtained using (a) MeOH and 33 mM salts, (b) EtOH and 33 mM salts, (c) EtOH and 20 mM salts, (d) PropOH and 33 mM salts, (e) PropOH and 20 mM salts, (f) PropOH and 10 mM salts, (g) BuOH and 33 mM salts, (h) BuOH and 20 mM salts and (i) BuOH and 10 mM salts. Collected with an FT-IR Bruker Alpha System spectrometer (64 scans).

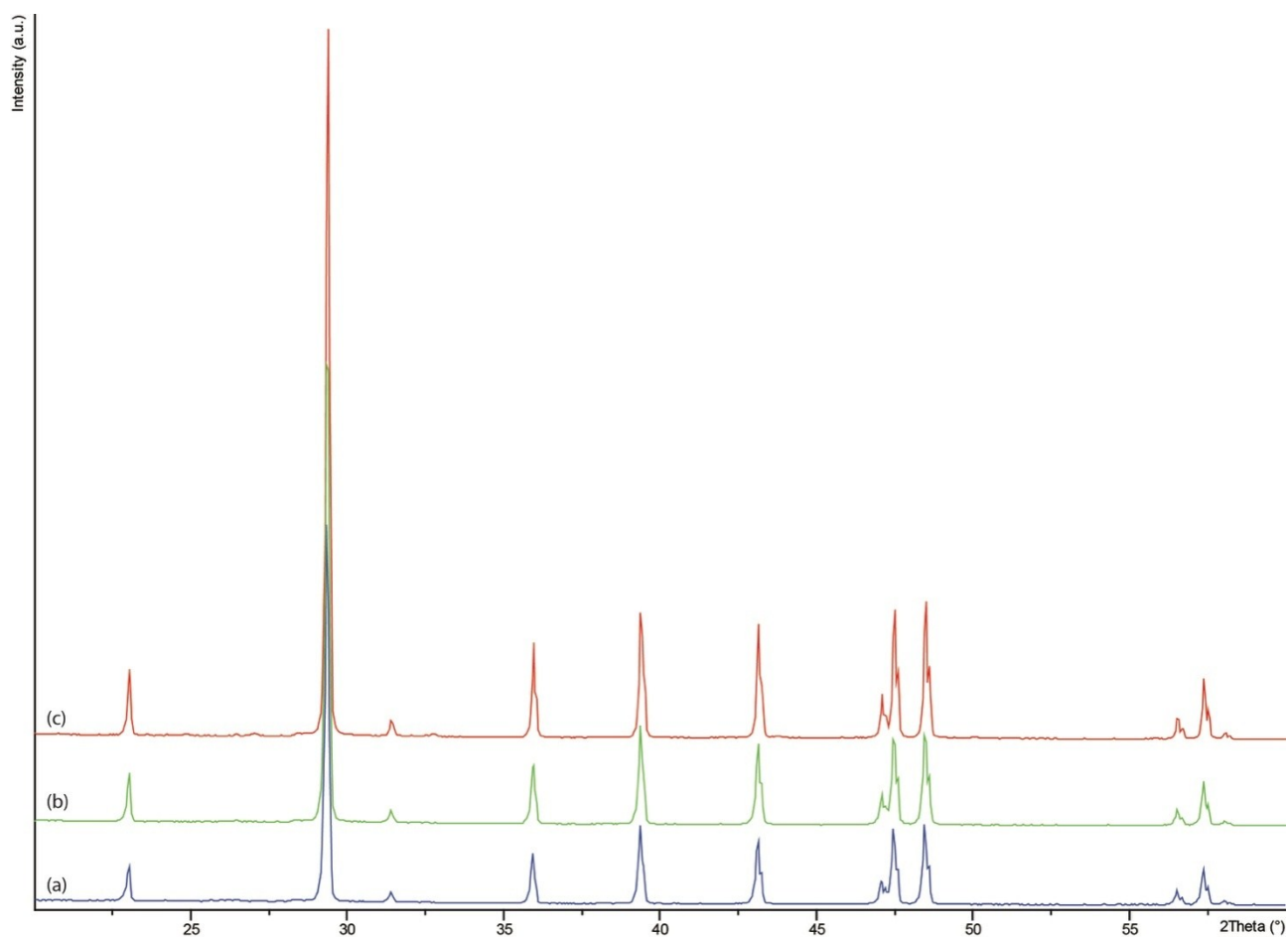


Figure S16 X-ray powder diffraction patterns of samples obtained in water with (a) 33 mM salts, with (b) 20 mM salts and (c) 10 mM salts using the same conditions used for the experiments with organic solvents. Only calcite peaks are present.

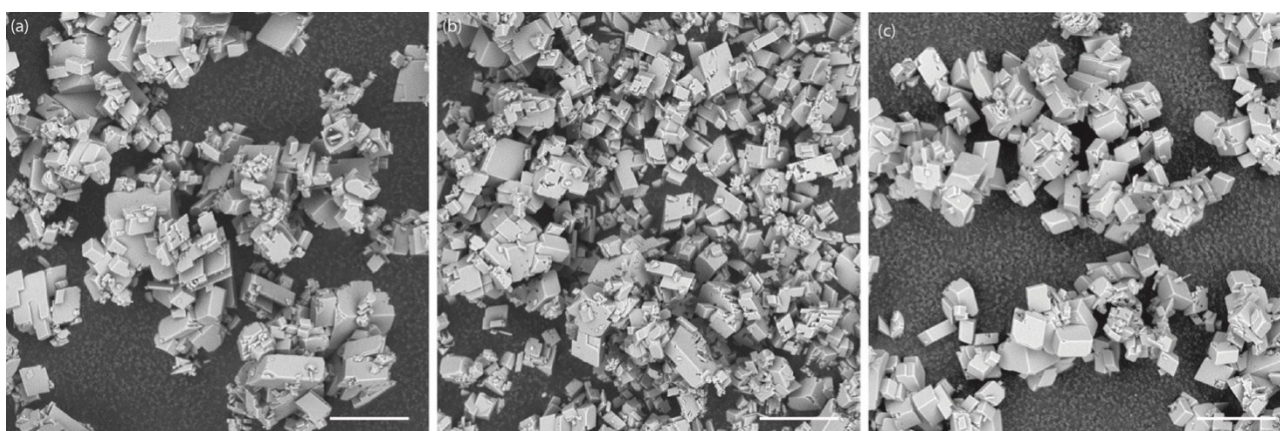


Figure S17 Scanning electron microscopy (SEM) of samples obtained in water with (a) 33 mM salts, with (b) 20 mM salts and (c) 10 mM salts using the same conditions used for the experiments with organic solvents. Only calcite rhombohedra are present. Scalebar is 10 μ m.