

Electronic Supplementary Information for “Estimation of the Growth and the Dissolution Kinetics of Ammonium Bicarbonate in Aqueous Ammonia Solutions from Batch Crystallization Experiments”

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Abstract

This is the *Electronic Supplementary Information* to the article “Estimation of the Growth and the Dissolution Kinetics of Ammonium Bicarbonate in Aqueous Ammonia Solutions from Batch Crystallization Experiments”. This document provides:

1. ATR-FTIR calibration sets of aqueous ammonia solutions of ammonium bicarbonate;
 2. Calculation of the standard deviation of steady-state ATR-FTIR concentration measurements;
 3. Solid Raman characterization of needle-like ammonium bicarbonate crystals;
 4. μ -DISCO camera images of the ammonium bicarbonate crystals;
 5. XRD patterns of crystal products obtained from the growth experiments;
 6. Fitting outcome of sub-sets of growth experiments at different nominal aqueous ammonia concentrations.
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Compound	Concentration [mol/kg _w]				Temperature [°C]			
<i>Sample No.</i>	1	2	3	4	1	2	3	4
NH ₄ HCO ₃ (aq) ($\omega_{\text{NH}_3}^\circ = 0\%$ wt)	1.76	2.02	2.31	2.64	5- 25	10 [†] - 25	10 [†] - 25	16 [†] - 25
NH ₄ HCO ₃ (aq) ($\omega_{\text{NH}_3}^\circ = 2\%$ wt)	2.64	2.89	3.05	3.17	5 - 25	8 [†] - 25	12 [†] - 25	14 [†] - 25
NH ₄ HCO ₃ (aq) ($\omega_{\text{NH}_3}^\circ = 3\%$ wt)	3.06	3.27	3.42	3.53	5 - 25	6 [†] - 25	8 [†] - 25	13 [†] - 25

Table 1: Set of standard concentrations of aqueous ammonia solutions of ammonium bicarbonate used for the ATR-FTIR calibrations (see Fig. 1); the variable $\omega_{\text{NH}_3}^\circ$ refers to the nominal ammonia concentration in the solvent (in weight percent). The symbol [†] refers to the temperature value corresponding to the onset of primary nucleation.

ATR-FTIR calibration sets of aqueous ammonia solutions of ammonium bicarbonate

The set of standard concentrations of aqueous ammonia solutions of ammonium bicarbonate used for the ATR-FTIR calibration procedure [1] are reported in Table 1.

Fig. 1 shows the range of ammonium bicarbonate concentrations used in this work.

The solid lines in Fig. 1 represent the solubility of ammonium bicarbonate at different nominal ammonia concentration $\omega_{\text{NH}_3}^\circ$. The ammonia concentration in the solvent is expressed on a weight percent basis. Both the supersaturated and the undersaturated regions of the phase diagram have been explored.

Calculation of the standard deviation of steady-state ATR-FTIR concentration measurements

Fig. 2 shows a series of ammonium bicarbonate steady-state ATR-FTIR concentration measurements in the range 120–240 g/kg_w. The data at each concentration has been mean-centered prior to computing the standard deviation of the measurements (cf. colored clusters in Fig. 2). The obtained value of standard deviation based on the whole experimental data set is 0.35 g kg⁻¹.

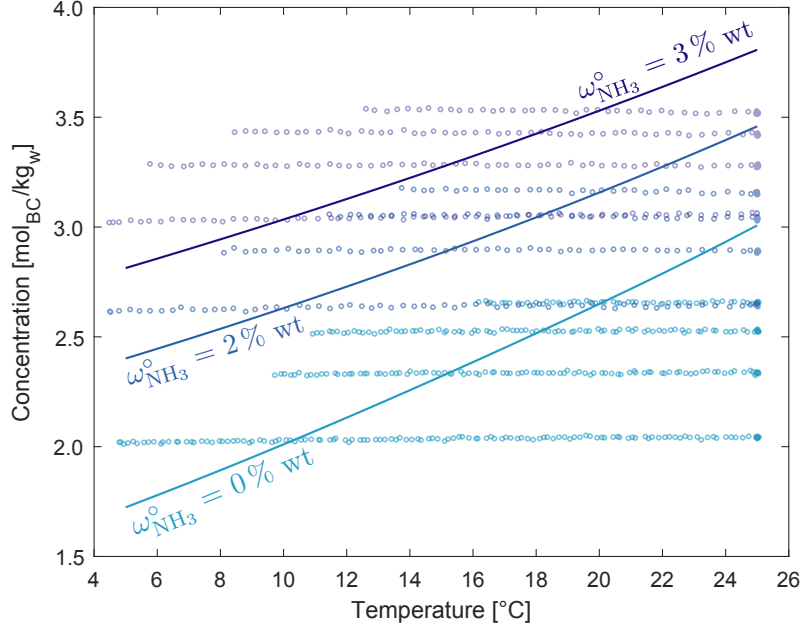


Figure 1: Set of ATR-FTIR calibrations of aqueous ammonia solutions of ammonium bicarbonate in the temperature range 5-25 °C; the variable $\omega_{\text{NH}_3}^0$ refers to the nominal ammonia concentration in the solvent (on a weight percent basis). Table 1 contains the nominal ammonium bicarbonate concentrations used for the calibration of the ATR-FTIR instrument. The concentration data collected after nucleation has been omitted in the figure and excluded from the calibration sets.

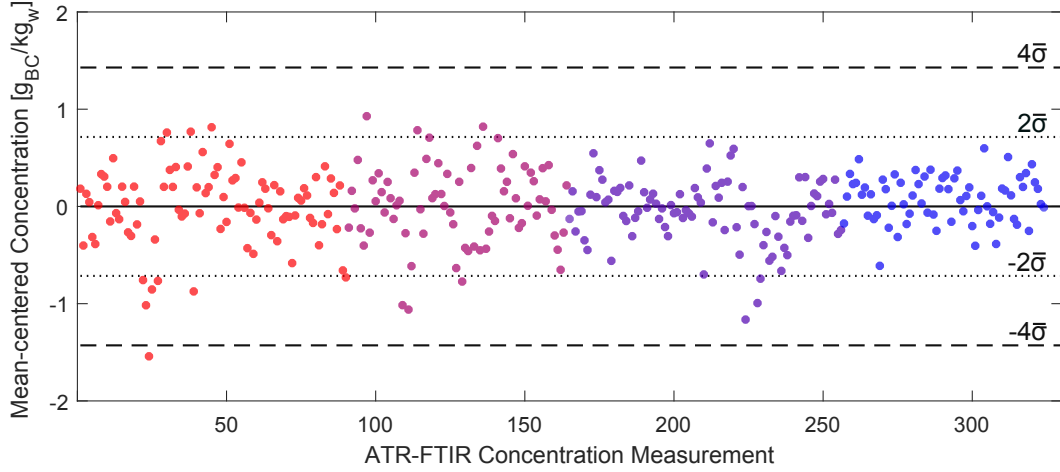


Figure 2: Mean-centered ATR-FTIR concentration measurements of aqueous ammonia solutions of ammonium bicarbonate. The nominal ammonium bicarbonate concentrations of the clusters, moving from the red one to the blue one, are 120 g kg⁻¹, 160 g kg⁻¹, 200 g kg⁻¹, and 240 g kg⁻¹, respectively. The standard deviation $\bar{\sigma}$ of the measurements based on the whole experimental data set is 0.35 g kg⁻¹. Bands are set to ± 2 and ± 4 standard deviations wrt to the mean-centered concentration.

Solid Raman characterization of needle-like ammonium bicarbonate crystals

Raman spectroscopy was employed to assess the composition of the needle-like crystals obtained from the experiment discussed in Sec. 5.1 of the article.

In this work, a RA 400 Raman spectrometer from Mettler-Toledo (Greifensee, Switzerland) equipped with a 250 mW frequency-stabilized laser diode at 785 nm and a thermoelectrically cooled CCD detector was used. In situ measurements were recorded using a 5/8 in. ball-type immersion probe (Inphotonics, Norwood, MA) connected via a fiber optic (thicknesses of collection and excitation fibers were 100 and 200 μm , respectively). Solid powder mixtures of the crystallization product as well as of the commercially available ammonium bicarbonate were analyzed, at ambient conditions, using a probe directly immersed in the solid phase. Raman spectra were collected at a laser intensity of 150 mW in the range 190 to 1600 cm^{-1} with a resolution of 0.5 cm^{-1} and were averaged over 10 scans using an exposure time of 5 s.

From the similarities between the spectra it can be inferred that the substance crystallized during the experiment is pure ammonium bicarbonate.

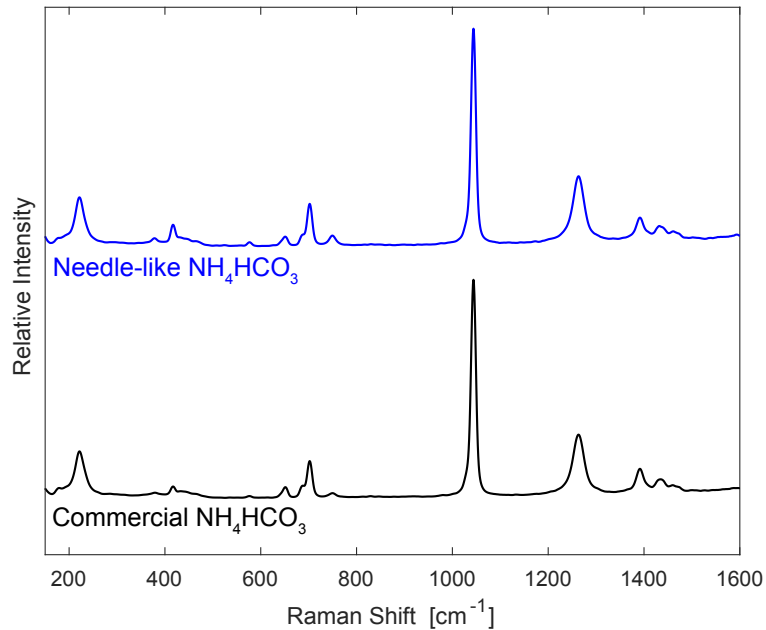


Figure 3: Solid-phase Raman spectra of ammonium bicarbonate collected at ambient conditions. The black curve refers to the commercial ammonium bicarbonate, while the blue curve refers to the product of the cooling crystallization experiment discussed in Sec. 5.1 of the article.

μ -DISCO camera images of the ammonium bicarbonate crystals

Fig. 4 shows the evolution of the crystal habit of ammonium bicarbonate as described in Sec. 5.1. In Fig. 4, from left to right, μ -DISCO camera images of the seed crystal population, of the seed crystals grown at a supersaturation $\sigma \leq 0.05$, and of a subsequent growth phase performed at a higher supersaturation ($\sigma \approx 0.07$) have been reported.

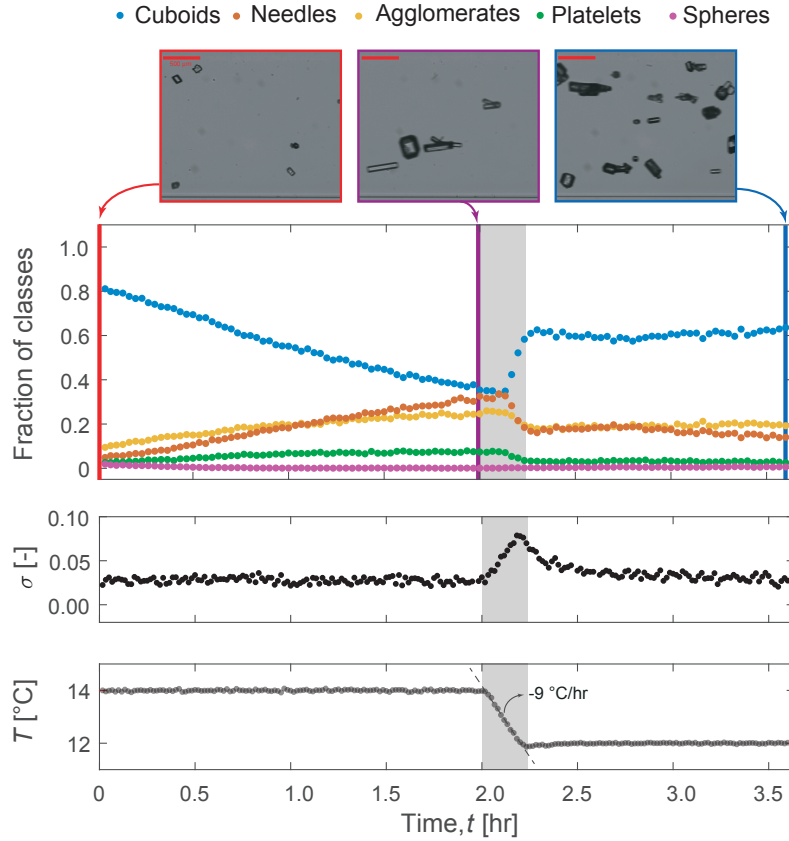


Figure 4: Time-resolved shape change of ammonium bicarbonate crystals during the growth experiment described in Sec. 5.1. Measurements have been performed every 2 min using the μ -DISCO acquiring 800 images per measurement. The number of sampled particles per measurement is roughly 25,000. The particle shape classification has been performed using an algorithm described elsewhere [2]. The μ -DISCO camera images relative to the different phases of the experiment are highlighted in red, purple, and blue respectively.

XRD patterns of crystal products obtained from the growth experiments

The nature of the crystals obtained from the desupersaturation growth experiments reported in Table 2 in the article was verified using powder X-ray diffraction, as shown in Fig. 5. Powder X-ray diffraction patterns were recorded after samples were spread uniformly over the sample holder using a diffractometer from Bruker (D2 Phaser, 30 kV, 10 mA, Cu KR; Karlsruhe, Germany). Patterns were recorded at 2θ between 10° and 80° with resolution of 0.02° and a scan speed of $5.83^\circ \text{ min}^{-1}$. The X-ray pattern of the crystal products matches qualitatively with the one of commercial ammonium bicarbonate (grey pattern in Fig. 5).

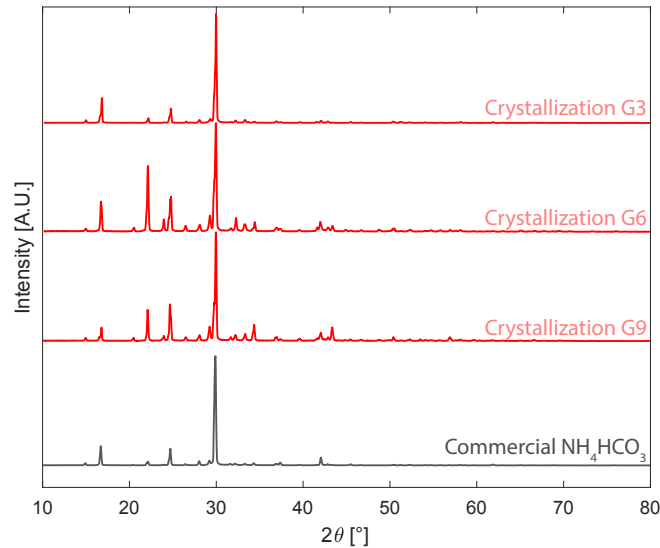


Figure 5: Powder X-ray diffraction patterns of the crystallization products obtained from the desupersaturation growth experiments reported in Table 2 in the article. The X-ray diffraction pattern of commercial ammonium bicarbonate is shown as reference.

Fitting outcome of sub-sets of growth experiments at different nominal aqueous ammonia concentrations

Fig. 6 shows the quality of fit of the growth model with respect to the desupersaturation growth experiments reported in Table 2 in the article. Four independent parameter estimations have been carried out using:

- the whole set of growth experiments at different aqueous ammonia concentrations in the solvent;
- the set of growth experiments at 0 % wt aqueous ammonia solution;
- the set of growth experiments at 2 % wt aqueous ammonia solution;
- the set of growth experiments at 3 % wt aqueous ammonia solution.

The respective values of the optimal growth kinetic parameter $\hat{k}_{g,1}$ are $(4.99 \pm 0.06) \cdot 10^{-6}$, $(6.68 \pm 0.07) \cdot 10^{-6}$, $(5.53 \pm 0.05) \cdot 10^{-6}$, and $(3.55 \pm 0.06) \cdot 10^{-6}$. As it can be noted, the optimal kinetic rate constant of the crystallization process tends to decrease as the nominal aqueous ammonia concentration increases.

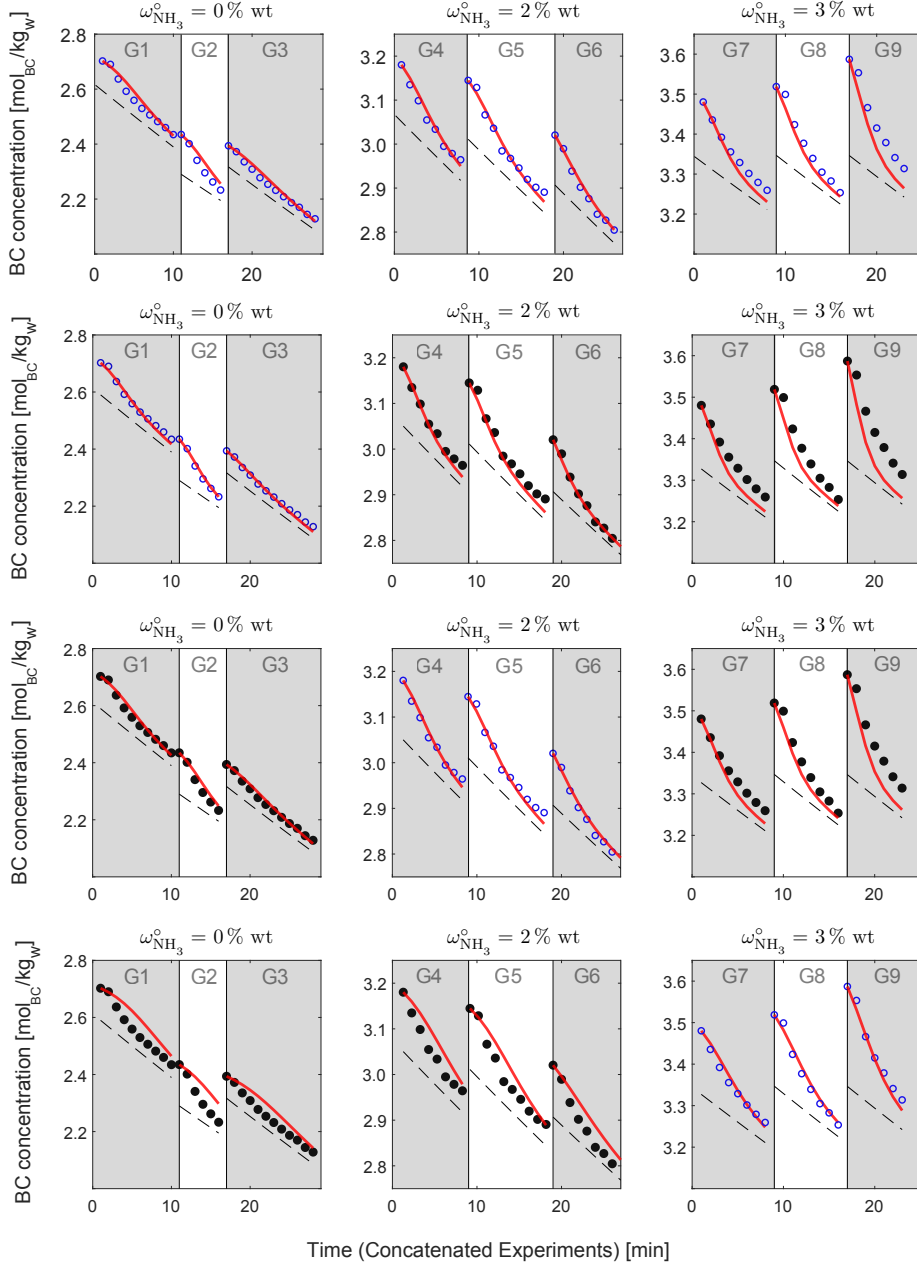


Figure 6: Concatenated seeded polythermal desupersaturation experiments in aqueous ammonia solutions of ammonium bicarbonate (BC) at 0% wt, 2% wt, and 3% wt ammonia, respectively (cf. Table 2 in the article). The hollow circular markers in blue color are the experimental BC concentration data points used for the kinetic parameter regression, while the black circular markers are the experimental data not included in the parameter estimation. The red curves are the fitted model's output, while the dashed lines indicate the BC solubility at the relevant temperature.

References

- [1] J. Cornel, C. Lindenberg, M. Mazzotti, Quantitative Application of in Situ ATR-FTIR and Raman Spectroscopy in Crystallization Processes, *Ind. Eng. Chem. Res.* 47 (14) (2008) 4870–4882. doi:10.1021/ie800236v.
- [2] A. K. Rajagopalan, J. Schneeberger, F. Salvatori, S. Bötschi, D. R. Ochsenbein, M. R. Oswald, M. Pollefeys, M. Mazzotti, A comprehensive shape analysis pipeline for stereoscopic measurements of particulate populations in suspension, *Powder Technol.* 321 (2017) 479–493. doi:10.1016/j.powtec.2017.08.044.