Supplementary information for: **Metastability Limit of Hydrated Phases of Sodium Sulfate under Temperature Cycling for Heat Storage**

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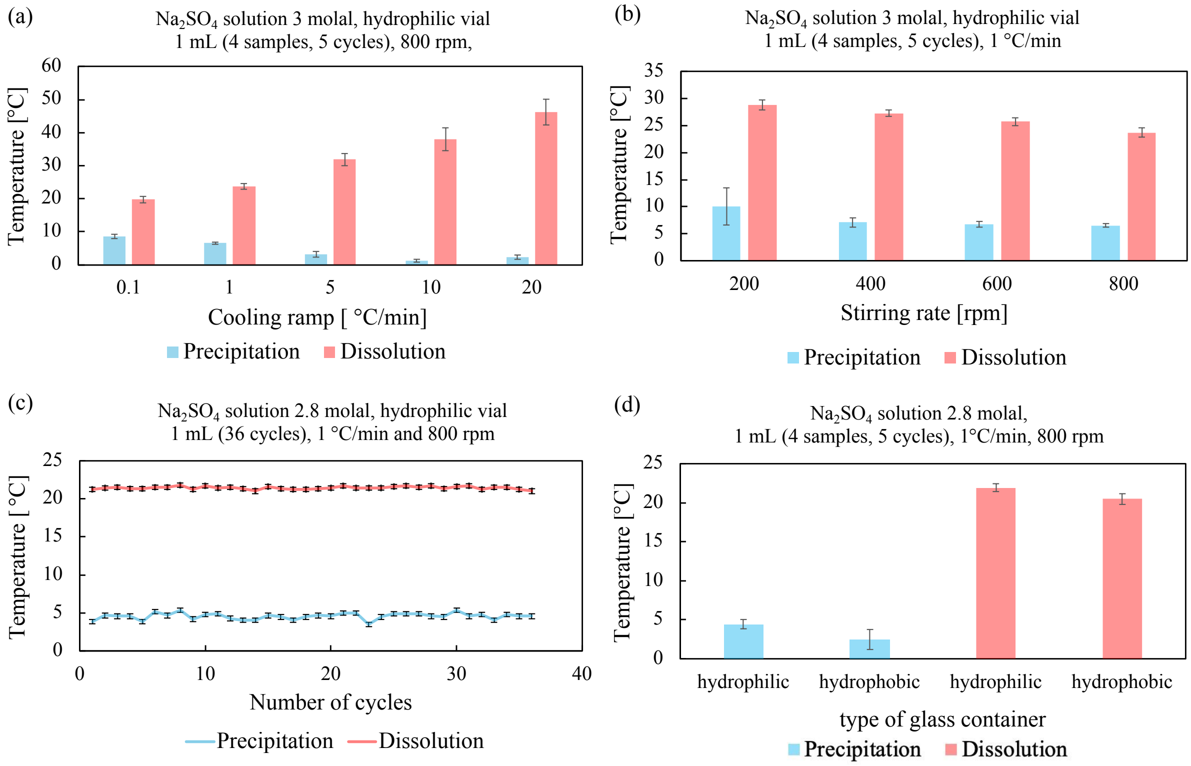

Figure S1. **Influence of the thermal cycling parameters on the temperatures of precipitation and dissolution of sodium sulfate heptahydrate in 1 mL samples**. (a) Cooling rate, (b) Stirring rate, (c) Number of cycles. (d) Influence of the type of glass container used.

Fig. S1a: The higher the cooling rate, the wider the MSZW. This result is in agreement with the study realized by Guisheng Zeng et al.[1] who worked with 100 mL solutions.

Fig. S1b: The impact of the stirring rate here is unsignificant. That's why the temperatures of precipitation obtained in the freezer (no stirring) and in the Crystal16 (800 rpm) presented Fig. 5 in the paper shows similar values. However, in the work of Guisheng Zeng et al. they have seen that the MSZW was very dependent on the stirring rate which is understandable as they have samples 100 times bigger than ours.

Fig. S1c shows that the temperatures of precipitation and dissolution remain stable over many cycles.

Fig. S1d was used to check if the hydrophobicity of the glass has an impact on the supercooling and on the mirabilite formation. The results show there is no influence of the hydrophobicity of the glass since we get the metastable heptahydrate with supercooling in both cases.

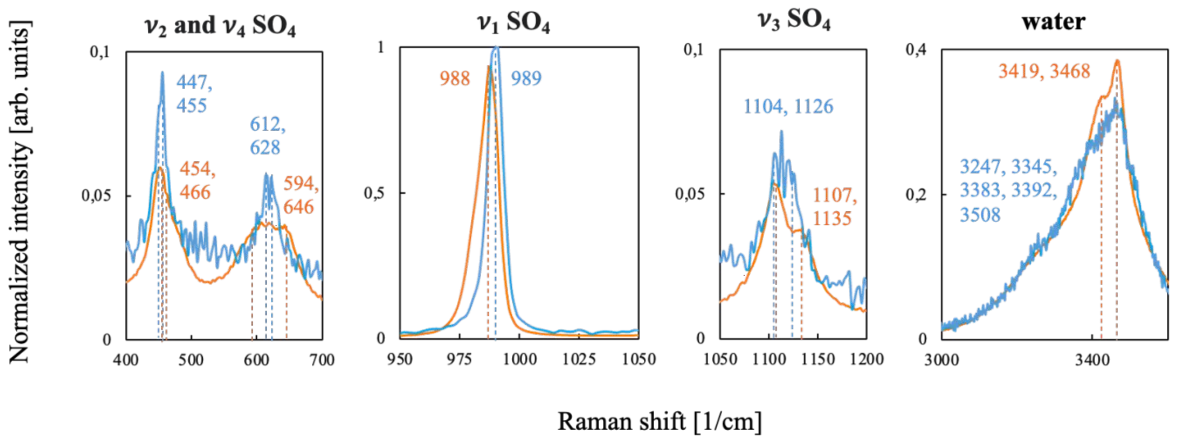

Figure S2. **Raman spectra of mirabilite (blue) and heptahydrate sodium sulfate (orange)**

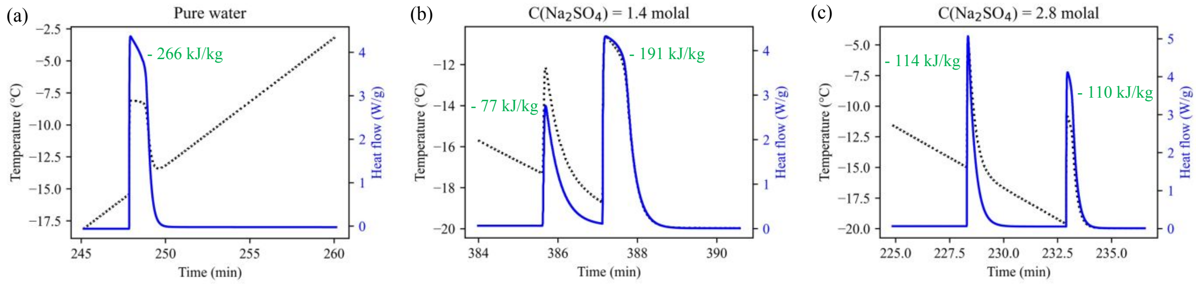

Figure S3. **Differential Scanning Calorimetry (DSC) conducted for three samples containing pure water (a), and sodium sulfate solutions at 1.4 molal (b) and 2.8 molal (c).** DSC measurements were performed on a DSC 25 - TA instrument with a ramp of cooling of 1°C/min, nitrogen flow fixed at 40.00 mL/min, on samples of 30 µL in aluminum pans, scanning between 50 and -20°C over 3 cycles. This figure is an extract from the data, where we show one representative cooling step of a cycle.

The analysis of the composition of each peak can be done by two methods: quantitative analysis based on latent heat, or comparative analysis based on peak's shape differentiation.

1. Quantitative analysis: latent heat calculation

Expected values of latent heat for:

- Ice: 334 kJ/kg [2]
- Mirabilite: 241 kJ/kg[3]

Relationship between the heat exchanged rate and the enthalpy of crystallization[4]:

- Derivative form: $\mathbf{Q} = \frac{dH}{dt}$ **(Equation 1)**
  where H (J) is the enthalpy of crystallization, Q (W) is the heat exchanged rate and t (s) the time.

By integrating Equation 1 over the phase change, and dividing by the mass of the sample, we get:

- Mass integrated form: $\boldsymbol{\Delta Q_m \times t = \frac{H}{m} = L}$ **(Equation 2)**
  With $\Delta Q_m = \frac{\Delta Q}{m}$, the heat flow (W/kg) and L (J/kg) the latent heat.

Using Equation 2, we should be able to identify each peak from Figure S3, since the area below the curve is proportional to the latent heat which is itself a signature of a chemical compound. The calculated values of latent heat are presented next to each peak in green on the previous figure. In our case, those values do not match with the expected ones, which may come from an inexact calibration of the DSC instrument.
Despite it all, the peak's attribution can still be carried thanks to peak's shape differentiation.

2. Comparative analysis: peak's shape differentiation

From the paper of Denecker et al.[5] who conducted DSC on the system Na_2SO_4-H_2O, they could see that:

a. The peak related to water is broader compared to the one mirabilite
b. Both peaks are asymmetric, and their right part of the peaks shows opposite concavities: ice has a convex shape while mirabilite is concave.

These two characteristic elements on the shape of the peaks are actually observed in Figure S3, which allow us to conclude that mirabilite forms before ice.

c. Conclusion

The comparative analysis based on the shape of the peaks obtained by DSC shows that the formation of mirabilite occurs prior to ice. This measurement is supporting the freezing experiments presented in the main text of this paper: visual and temperature monitoring performed in the freezer, and the microcapillary experiment using the Peltier module.

Supplementary references

1. Zeng, G., Li, H., Huang, S., Wang, X. & Chen, J. Determination of metastable zone width and the primary nucleation kinetics of sodium sulfate. *Theor Found Chem Eng* **49**, 869–876 (2015).
2. Kumano, H., Asaoka, T., Saito, A. & Okawa, S. Study on latent heat of fusion of ice in aqueous solutions. *International Journal of Refrigeration* **30**, 267–273 (2007).
3. Sharma, A., Tyagi, V. V., Chen, C. R. & Buddhi, D. Review on thermal energy storage with phase change materials and applications. *Renewable and Sustainable Energy Reviews* **13**, 318–345 (2009).
4. Ghanbari, E., Picken, S. J. & van Esch, J. H. Analysis of differential scanning calorimetry (DSC): determining the transition temperatures, and enthalpy and heat capacity changes in multicomponent systems by analytical model fitting. *J Therm Anal Calorim* **148**, 12393–12409 (2023).
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