

1. Materials and sample preparation

NaCl, NaSCN, Na₂SO₄, NaI and NaNO₃, were obtained from Merck (Darmstadt, Germany) and were of analytical grade except NaSCN, which was of *purum* quality.

Water was distilled and further purified on a Purelab Plus apparatus, equipped with a final filter with a pore size of 0.1 μm. D₂O with an isotopic purity of 99 % was purchased from Cambridge Isotope Laboratories. Chloroform was obtained from Merck (Darmstadt, Germany) and was of analytical grade.

Freeze-drying was performed on Christ Alpha freeze-drier. The powders were completely dissolved in *tert*-butanol at room temperature in round bottom flasks. The solutions were rapidly quenched on an isopropanol/dry ice bath while constantly rotating the flask. Drying was performed under vacuum (> 0,5 mbar) for at least 24 h.

2. Solid-State Differential Scanning Calorimetry

Solid-state DSC experiments were conducted on a TA Instruments Q1000, equipped with modulation option and refrigerated cooling accessory. Experiments were carried out with a modulation of ± 0.5 °C every 40 s with an underlying heating rate of 2.5 °C/min. The heating rate was in a heat-only mode, *i.e.* the overlaid temperature was always positive. The cell was purged with dry nitrogen at an average rate of 50 mL/min.

The presence of water (which may be retained bulk water and/or water of crystallisation) obviously have a major impact on the phase behaviour of solid materials and therefore on their DSC characteristics. For this reason, DSC measurements were conducted according to three complementary protocols:

1. Experiments with the sample enclosed in aluminium pans with a loosely fitted lid, which allowed for any released water to escape from the sample during heating. After ensuring that no thermal events occurred below 40 °C, the experiments were started by drying the sample in the pan for 60 minutes at 40 °C under a flow of dry nitrogen. It then continued with a heat ramp up to a final temperature of *ca* 300 °C.
2. Experiments with the sample enclosed in aluminium pans that were sealed after drying the sample in the pan for 60 minutes at 40 °C as in Protocol 1. After sealing, the heat ramp was started and continued up to *ca* 120 °C. The walls of the pans used in these experiments are somewhat thicker than those in the pans used in Protocol 1, which lowers the sensitivity of the measurement.
3. As in Protocol 2, but without the initial drying step, *i.e.* the material under investigation was transferred directly to the pan and the pan was sealed.

In modulating DSC, it is possible to split the heat flow signal into two components, usually referred to as the *reversing* and the *non-reversing* heat flow. The total heat flow signal may be expressed as

$$dQ/dt = C_p b + f(t,T) \quad (1)$$

where dQ/dt is the total heat flow, C_p is the heat capacity of the sample, b is the rate of temperature change (dT/dt). $f(t,T)$ represent the heat flow from events that are a function of time and absolute temperature (kinetic events). In other words, the total heat flow is expressed as a sum of a heat capacity component ($C_p b$) or *reversing heat flow*, and a kinetic component $f(t,T)$ or *non-reversing heat flow*. This separation of components greatly facilitates the interpretation of the thermal events. For instance, glass transitions are predominantly affecting the reversing heat flow, since they are related to the changes in heat capacity. On the other hand, processes such as enthalpic relaxation, evaporation, crystallisation and decomposition are detected in the non-reversing heat flow signal.

Transition temperatures reported in this work correspond to the maximum of the corresponding peak in the thermogram.

3. Liquid Differential Scanning Calorimetry

A MCS DSC instrument from Microcal Inc. (Northampton, MA) was used for DSC studies of liquid samples. The sample cell volume was 1.160 mL. In a typical experiment, surfactant was dissolved in water or salt solution to a concentration of 1.0 g/L and then equilibrated either at room temperature or at 6 °C until a precipitate formed. Before DSC measurement, the samples were homogenised on a vortex stirrer and de-aerated under vacuum for half an hour. The reference cell was filled with water or the appropriate salt solution. The sample was injected to the sample cell and scanned at a rate of 60 °C/h in the temperature interval 15-60 °C.

In the present work, the *Krafft boundary* is defined as the temperature corresponding to the maximum of the endothermic peak.

4. Powder X-Ray Diffraction (PXRD)

All X-ray diffraction experiments conducted at room temperature were performed on a Scintag XDS 2000 θ - θ diffractometer (Scintag Inc., USA), whereas experiments at elevated temperatures were performed on a Panalytical X'Pert Pro. The Scintag diffractometer was equipped with a liquid-nitrogen-cooled solid-state germanium detector and spinning sample holders. Measurements were performed over an angular range of 2-35° (2θ), using CuK $_{\alpha}$ radiation (1.5418 Å, 45 kV, and 30 mA). A continuous scan rate of 1°/min and a step size of 0.03° were used. On the primary side, 2- and 4-mm slits were used, whereas the secondary side used 0.5- and 0.3-mm slits. The Panalytical X'Pert Pro θ - θ diffractometer was equipped with X'Celerator detector and was used with an increasing temperature of 1 °C/min with a continuous scan rate of 6.1 °/min and a step size of 0.017°. The angular range was 2-40° (2θ) and the radiation was CuK $_{\alpha}$ (1.5418 Å, 45 kV and 40 mA). Measurements were performed without spinning the sample holder.

5. Small and Wide Angle X-ray Scattering (SAXS and WAXS)

A Kratky compact small-angle system with linear collimation and a position sensitive detector was used in the SAXS and WAXS experiments. Measurements were performed between 25 and 130 °C using CuK $_{\alpha}$ radiation (1.5418 Å). SAXS and WAXS data were recorded simultaneously. The sample cell was equipped with mica windows and sealed with rubber O-rings.

6. Gravimetric Vapour Sorption (GVS)

GVS experiments were conducted on a SGA 100 symmetrical water vapour sorption system from VTI Corp. The equipment was located in a room with a controlled relative humidity of 20 %. The analyses were carried out at 25 °C and the relative humidity was adjusted in steps of 5 %-units from 0 % to 95 %. At each level, the equilibration criterion was that the weight should remain constant within 0.0100 wt-% in 10 min for freeze-dried material and 0.0002 wt-% in 5 min for crystalline precipitate. If equilibrium was not achieved within a time limit of 720 min, then the next level of relative humidity was entered. The reference- and sample cups were identical metal cups in experiments on the starting material and identical glass cups in the experiment with precipitate.

7. Thermogravimetric analysis (TGA)

TGA experiments were executed on a TA Instrument Q500 thermogravimetric analyser. In order to properly distinguish between retained bulk water and waters of crystallisation, it proved necessary to conduct the measurements according to two different, but complementary protocols. In the first protocol, the material under study was dried in the sample compartment at 30 °C for 60 min under a flow of dry nitrogen. The sample was then heated at 5 °C/min from 30 to 200 °C. In the second protocol, the drying step was omitted and the heat ramp started directly after the sample had been placed in the sample compartment. During the measurement and the initial drying step (if applicable), the sample compartment was flushed with dry nitrogen at a rate of 60 mL/min.

8. Elemental Analysis

Elemental analyses were performed by Mikrokemi AB, Uppsala, Sweden. Four independent samples were analysed for the precipitates formed at room temperature and at 6 °C. Prior to the measurement the samples were dried at 40 °C in vacuum.