Non-equilibrium Phase Diagram of Sucrose-Water System

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The measurement of the thermal events in dilute solutions is a challenge for the conventional DSC. Because of the small amount of active substances the thermal effects are related to heat flow changes of few micro watts or less. Increasing the sample mass, however, leads to larger temperature gradients within the sample. To prevent this, small heating rates have to be used. Consequently, the amplifying effect of the high sample mass reduces. Therefore, in the case of small heat flow signals (in the micro watt range) the only way to measure these signals is to use an instrument with an excellent signal to noise ratio and outstanding sensitivity. These requirements are matched by the new HSS7 sensor offering a combination of low noise, high sensibility and short time constant.

Sucrose water solutions show very week transitions at low concentrations which are not related to the normal equilibrium eutectic phase behavior. Therefore, additional non-equilibrium transitions have to be implemented the phase diagram.

EXPERIMENTAL

Sucrose (99.5% GC) delivered by SIGMA with a molar mass of 348 g/mol was used for the sucrose solution. Concentrations between 0.007 and 3.36mol% were prepared. Samples with a typical mass of 15 mg were filled in 40 µl Al-crucibles. Typical, the samples were cooled with –2 K/min to -100 °C and then heated at 5 K/min. The measurements were performed using a METTLER TOLEDO DSC822^{e} with a HSS7 sensor and liquid nitrogen cooling.

RESULTS AND DISCUSSION

Below 80wt% sucrose the system sucrose/water shows meta-stable phases and consequently a distinct time dependence in the phase behavior. This can easily be detected by DSC measurements using different cooling rates.

In this work we are interested in the phase diagram of the sucrose/water system for small sucrose content. To determine a representative phase diagram, samples with different sucrose content were measured in the DSC after slow cooling (-2 K/min). A collection of DSC curves is shown in Figure 2. Besides the melting peak the curves show two endothermal steps, which we denote as transition 1 (around –44 °C) and transition 2 (around –35 °C). For clarification the relevant curve sections are shown in Figure 1 diagram (A) and (B). The curve of the sample with 0.14wt% sucrose is shown after a slope correction in diagram (B). The slope correction was necessary because of the temperature dependence of the heat capacity of water. This curve shows a reproducible step height at transition 2 of 11.6 µW (or 480 µW/g).

From these curves, the interesting part of the phase diagram can be determined:

The liquidus line in the phase diagram was determined from the melting peaks at consideration of the slope of the curve of pure water.

The transition 1 can be clearly identified as a glass transition. During slow cooling a glass is formed by freezing the associated glucose water solution. Most of the water freezes as pure ice, but a residual amount is strongly associated to the sucrose molecules. This associated liquid solution forms

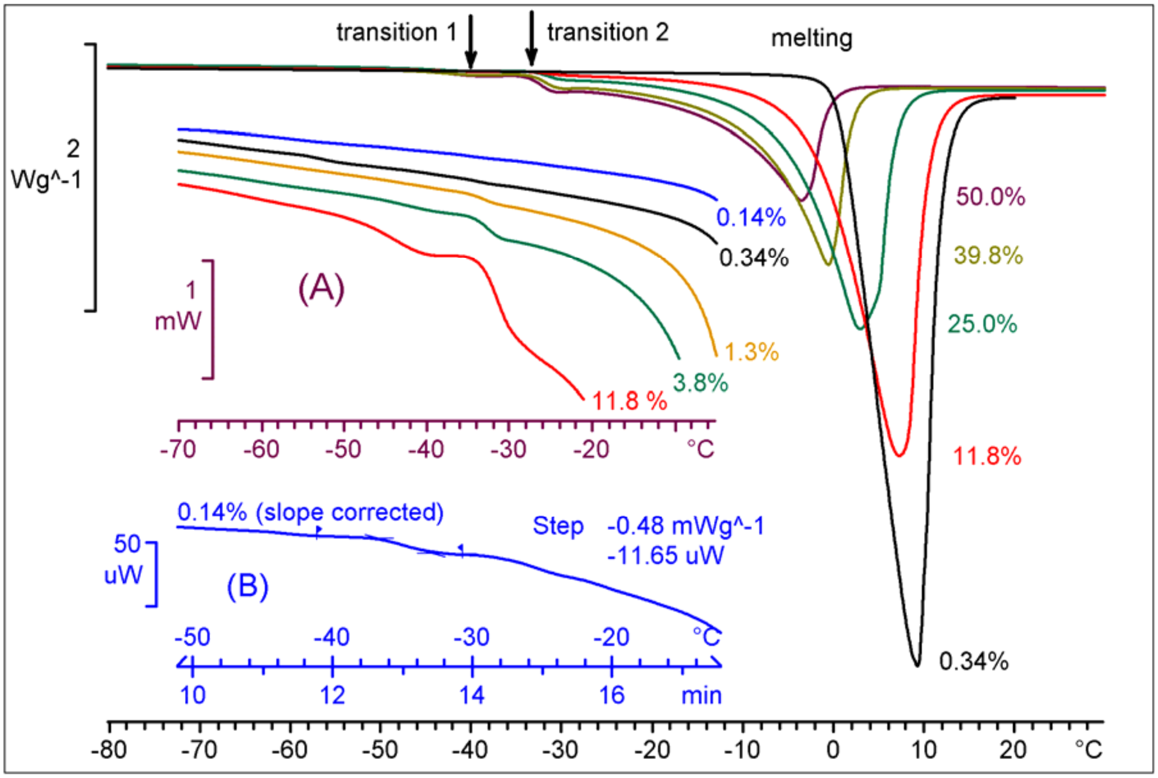

Figure1: DSC curves (exo up) of different sucrose solutions measured at 5 K/min. The curves show two endothermic steps at around –44 °C (transition 1) and –35 °C (transition 2) and a melting peak. In diagram (A) the region of the transitions 1 and 2 are magnified for clarification. Diagram (B) shows a slope corrected curve of the solution with 0.14wt% sucrose.

an unstable phase which crystallizes only by phase separation into pure ice and the eutectic mixture, if very long time is given. At the transition 1 (-44 °C), the glass transforms to liquid. For all measured concentration this glass transition temperature, T_{g1}, is almost constant.

The transition 2 is also at almost the same temperature for all samples (-33 °C) and seems to be an other glass transition. But, the intensity of this transition is relatively large in case of high sucrose content. For the 50wt% sucrose sample Δc_p was determined to be 1.3 J/gK, too high for a simple glass transition. Thus, this transition is a fusion process of the pure ice into the associated liquid solution as temperature-modulated DSC (TOPEM® [1]) measurements have shown [2]

CONCLUSIONS

To measure weak thermal events in dilute systems by DSC, high sensitivity, good baseline stability, low noise and short time constants are crucial. The new DSC sensor HSS7 outstanding complies with these requirements. The temperature modulated DSC (TOPEM®) helps to identify the nature of some of the weak transitions. Detailed evaluation of the transitions delivers the composition of the associated solution of sucrose and water.

References

[1] J.E.K.Schawe et. al., Stochastic temperature modulation : A new technique in temperature-modulated DSC, Thermochimica Acta, 442 (2006) 230

[2] Y.Roos, M.Karel, Amorphous state and delayed ice formation in sucrose solutions, Int. J. Food Sci. Technol. 26 (1991) 553