Journal of Thermal Analysis, Vol. 52 (1998) 109-113

Dedicated to Prof. Antonius Kettrup on the occasion of his 60th birthday

THE GLASS TRANSITION OF WATER AND AQUEOUS SYSTEMS

G. Widmann and R. Riesen

Mettler Toledo Analytical, CH-8603 Schwerzenbach, Switzerland

Abstract

After a brief introduction of the terms supercooling, amorphous solid state, glass transition and devitrification, the known ways of production of amorphous solid water are discussed. DSC experiments with quench cooled aqueous solutions show the phenomenon of glass transition and devitrification.

Keywords: amorphous solid water, aqueous systems, DSC, glass transition, supercooling

Introduction

In the solid state of aggregation most substances of low molar mass are crystalline. Crystallization usually takes place when a molten substance is cooled below the melting point. It usually does not occur spontaneously at the temperature of fusion: there is the well known phenomenon of supercooling due to the limited rate of nuclei formation and growth. Supercooling increases with increasing cooling rate. With high enough cooling rates most substances remain in the amorphous state [1], they form a glass or 'vitrify'. The necessary cooling rates range from 1 to 10^7 K min^{-1}.

In the glassy solid state the mobility of the molecules or atoms is too small for crystallization, thus the substance remains in the amorphous state. On heating, the mobility increases at the so-called glass transition temperature. Above this glass transition temperature, substances of low molecular weight form a more or less viscous liquid, polymers become rubber-elastic. In this state most substances form crystals: 'devitrification' or 'cold crystallization' takes place. According to Ostwald's rule often metastable crystalline phases are formed. On further heating the crystals melt at the temperature of fusion of the respective modification.

Even though water shows marked supercooling (Fig. 1) it is extremely difficult to quench cool the liquid phase in order to obtain the amorphous solid water

1418-2874/98/ $ 5.00

Akadémia Kiadó, Budapest
Kluwer Academic Publishers, Dordrecht

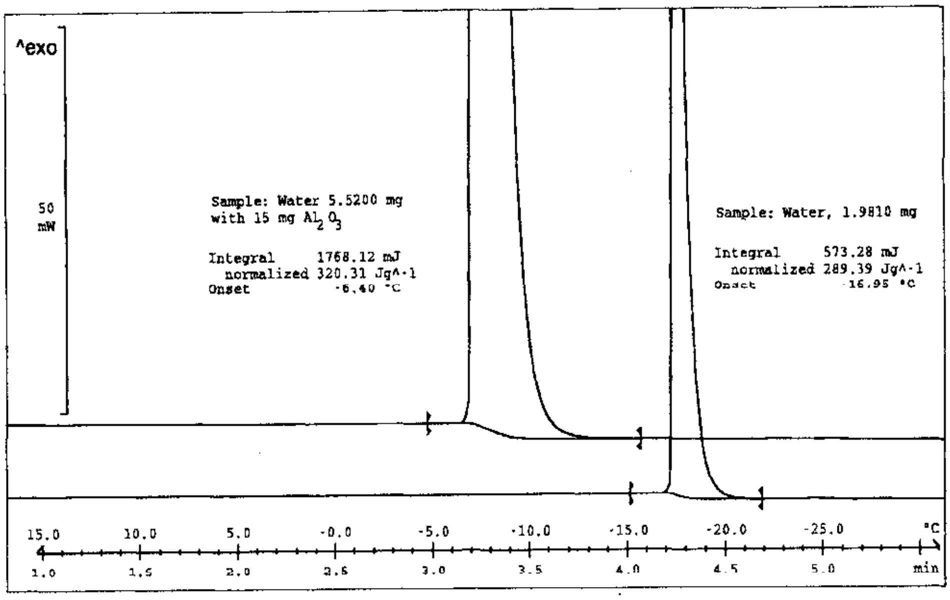

Fig. 1 Two DSC cooling curves of distilled water measured at a cooling rate of 10 K min^{-1}. The small water sample begins to crystallize at –16.9°C. The earlier crystallization is caused by the addition of 15 mg α-alumina powder as a crystallization aid. Only the lower part of the peaks are shown to demonstrate the change in heat capacity between liquid and crystalline state. The integral baseline enables a correct determination of the enthalpy change

(ASW): droplets of approx. 3 μm diameter thrown at supersonic speed towards a metallic wall cooled by liquid nitrogen (hyper quenching) form a layer of ASW. With this treatment cooling rates of approx. 10^6 K min^{-1} are reported [2]. Another quite complicated method is by compression of hexagonal ice at 77 K [3]. Condensing water vapor on a surface cooled by liquid nitrogen [4] seems to be the easiest way of preparation of ASW. The expected value of the glass transition temperature is –137°C.

Binary systems on the other hand are known to crystallize not readily, e.g. molten eutectic compositions often do not crystallize: impure organic compounds are sticky and tacky due to resin like parts. This effect also is true for aqueous solutions. Some solutions only need cooling rates below 1000 K min^{-1} achievable by quench-cooling in the pre-cooled DSC cell or in liquid nitrogen.

The heat of crystallization depends on the actual supercooling (Fig. 2).

Experimental and results

The measurements have been performed in a Mettler-Toledo STAR^e system with DSC821 and liquid nitrogen cooling.

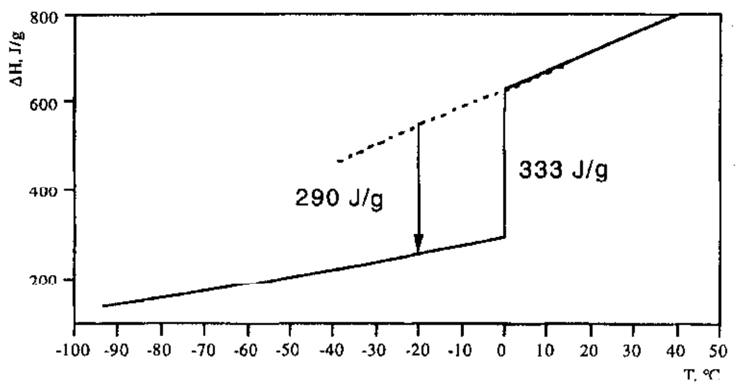

Fig. 2 The enthalpy temperature plot of water [5]. The enthalpy of fusion is 333 J g^{-1} at 0°C. The slope of the water line is 4.18 J $g^{-1}K^{-1}$ (c_p of water), the one of the ice line near 0°C is 2.0 J $g^{-1}K^{-1}$ (c_p of ice) only. Since the enthalpy follows the dotted line on (super)cooling the heat of crystallization decreases

The supercooling of pure water was measured at a constant cooling rate of 10 K $\min^{-1}$.

To produce ASW the condensing water vapor method has been tested: a copper cylinder of 20 mm diameter and 60 mm height was placed in a small Dewar container with an inner diameter of 40 mm and a height of 100 mm. The Dewar was filled with liquid nitrogen until only the top surface of the copper cylinder is outside the liquid. When a DSC pan was placed on this plane surface it reached approx. –190°C. Then a flow rate of 30 ml $\min^{-1}$ of nitrogen saturated with water vapor at 25°C in a gas wash bottle was blown through a stainless steel capillary of 0.4 mm diameter. The jet was directed vertically down to the cold pan, where condensation took place. To suppress condensation in the capillary it was insulated with several plastic pipes. After a few minutes the pan was quickly transferred into the DSC cell pre-cooled to –150°C. The pan was picked up by means of liquid nitrogen cooled tweezers. An endothermal peak ensures the pan has remained below –150°C during transfer. The dry nitrogen used as purge gas hindered condensation of air humidity when the DSC cell was open for a few seconds. After equilibrating the sample at –150°C during 1 min, the heating started at 10 K $\min^{-1}$. Despite of many experiments we have not yet been able to get pure ASW by the described vapor deposition method until today. The condensed product always has been crystalline. We assume there has been some ice formation in the nitrogen jet stream.

There are two common ways of quench-cooling the samples of aqueous solutions:

1. Cooling the DSC to e.g. –150°C (equal to the start temperature of the following temperature program). Then the sample (kept at ambient temperature, 25°C) is introduced into the DSC cell. With a typical time constant of the heat

transfer (or signal time constant, τ) of 2 s and an initial temperature difference, ΔT, of 175°C the sample is quenched with a maximum cooling rate of $\Delta T/\tau$= 87.5 K s^{-1} or approx. 5000 K min^{-1}. Within 10 s the sample temperature is $(1/e)^5 \cdot \Delta T$=1.0°C above –150°C (Newton's law of cooling) corresponding to a mean cooling rate of 1000 K min^{-1}.

2. Holding the sample crucible into liquid nitrogen with a pair of light tweezers is even faster (dropping is not very efficient: the pan swims on the boiling nitrogen, Leidenfrost's phenomenon).

Table 1 Heats of crystallization as a function of the temperature of crystallization

Temperature of crystallization/°C	Heat of crystallization [5]/J g^{-1}	Measured heat of crystallization/J g^{-1}
0	333	333*
–6.4	219	320.3
–10	311.5	–
–16.9	297	289.4
–20	290	–
–30	269	–

*actually measured by integrating the fusion peak

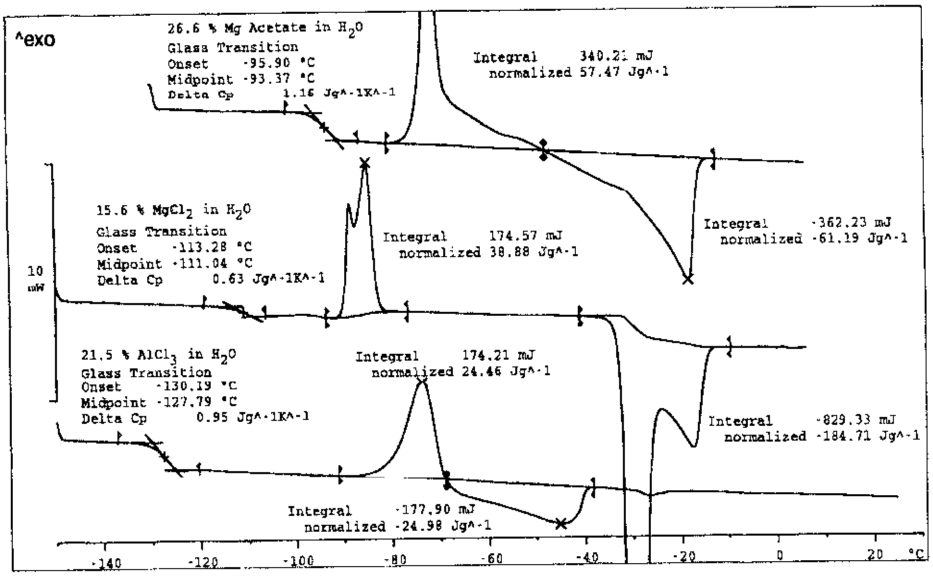

Fig. 3 Amorphous aqueous solutions.Salt solutions that have been quench cooled in the DSC cell at –150 and –130°C, respectively. On heating they undergo glass transition (see evaluations). Between –90 and –70°C crystallization takes place. Due to the discussed reasons (Fig. 2) we expect a heat of crystallization that is smaller than the heat of fusion

As the experiments have shown, quenching certain aqueous solutions in the DSC-cell is good enough to get them in the amorphous solid state. In addition to the in Fig. 3 presented solutions, for instance calcium acetate and aluminium nitrate have given amorphous products (others are reported in [6]). It is interesting that the heats of fusion are much smaller than 333 J g^{-1}. This indicates incomplete cold crystallization of the samples.

Conclusions

Certain aqueous solutions are easily obtained by quench cooling the sample in a pre-cooled DSC cell. The glass transition and the devitrification are observed on heating the sample. The amorphous solid state of aqueous systems becomes more and more important in processing of food [7] and pharmaceuticals, e.g. freeze drying.

References

1 G. Widmann, Thermochim. Acta, 112 (1987) 137.
2 G. P. Johari, A. Hallbrucker and E. Mayer, Nature, 330 (1987) 552.
3 O. Mishima, L. D. Calvert and E. Whalley, Nature, 314 (1985) 76.
4 B. Schmitt, J. Ocampo and J. Klinger, J. Phys., (Paris), Suppl. C1, 48 (1987) 519.
5 Landolt-Börnstein, 6th edition, Vol. II, Part 4.
6 B. Conde-Petit and F. Escher, Lebensmittel-Technologie 28, Nr. 3 (1995).
7 C. A. Angell and J. C. Tucker, J. Phys. Chem., 84 (1980) 268.