Heat capacity anomaly in a large sample of supercooled water

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Abstract

A glass ampoule of water 10 cm^3 in volume has been brought down to and maintained at a temperature of $-30°C$ in the liquid state, and its heat capacity has been measured between $-28.5°C$ and $+10°C$. The experimental data show an anomalous behaviour of the heat capacity of water in the supercooled regime, more pronounced than that previously observed from experiments on water emulsions. © 1999 Elsevier Science B.V. All rights reserved.

1. Introduction

A significant part of the studies aimed to explain the anomalous properties of water have been considering liquid water below 0°C, in the metastable regime [1]. The experiments with bulk water have generally been performed at temperature higher than $-13°C$ owing the spontaneous freezing of the sample, provoked by the presence, in water or on the sample container, of microscopic impurities which are able to trigger the growth of ice on their surfaces. Freezing can also occur as a consequence of local density fluctuations which create embryos of ice in the liquid phase [2]. The probability of freezing linked to these two mechanisms increases with the sample volume; thus researchers have been compelled to work either with very small water samples in thin capillary tubes [3] or with emulsions in which water is dispersed in tiny droplets [4], to reach temperatures lower than $-20°C$, where the anoma-

lous behaviour is more evident. These constraints have placed severe limitations on the experimental methods that can be used, restricting the possibilities of investigation and making measurements more difficult to carry out and interpret. Indeed, a recent paper [5] has examined critically the heat capacity, C_p, measurements on water emulsions and concluded that C_p of bulk water needs to be determined to verify the anomalous behaviour of the heat capacity based on some differential scanning calorimetric (DSC) measurements on emulsions [4].

In order to measure C_p of pure bulk water, we have designed and built an adiabatic calorimeter capable of measuring the heat capacity of large water samples that have been supercooled and maintained at temperatures below $-20°C$ for long periods of time. Glass ampoules containing double-distilled water (10 cm^3) produced by Angelini SpA (Verona, Italy) for medical purposes are known to have the property of remaining liquid even below $-20°C$ [6]. We found that, due to the exceptional purity (to a degree unobtainable in the laboratory [7,8]) of these samples, water remained in the liquid state in ∼ 10% of the glass ampoules after 24 h at $-24°C$. The

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contents of three among ten ampoules so selected were found to still be liquid after 43 h, and these ampoules were chosen for the subsequent heat capacity measurements.

2. Experimental

In the design of the adiabatic calorimeter, the heater and sensor were wound uniformly on the same aluminium cylinder of the calorimetric cell. This was held in good thermal contact with the sample-containing ampoule and concentric to an active thermal shield, maintained continuously at the temperature of the external surface of the calorimetric cell. This produced the adiabatic conditions necessary for the experiment without the use of vacuum [9]. In the heat capacity measuring procedure, the temperature of the cell containing the sample ampoule was increased by incremental steps (ΔT) of $\sim 0.5°C$, starting from the minimum temperature. To do so, equal heat pulses (Q) lasting 90 s per pulse were applied at time intervals of 900 s to the sample cell. The time duration of each step was much longer than the relaxation time of the temperature gradients inside the sample cell (70 s). The adiabatic condition was established so efficiently that

Fig. 2. Heat capacity of supercooled water from literature and present study. Full squares: bulk water reference data from Ref. [10]; full circles: bulk water data from Ref. [11]; full triangles: data for water in capillary tubes from Ref. [3]; open triangles: data for water in emulsions from Ref. [11]; full line: curve fitting the experimental points of this study; dashed line: extrapolation of the fitting curve.

the ΔT value remained practically constant ($\pm 0.001°C$) during the last 300 s of each step. The accuracy of the Q and ΔT measurements were better than ± 0.001 J and $\pm 0.003°C$, respectively.

The temperature sensors of the calorimeter were calibrated to a Hart Scientific 1502 platinum resistance thermometer and the absolute temperature of the water sample was calculated by shifting the measured triple point temperature of water to $0.01°C$ (the standard value). This temperature marker was spontaneously created during the calorimetric run. Indeed, when the supercooled water occasionally froze in the ampoule, the sample cell temperature rapidly rose to the triple point, which meant that ice, liquid water and vapour could be found coexisting in the ampoule. Thus, the temperature accuracy was better than $\pm 0.01°C$.

The heat capacity of the water was determined as follows. In a first run, the heat capacity of the sample cell containing the ampoule of water was calculated over the range of interest from the ratio $Q/\Delta T$. The ampoule was then weighed together with its contents, opened, drained, dried and weighed again in order to obtain the exact mass of the water it
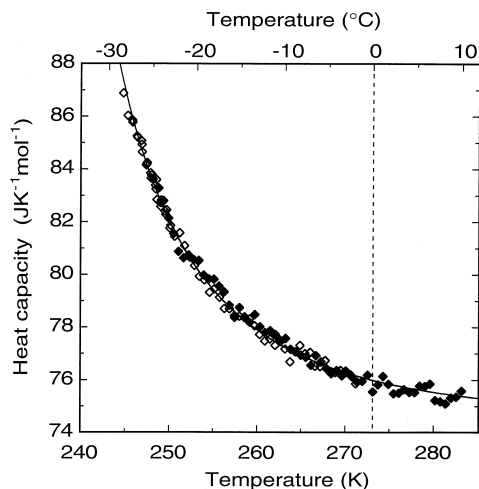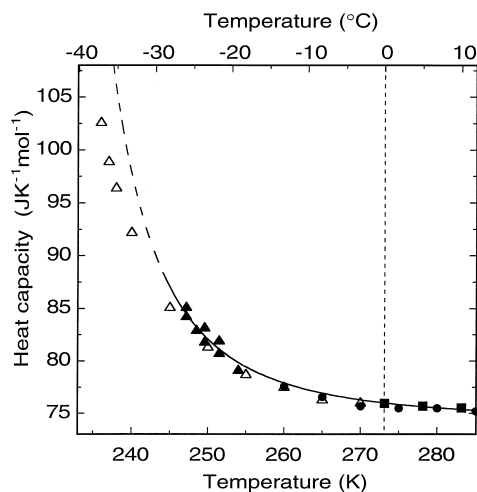

Fig. 1. Heat capacity of water measured as a function of temperature. Full and open diamonds: data obtained in this study with two different samples; full line: curve fitting the experimental points [$C_p = 0.44 * (T/222 - 1)^{-2.5} + 74.3$].

had originally contained. Then the empty ampoule was placed in the calorimeter for a second run in order to obtain the heat capacity of the empty cell under the same conditions. By subtracting the values measured in the second run from those in the first one, the heat capacity of the water (C_p) was obtained.

3. Results and discussion

C_p values, measured in successive runs with two different ampoules, are shown plotted against temperature (T) in Fig. 1. The data reported in the literature for water supercooled in capillary tubes [3] and in emulsions [4] are shown in Fig. 2, together with the fitting curve of the data in Fig. 1. The good agreement found between the C_p values obtained in this study and the reference data for liquid water [10] above 0°C (Fig. 1) represents an intrinsic accuracy check.

As emerges clearly from Fig. 2, C_p data from studies based on samples of different shapes and sizes, prepared according to different procedures, confirm the heat capacity anomaly of water in the supercooled regime. To enter into details of Fig. 2, a systematic deviation of emulsion data from the bulk data is evident. It increases at temperature lower than -30°C, though the extrapolation of the fitting curve to this region is questionable. The origin of this disagreement must be investigated in relation with possible surface effects [5]. Anyway, data in Fig. 2 show the thermodynamic equivalence at least of bulk water, and water in capillaries.

The fitting equation in Fig. 1 must be considered only as the best representation of the experimental data. Indeed the origin of the water anomaly, that is the existence of a singularity, as the fitting equation could suggest, or of a liquid–liquid phase transition remains an open question [12], beyond the limited aim of this Letter. The results obtained here for the first time with bulk water at temperatures much lower than the previous limit (-13°C) [11] suggest that double-distilled water samples, such as those used in this study, should be more broadly applied in future research on the properties of deeply supercooled water.

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