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CHARACTERIZATION OF ANOMALOUS OR POLYWATER BY DIFFERENTIAL THERMAL ANALYSIS

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ABSTRACT

Micro amounts of anomalous or polywater have been prepared in micron sized capillaries. The capillaries were transferred directly to the apparatus where differential thermal analysis was carried out. The thermograms obtained show the substance to melt at approximately −30 °C, and boil and/or decompose at temperatures in excess of 300 °C, depending upon the degree of anomality or polymerization. These properties differentiate it from normal water and show it to be anomalous water or a polymer of water.

Deryagin[1] and coworkers have referred to a form of water as "anomalous water" because of the different and distinct physical properties it has exhibited as opposed to those of ordinary water.

This material has been prepared in similar ways by several investigators[2–4]. The amount of material obtained in every case has been exceedingly small which makes analysis and characterization difficult.

A recent study of anomalous water by Lippincott *et al.*[4] has been performed. From the Raman and infrared spectra of this material, these investigators concluded that this material is truly a polymer of water as opposed to anomalous water.

Because of the micro quantities of material that can be obtained for analysis and in view of the unusual reported physical properties which define the substance (freezing point below −10 °C, and stability to temperatures of 300–500 °C)[4,5], differential thermal analysis appeared to be a technique that provided the required sensitivity and temperature range for investigating the properties of anomalous or polywater.

EXPERIMENTAL

Preparation

The material was prepared generally by the standard methods that have been described previously[4,5]. In this instance, Pyrex tubing was chemically cleaned, dried, and drawn into capillaries with a small internal diameter. The capillaries, along with

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a beaker of water saturated with potassium sulfate, were placed in a desiccator which was then evacuated.

Approximately one week was required for the material to form. It formed, generally in small quantities, in the ends of the capillaries; although occasionally a minute column of liquid was found growing away from the ends in the smallest capillaries.

The material was found to be present in a small percentage of the capillaries ranging in size from 0.5 microns to 5 microns. During this time period, it was rare that material was observed in capillaries having an inside diameter greater than 5 microns. When material was present it generally proved to be normal water as evidenced by boiling point. One explanation for this is that the –Si–O–Si– bonds of the glass cannot act as a template in this case, and normal condensation occurs. In some cases, the material was carefully sealed in the capillaries to facilitate further examination without subsequent losses.

Apparatus

An R. L. Stone model LB-202 Recorder Controller, a JP-202 Furnace Platform, and an H-5 Subambient DTA were used in this study. These instruments are manufactured by the Analytical Instruments Division, TRACOR, Inc., Austin, Texas. A sample holder that contained ring-type thermocouples (SH-11BR Ni) was used in conjunction with the JP-202 Furnace Platform.

RESULTS AND DISCUSSION

A small quantity of distilled water was introduced into a capillary of similar size as those used for the preparation of anomalous water. This, and additional capillaries, were run by placing them directly on the sample side of the ring-type differential thermocouple within the H-5 sample holder. It was found that the sample holder accommodated direct handling of samples in this manner; and as long as the number of capillaries placed on the sample ring was kept few, and the capillaries were no longer than 3/4 inch, reference capillaries or alternate inert reference materials were not required. This facilitated sample analysis, since as little handling as possible of the fragile capillaries is best because of the possibilities of loss and/or contamination.

When several capillaries were used at very sensitive ranges of ΔT, additional drift was introduced due to improper heat balance of each side of the differential couple since no attempt was made to match precisely each side with respect to heat capacity, but this did not preclude clear interpretation of the thermograms.

The thermograms shown in Fig. 1a were obtained using the distilled water sample contained in a closed capillary.

The freezing point is typical of those obtained on other samples using distilled water. Freezing points between -30 and -40°C were obtained. This is not unusual, since droplet size and extent of supercooling influence the freezing point.

It will be observed that the ice sample melts at precisely 0°C, or at its normal melting point. Boiling, however, is not observed below the upper temperature limit

of the H-5 Subambient DTA, which is 300 °C. It would be expected that boiling would be observed over a rather wide temperature range; since the temperature at which boiling occurs will be dictated by the pressure developed within the closed capillary which is, in turn, determined by the extent of filling.

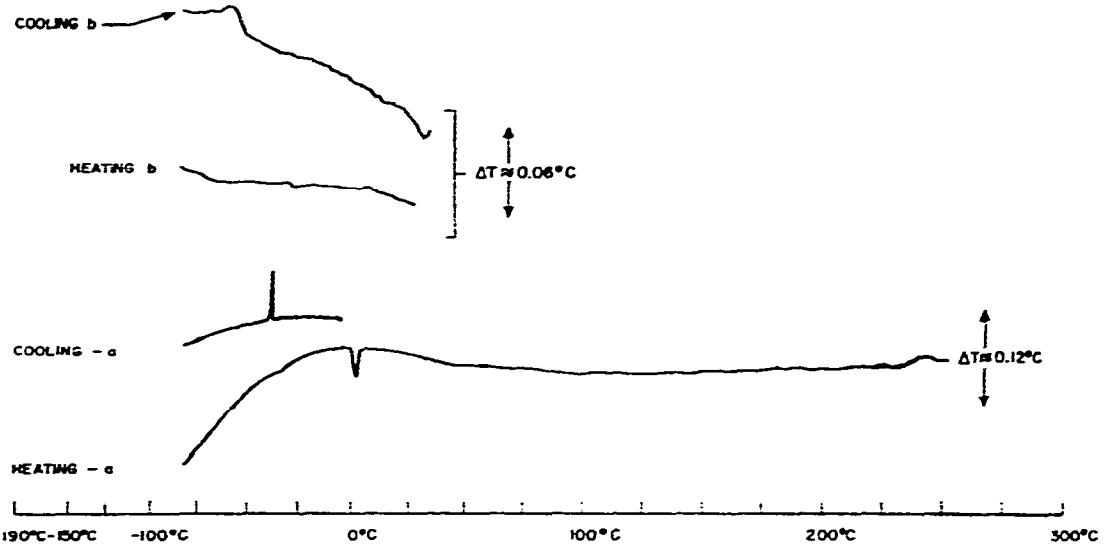

Fig. 1. Low-temperature thermograms of normal and polywater; (a) normal water (closed capillary); (b) polywater (open capillary). Program rate: 10°/min.

Several open capillaries, which were found to contain minute amounts of condensed material after preparation, provided the thermograms shown in Fig. 1b. The freezing now occurs at lower temperatures (−55 and −65 °C), which could again be explained by the small droplet size and the possibility of undercooling. Although it is felt that the amount of material used for this run represents roughly the amounts of normal water used to obtain the thermograms in Fig. 1a, the freezing is ill-defined and melting is practically not observed. The nebulous melting endotherm, or poorly defined change of state at −30 °C, was observed in other runs and is consistent with the properties reported previously[1].

Fig. 2a shows the boiling of water in an open capillary, using the JP-202 Furnace Platform and the SH-11BR Ni Sample Holder as described previously. The normal water begins vaporizing from the capillary below its boiling point; and thus, boiling begins about 2 °C below the true boiling point, or at 98 °C. The thermogram in Fig. 2b shows the boiling and/or decomposition of anomalous or polywater which formed in several capillaries during the preparation; which were placed, without sealing the ends, on the sample side of the ring thermocouple.

Naturally, some drift is encountered at the sensitivities used since only qualitative heat balancing of reference and sample sides was attempted. Nevertheless, boiling and/or decomposition endotherms are clearly evident at 328, 364, 390, and 410 °C.

The interesting aspect is that multiple capillaries can be examined simul-

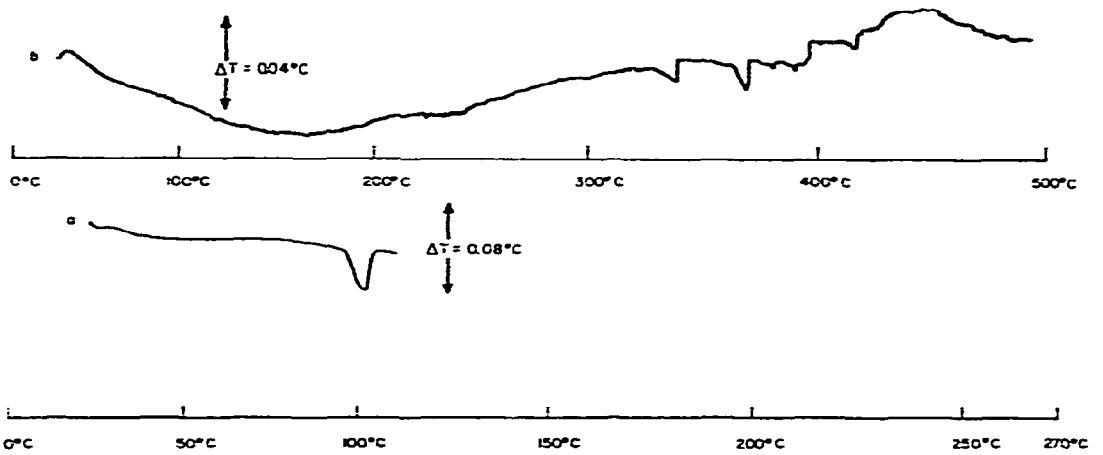

Fig. 2. High-temperature thermograms of normal and polywater; (a) normal water (open capillary); (b) polywater (open capillary). Program rate: 10°/min.

taneously by simply placing them directly on the sample side of the ring differential couple. At high sensitivities, in this manner, individual differences in the degree of anomality or degree of polymerization between capillaries can be observed.

It is difficult to account for these results in terms other than those mentioned above in view of the starting material (normal water) and the precautions of cleanliness observed, although the liquid was not analyzed for purity. The small size of the capillary, used as the control in the case of normal water, had no effect on the normal boiling point. The boiling point shows that the material is vastly different from normal water. Melting point, boiling point and/or decomposition show the prepared material to be anomalous water and similar to what might be expected for polywater; or, as other investigators have termed it[4], a polymer of water.

Comparisons between heats of vaporization of normal water and anomalous water could not be made quantitatively because the amount of material present could not be weighed with accuracy. However, it appears qualitatively that more energy is required for the vaporization of polywater.

The described closed-capillary technique has been used successfully on a macro scale by using ordinary melting-tube capillaries for determining the melting point of sensitive organic compounds which decompose or sublime when the usual DTA techniques are applied.

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