Thermal Expansion Behaviour of SiO_2–H_2O and SiO_2–NaOH–H_2O

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Summary The thermal expansion behaviour of water solutions containing various percentages of SiO_2 or SiO_2 and NaOH has been studied; the behaviour of mixtures of NaOH, SiO_2 and water closely resembles that reported for anomalous water.

The existence of an alleged stable allotropic modification of ordinary water, most often called anomalous or polywater, has recently been questioned. This material has been reported to form when water vapour, introduced into an evacuated chamber at pressures less than the saturation vapour pressure of water at a particular temperature, condenses inside fused silica capillaries.

A key property supporting the existence of this "anomalous" form of water is its unusual expansion behaviour at temperatures below 0 °C. In this paper the expansion

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behaviour of various mixtures of silica and water, and silica, water and sodium hydroxide has been investigated, and is compared with the behaviour for anomalous water reported by Deryaguin.[1,2] The thermal expansion behaviour of anomalous water reported by Deryaguin[2] appears in Figure 1A, and the results of our investigation appear in Figures 1B, C, and D, and Figure 2.

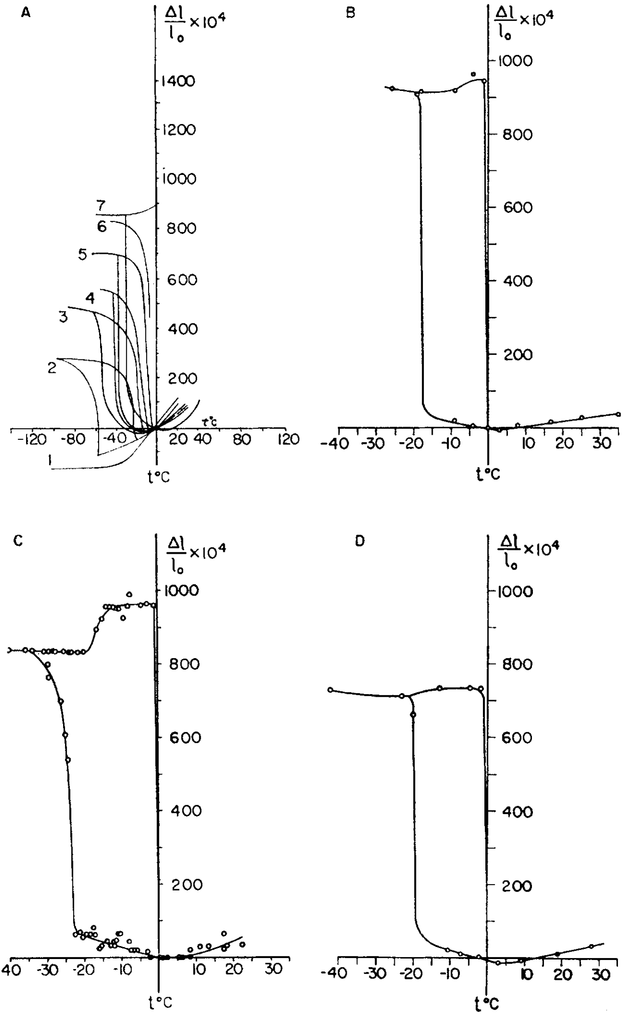

FIGURE 1. *Thermal expansion curves.* A *Modified water with different concentrations of anomalous component obtained by Deryaguin*[2] *from* 100% *anomalous component, curve* 1, *through* 0% *(ordinary water), curve* 7. *(Used by permission of the author.)* B 1% *Cab-O-Sil dispersed in water. (lower left curve, cooling; upper right curve, warming for Figure* 1, B, C, *and* D). C 5% *Cab-O-Sil dispersed in water.* D 10% *Cab-O-Sil dispersed in water.*

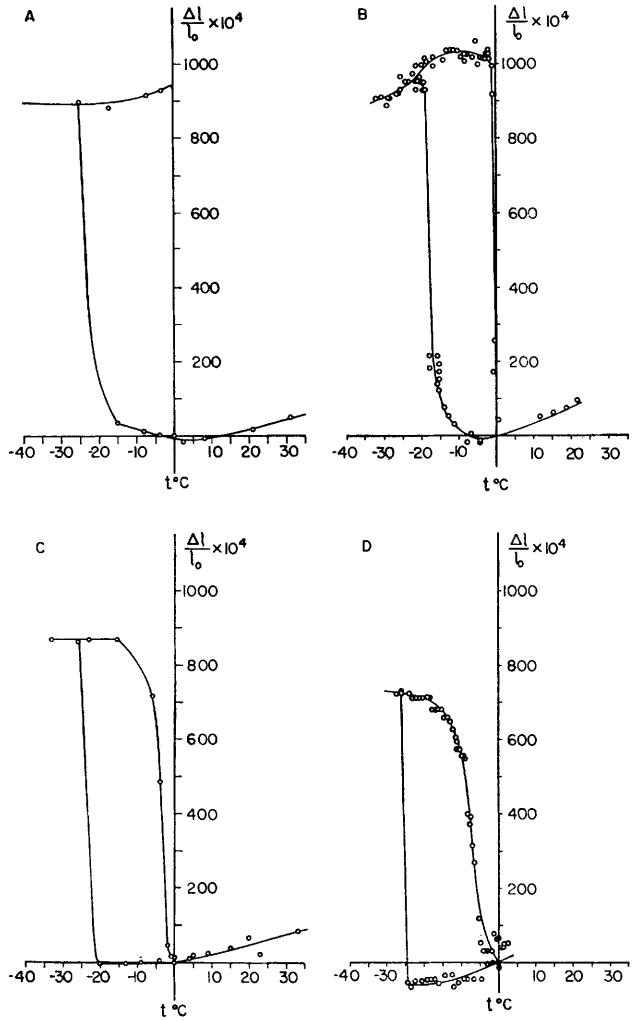

FIGURE 2. *Thermal expansion curves.* A *Distilled water (lower left curve, cooling; upper right curve, warming in all cases).* B 1% *each sodium hydroxide and Cab-O-Sil dispersed in water.* C 5% *each sodium hydroxide and Cab-O-Sil dispersed in water.* D 10% *each sodium hydroxide and Cab-O-Sil dispersed in water.*

Dispersions of silica and quintuply distilled water were prepared by weighing Cabosil (a highly pure, colloidal form of silica supplied by Cabot Corp.) and adding weighed amounts of water. Because it is so finely divided, Cabosil readily disperses in water. Sodium hydroxide, dried at 110 °C for 3 h, and subsequently stored in a desiccator, was weighed at the same time as the silica and water when ternary mixtures were desired. The resulting dispersions rose quickly into freshly-pulled quartz capillaries of *ca.* 100 μ ID when one end of a capillary was immersed in the dispersion. Capillary columns used for thermal expansion measurements were *ca.* 2 cm in length. Dispersions containing more than 10% silica set to a gel soon after being formed, and consequently could not readily be introduced into capillaries, but dispersions containing equal amounts of SiO_2 and NaOH did not gel.

Temperature control of the sample was accomplished by circulating toluene from a temperature-controlled, refrigerated bath through a tube which contained the capillary with the sample sealed inside. Condensation of moisture on the toluene-containing tube was prevented by surrounding it with an evacuated, gas-tight larger tube. Measurement of the sample temperature was made by means of a chromel–alumel thermocouple located in the toluene tube immediately upstream from the sample.

The two concentric tubes which surrounded the sample-containing, sealed capillary were placed on top of the lens of a photographic enlarger. The lamp of the enlarger was replaced by a 300 W, reflector lamp in order to secure more brilliant illumination. The enlarger image was projected on to a linear scale about 5 ft below the sample position, so that a sample column 2 cm long appeared to be 3 ft long, allowing accurate column length measurement.

All measurements were made starting with a warm sample. This was cooled until freezing occurred, accompanied by a sudden increase in volume. Cooling was continued until little further change in volume was observed, then the sample was warmed by turning on a 100 W heating element immersed in the toluene bath. On each cooling curve, therefore, the supercooling occurs during cooling and the phase transition near 0 °C was observed during warming. All measurements plotted on a particular cooling–warming curve were obtained during a single run.

The depressed freezing temperature observed by us during cooling measurements is much lower than would be predicted from cryoscopic calculations utilizing the molarity of the solution. Freezing point lowering calculations based on molarity are of course not valid for a silica system such as the one employed because colloidal silica dispersions were formed. These exhibit large increases in viscosity which interfere with the freezing process and result in the hysteresis-type of freezing behaviour which has been observed by us.

Our thermal expansion measurements on water closely resemble those made by Deryaguin, but with less supercooling. Although we did not verify it for their system, the extent of supercooling depends on the rate of cooling[3] as well as the presence of nuclei, and also on capillary diameter.[4] Our cooling from 0 to -40 °C was very slow, requiring *ca.* 8 h, and such cooling would tend to reduce the amount of supercooling. Furthermore, the capillaries used by us were consideraby larger than the capillaries used by Deryaguin, and are very possibly also a factor in reducing the amount of supercooling observed. The cooling curve produced by the solution with the largest concentration of impurities, 10% NaOH and 10% SiO_2, closely resembles Deryaguin's cooling curve for highly modified water. The curves produced by cooling mixtures of water, silica and sodium hydroxide reproduce more closely the behaviour of highly modified water than do those produced by silica-water mixtures, although neither type shows freezing point lowering of the solution, on the melting curve, of the magnitude observed by Deryaguin. This may indicate that samples used by him contained more dissolved impurities than those used by us.

We conclude that water containing equal amounts of silica and sodium hydroxide, when introduced into capillaries, closely reproduces the freezing expansion behaviour observed by Deryaguin[2] for samples of highly modified water. This result supports the contention[5] that silica–sodium hydroxide–water mixtures exhibit all the properties of anomalous water, and agrees with the electron microprobe analysis[5] of samples prepared by the method used by Deryaguin to prepare anomalous water, in which equal amounts of sodium and silica were found.

It is therefore not necessary to postulate an additional allotropic modification of water to explain the thermal expansion behaviour of anomalous water. This property is exhibited by silica–sodium hydroxide–water mixtures.

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