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The Oxygen Content in Supercooled Water**

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Summary. The oxygen content in liquid water has been measured in the temperature range between 0 °C and −7 °C. The measurements have been carried out with an amperometric needle sensor in glass-capillaries with an inner diameter of 1.7 mm. It has been obtained that the oxygen content in water is rapidly increasing as the temperature is lowered below 0 °C. At −5 °C the concentration of oxygen in water at constant partial pressure of oxygen is by 13% higher than that at +3 °C. The increase of oxygen content seems to be related to the unusual temperature dependence of heat capacity, density and isothermal compressibility of supercooled water.

Keywords. Supercooled water; Oxygen content; Supermolecular system organization.

Der Sauerstoffgehalt von unterkühltem Wasser

Zusammenfassung. Es wurde der Sauerstoffgehalt in flüssigem Wasser innerhalb des Temperaturbereichs von 0 °C bis −7 °C gemessen. Die Messungen wurden in Glaskapillaren mit einem Innendurchmesser von 1.7 mm mit Hilfe einer amperometrischen O_2-Feinnadelsonde durchgeführt. Es wurde festgestellt, daß der Sauerstoffgehalt des Wassers stark zunimmt sobald die Temperatur unter 0 °C sinkt. Bei konstantem Sauerstoffpartialdruck über der Flüssigkeit ist die Sauerstoffkonzentration im Wasser bei −5 °C im Mittel um 13% höher als bei +3 °C. Die extreme Zunahme des Sauerstoffgehaltes scheint mit den außergewöhnlichen Temperaturabhängigkeiten der Wärmekapazität, der Dichte und der isothermen Kompressibilität des unterkühlten Wassers in Relation zu stehen.

Introduction

It has been suggested that the liquid state of supercooled water [1–3] is due to a considerable loosening of the water structure and improved dynamic properties [4]. This may be related to the increased gas solubilities, which are known to have negative temperature coefficients. In absence of solubility data below 0 °C, we wish to report about the measurements of the oxygen content in supercooled water in the temperature range between 0 °C and −7 °C.

Experimental Part

The concentrations of oxygen have been measured by an amperometric membrane-covered needle-oxygen-sensor obtained from Fa. Eppendorf. Sensors of this type are normally used in medicine

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** Herrn Professor Ulrich Wannagat in alter Verbundenheit zum 70. Geburtstag gewidmet.

to measure oxygen concentrations in blood and tissues. The measured values were registered by a self-constructed electronic instrument which generated a bias of 700 mV for the working electrode relative to the reference electrode. The measured values were recorded on a *x–t*-writer. The needle-oxygen-sensor was not a Clark-type-sensor. This means that (i) the liquid to be measured is simultaneously the electrolyte and (ii) an external Ag/AgCl-reference electrode has to be used. Because of this facts, measurements were made not in pure water but in 0.1 molar NaCl-solutions which was taken into account in the calibration procedure described below. The solutions had been prepared freshly before each measurement using NaCl p.a. by Merck and freshly double-distilled water.

The needle-oxygen-sensor was calibrated by measuring the values of 0.1 molar NaCl-solutions with different oxygen concentrations which in turn had been measured by an conventional (Clark-type) oxygen sensor (obtained from Fa. WTW) at 5 °C. Both the needle sensor and the conventional sensor respond to the oxygen partial pressure in the liquid and hence do not realize the salting-out-effect. Therefore the displayed values refer to the oxygen concentration in pure water. Hence, the measured values of oxygen concentration given in Table 1 also refer to that of pure supercooled water.

The measurements were carried out in Duran-glass-capillaries with an inner diameter of about 1.7 mm. This minimum diameter was given by the geometry of the oxygen sensor and the reference electrode, respectively. Before use the capillaries were cleaned with chromic-sulfuric acid and well rinsed with double-distilled water. The capillaries were placed in a special temperature control device. The temperature was set by a methanol filled Lauda-kryostat (TUK30) and displayed by a Lauda-Pt-resistance-thermometer with a precision of ±0.01 °C.

The measurements were made under constant atmospheric conditions according to the following procedure: First the needle-oxygen-sensor was calibrated as described above and placed inside the freshly filled capillary. When a constant temperature had been reached the oxygen concentration was measured. Now the temperature was lowered by 1 °C. Again the measurement was made at constant temperature. In this way the concentration of oxygen could be measured down to −7 °C. At this temperature the solution froze. Deeper freezing temperatures had not been reached because of the given minimum diameter of the glass capillaries and because the electrodes acted as nucleus. During the measurements neither the temperature nor the atmospheric pressure changed so that the partial pressure of oxygen remained constant.

The error of measuring the oxygen concentration was smaller than 2%.

Results and Discussion

In Table 1 the measured values of oxygen content in supercooled water are given. For the purpose of clear representation only one measurement is displayed in Fig. 1. The other measurements yield almost the same curvature. Figure 1 shows that the oxygen content in water is drastically increased as the temperature is decreased below 0 °C: at −5 °C the concentration of oxygen in water is by 13% higher than at +3 °C (all measurements have been taken into account).

The increase of oxygen content in the supercooled state is an indication for the increase of the solubility of oxygen in liquid water below 0 °C, as has been extrapolated from solubility data for gases in water by Benson and Krause [5, 6].

Figure 2 reveals that the increase in concentration of dissolved oxygen is related to the increase of heat capacity in supercooled water [7]. Results of the calculation of the difference between the partial molar heat capacity of oxygen in aqueous solutions at infinite dilution and that in the ideal gas state for different temperatures above 0 °C showed that the heat capacities of oxygen dissolved in water is even higher than in the gaseous state [8]. According to the theorem of additivity of heat capacities for solutions an increase in concentration of dissolved oxygen should lead

Table 1. Concentration of oxygen dissolved in water at different temperatures, t_i... temperature in °C, c_i... concentration of oxygen in mg/l

t_1	c_1	t_2	c_2	t_3	c_3	t_4	c_4	t_5	c_5
5.07	8.26	3.05	10.39	4.10	10.01	1.46	10.10	3.44	8.35
4.06	8.34	2.05	10.46	3.10	10.30	−0.44	10.29	2.53	8.41
3.07	8.37	1.05	10.53	2.10	10.20	−1.58	10.48	1.83	8.56
2.06	8.57	0.03	10.63	0.85	10.42	−2.45	10.81	0.78	8.67
1.06	8.64	−0.49	10.69	−0.01	10.41	−3.29	11.13	−0.33	8.82
0.05	8.72	−1.96	10.80	−0.96	10.60	−4.29	11.52	−1.44	9.05
−0.95	8.97	−2.95	10.91	−2.06	10.73	−5.34	12.01	−2.56	9.19
−1.95	9.31	−3.97	11.03	−2.89	10.87			−3.42	9.34
−2.95	9.36	−4.96	11.16	−4.08	11.17			−4.33	9.62
−3.95	9.85	−5.93	11.45	−5.15	11.34			−5.43	10.12
		−6.98	11.84	−5.72	11.65				

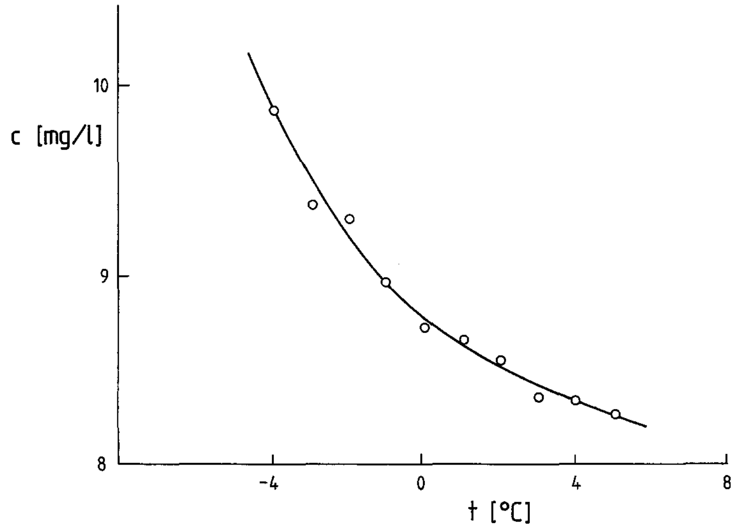

Fig. 1. Concentration of oxygen dissolved in water at different temperatures

to an increase in the heat capacity of the solution. As the absorption of oxygen by supercooled water increases dramatically with decreasing temperature the "abnormal" increase of heat capacity becomes understandable.

The gas molecules dissolved in water are known to librate within the voids, the size of which is greater than necessary for the accommodation of the gas molecules [9,10]. The water molecules surrounding the gas molecules provide inner surfaces, by which the librations of the gas molecules are in harmony with the oscillating pattern of the liquid. By their mutual interactions the dynamic features of the gas molecules influence the whole water structure leading to its loosening. This is also related to the decrease in density [11] (Fig. 3) and the increase of the isothermal

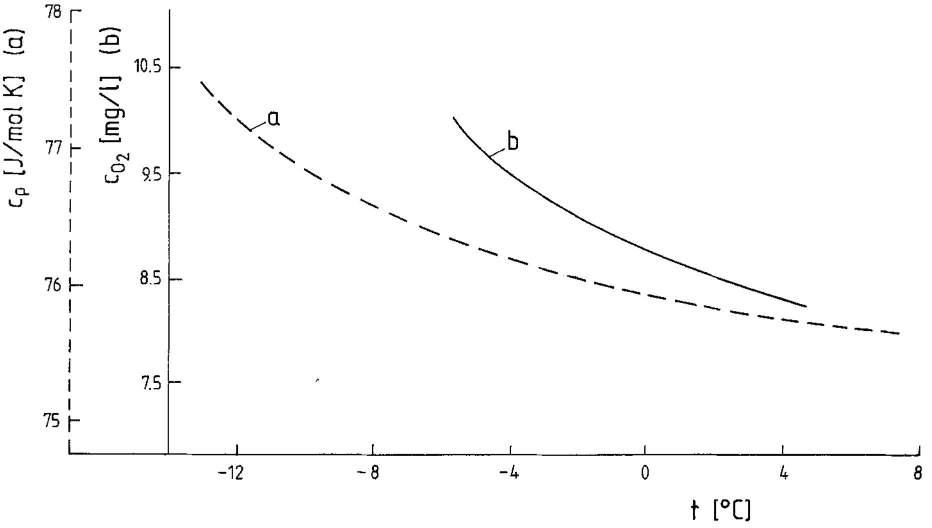

Fig. 2. Relation between oxygen concentration and molar heat capacity c_p of supercooled water. Curve a) refers to the c_p-values and curve b) to the concentration of oxygen

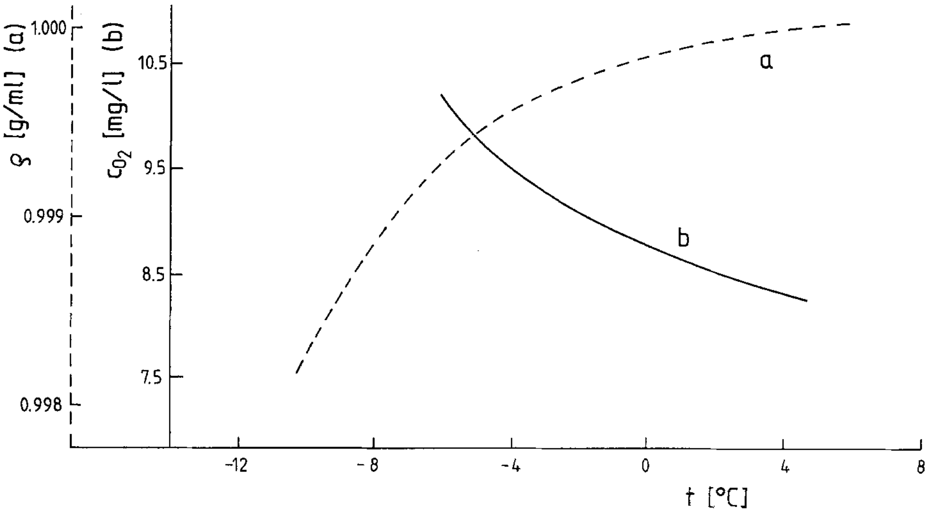

Fig. 3. Relation between oxygen concentration and density of supercooled water. Curve a) refers to the density and curve b) to the oxygen concentration

compressibility [12] (Fig. 4). In supercooled water the absorption of gases is favoured by increasing the number of molecules at the interface. The results are in accordance with the concept of supermolecular system organization of liquid water and its improvement in supercooled water which has recently been described in some detail [4].

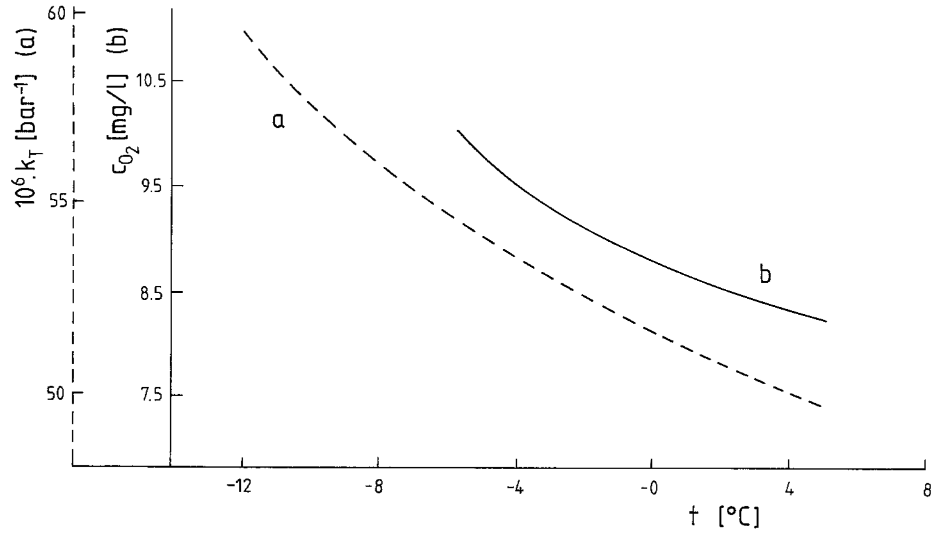

Fig. 4. Relation between oxygen concentration and isothermal compressibility of supercooled water. Curve a) refers to the isothermal compressibility and curve b) to the oxygen concentration

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