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THE EFFECT OF OXYGEN CONTENT ON THE MELTING OF THE EUTECTIC OF PHYSIOLOGICAL SALINITY SOLUTION

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The effect of oxygen concentration on the melting of this eutectic was investigated by DSC. In the deoxygenized solution, an endothermic peak attributed to the eutectic transition was observed in the course of heating, and its peak temperature is around –21.5°C. Another endothermic peak appeared at lower temperature in the presence of oxygen. As the oxygen content in the solution increases, the temperature of this peak is shifted to lower temperature. The transition at the lower temperature are associated with the melting of eutectic carrying oxygen. The same results are given in the NMR data.

Keywords: DSC, effect of oxygen content, eutectic, NMR

Introduction

The investigation of eutectic forming solutions is important for pharmaceutical preparation to be lyophilized. So some experimental studies have been reported on the eutectic forming solutions by differential scanning calorimetry (DSC) [1, 2]. However, most of these investigations are concerned with concentrated solutions. In this study, aqueous sodium chloride solution was chosen as the eutectic forming solution because of its physiological importance, and the effect of oxygen content on the melting of the eutectic compound of physiological saline water was investigated.

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Experimental

Reagents

Analytical grade sodium chloride was purchased from Wako Pure Chemical Industries, Ltd. and used without further purification. The purity of sodium chloride was 99.99%. Water was purified with a Millipor Milli-Q SP system.

Apparatus

Measurements were made with a SEIKO DSC SSC5000 DSC100, and a JEOL NMR JNM EX400. The oxygen holding solution was made by bubbling oxygen gas into the solution. The oxygen content control solutions were made by a membrane deoxygenizer of the ERMA Inc. made. The oxygen contents of the solutions were 0.7 μg/ml, 4.0 μg/ml and 8.5 μg/ml.

DSC and NMR measurements were made on the aqueous sodium chloride solutions at the concentration of 0.1 mol/l. The solution was sealed in a silver metal container with the size of 6 mmø x 4 mm, and weighed ± 1 μg.

The NMR measurement have been made on the same solutions as the DSC measurements. The solution was cooled down to –60°C and kept at this temperature for 20 min, and then brought up to the measuring temperature. To balance the heat capacities between the sample and reference holders, a sapphire stone was used as the reference. The solution was cooled at a rate of 2 deg·min^{-1} and subsequently heated at a rate of 1 deg·min^{-1}.

Results and discussions

The DSC carve of an aqueous sodium chloride solution give a small peak due to heat absorption at around –22°C and a main endothermic peak at around 0°C. The former peak is attributed to the melting of the eutectic compound of sodium chloride and water, and the latter peak is due to the melting of ice.

Sodium chloride is the main component of the human blood. The concentration of sodium chloride in the physiological saline water is about 0.14 mol/l. We have reported that the fluctuation of the refractive index is anomalously enhanced at this salt concentration. When oxygen was removed from the solution, this enhancement did not occur [3, 4]. Therefore, the effect of oxygen concentration on the melting of this eutectic compound was investigated by DSC (Fig. 1). In the case of the deoxygenized solution, an endothermic peak which is attributed to the

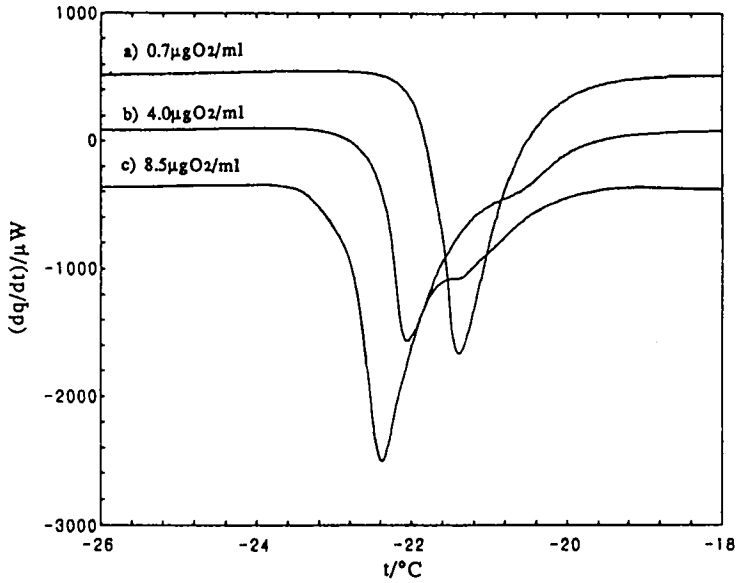

Fig. 1 The effect of oxygen content on the DSC melting curve for the eutectic compound. Oxygen content; a) 0.7 μg/ml, b) 4.0 μg/ml, c) 8.5 μg/ml

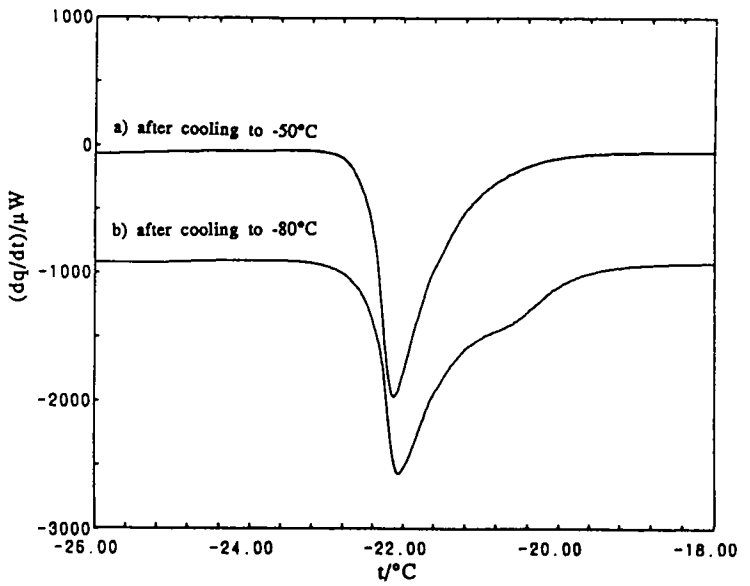

Fig. 2 DSC curve of eutectic compound measured in the course of heating. a) After cooling to –50°C, b) after cooling to –80°C

eutectic transition was observed in the course of heating, and its peak temperature is around –21.5°C. Another endothermic peak appeared at lower temperature in the presence of oxygen. As the oxygen content in the solution increases, the temperature of eutectic transition peak is shifted to lower temperature. The transition at the lower temperature are associated with the melting of eutectic compound carrying oxygen as reported previously [5]. To examine these transitions, two kinds of DSC measurements were carried out on the same solution holding 4 μg/ml oxygen. In the one method, the solution was cooled to –50°C and the heating curve was recorded. In the other, the cooling temperature was lowered to –80°C. When the sodium chloride solution is cooled from room temperature, several transitions will be observed. The first one is the crystallization of water, then the eutectic compound holding oxygen crystallizes, and the last one is the crystallization of the eutectic compound itself. As can be seen from Fig. 2, the lower temperature transition is associated with the melting of eutectic compound holding oxygen, while the higher temperature transition is due to the melting of the eutectic compound itself. The difference of transition temperatures by varying the cooling temperature is caused by that of the crystal size of the eutectic com-

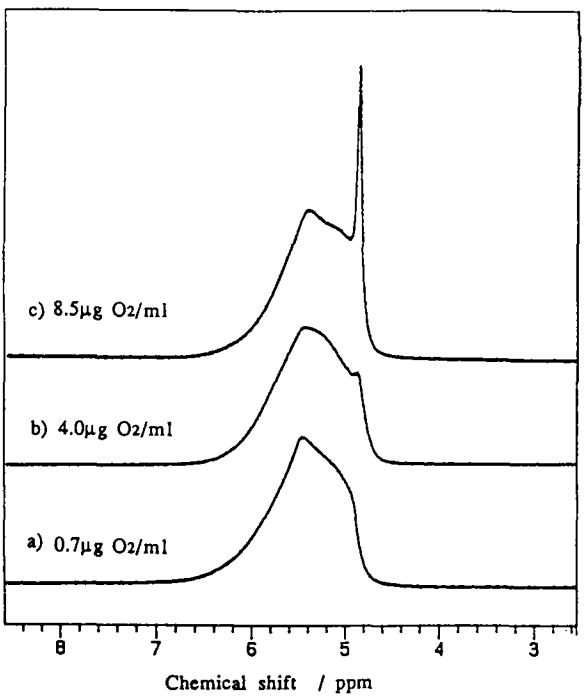

Fig. 3 The effect of oxygen content on the ^{1}H NMR spectrum of eutectic compound at –20°C. Oxygen content: a) 0.7 μg/ml, b) 4.0 μg/ml, c) 8.5 μg/ml

pounds. Swerme *et al.* has reported that the crystal size of $NaCl{\cdot}2H_2O$ is about 10 μm at first, gradually growing to the final size of about 100 μm on standing [6]. Namely, when oxygen is added to the saline solution, the crystal growth of the eutectic compound is prevented by oxygen.

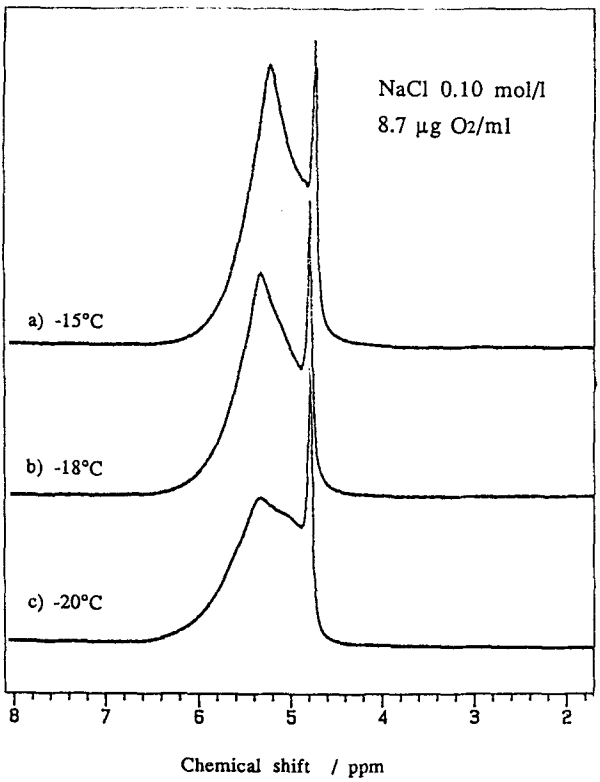

Fig. 4 The effect of temperature on the ^{1} HNMR spectrum of eutectic compound. Temperature; a) –15°C, b) –18°C, c) –20°C

To further examine the melting of the eutectic compound, the NMR measurements were made on these solutions. Figure 3 shows the effect of oxygen concentration on ^{1}H NMR spectra at –20°C. As the reference, tetramethylsilane dissolved in deuterium chloride was used externally. The NMR spectra for the oxygen holding solutions are the overlap of two or three lines, one is sharp line at 4.7 ppm, which is the resonant position of pure water and the other are broad lines at 5.0~5.5 ppm. The sharp line was remarkably affected by the oxygen content, so it is due to the molten eutectic compound, which holds oxygen, in the ice.

As seen in Fig. 4, this sharp line is independent of measuring temperature, while, the broad lines are dependent on temperature. As the crystal size of the eutectic compound holding oxygen is small enough to move in the ice, the line becomes sharp.

From these results, the oxygen content in the solution has a significant effect on the melting of the eutectic compound of sodium chloride and water.

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Zusammenfassung — Mittels DSC wurde der Einfluß der Sauerstoffkonzentration auf das Schmelzen dieser eutektischen Verbindung untersucht. In von Sauerstoff gereinigter Lösung wurde beim Erhitzen ein endothermer Peak in Verbindung mit der eutektischen Umwandlung beobachtet, die Peaktemperatur liegt bei etwa –21.5°C. Ein weiterer endothermer Peak erscheint in Gegenwart von Sauerstoff bei tieferen Temperaturen. Nimmt der Sauerstoffgehalt der Lösung zu, wird die Temperatur dieses Peaks in Richtung niedrigerer Temperaturen verschoben. Die Umwandlung bei der tieferen Temperatur steht im Zusammenhang mit dem Schmelzen einer sauerstofftragenden eutektischen Verbindung. Gleiche Resultate erhält man mittels NMR-Studien.