CHEMISTRY LETTERS, pp. 2311-2314 1992.

Measurement of Ice Fraction in NaCl Solution with FTIR

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Infrared spectra of 0.12 mm thick frozen NaCl solution from 1600 to 4000 cm^{-1} were obtained at sub-zero temperature with a FTIR spectrometer. The transmittance of the sample decreased sensitively with decreasing temperature around the frequency of 2700 cm^{-1}. The volume fraction of ice in the NaCl solution, calculated from the absorbance at 2700 cm^{-1}, agreed well with the values predicted from a phase diagram of the system H_2O-NaCl.

Infrared spectroscopy method is useful for studies on the structure of ice, liquid water and absorbed water on clay particles.[1,2] Absorption peaks of infrared are different for liquid water and ice.[3] Therefore, if the difference in the peak between liquid and ice are observed for a frozen sample, the method can be used to determine ice content in the sample. For infrared spectrum of water, normally, attention is given to the frequencies of OH stretching or OH bending bands. However, because several absorption peaks of both liquid water and ice coexist at the narrow range of each frequency, it is difficult to distinguish the peaks and to analyze them quantitatively. In addition, the absorptions at the frequencies of OH stretching and OH bending bands are so intensive that only a thin sample containing less water must be prepared for the measurement of the absorption peaks. For such a thin sample, however, it is difficult not only to distinguish ice from liquid water but also to determine the water content in the sample. In this study, a new infrared spectroscopic method is presented to determine the ice fraction in a thicker frozen sample of NaCl solution. Then the method is shown to be promising for the measurement of ice fraction in a frozen sample.

The absorbance of a frozen sample, A_f, can be expressed by the Beer-Lamber's law:

$$A_f = \mu_L(m_L/V)l + \mu_i(m_i/V)l + \mu_c(m_c/V)l \qquad (1)$$

$$= (\mu_L l/\bar{v}_L)(m_L\bar{v}_L/V) + (\mu_i l/\bar{v}_i)(m_i\bar{v}_i/V) + (\mu_c l/\bar{v}_c)(m_c\bar{v}_c/V) \quad (2)$$

where μ is the mass absorption coefficient (cm^2/g), m is the mass of constituent (g), V is the total volume of the sample (cm^3), $\bar{v}$ is the partial specific volume (cm^3/g), and l is the the thickness of the sample (cm). The subscripts L, i and s indicate liquid water, ice and solute, respectively. To apply Eq. 2 to the measurement of ice content, we define here the specific absorbance which is determined experimentally for each specific constituent with the thickness of l, namely,

$$A_L \equiv \mu_L l/\bar{v}_L, \quad A_i \equiv \mu_i l/\bar{v}_i, \quad A_c \equiv \mu_c l/\bar{v}_c. \quad (3)$$

Since $m\bar{v}/V$ in Eq. 2 is equal to the volume fraction of each constituent, θ , Eq. 2 becomes:

$$A_f = A_L\theta_L + A_i\theta_i + A_c\theta_c. \quad (4)$$

The sum of the volume fraction of each constituent must be unique; that is,

$$\theta_L + \theta_i + \theta_c = 1. \quad (5)$$

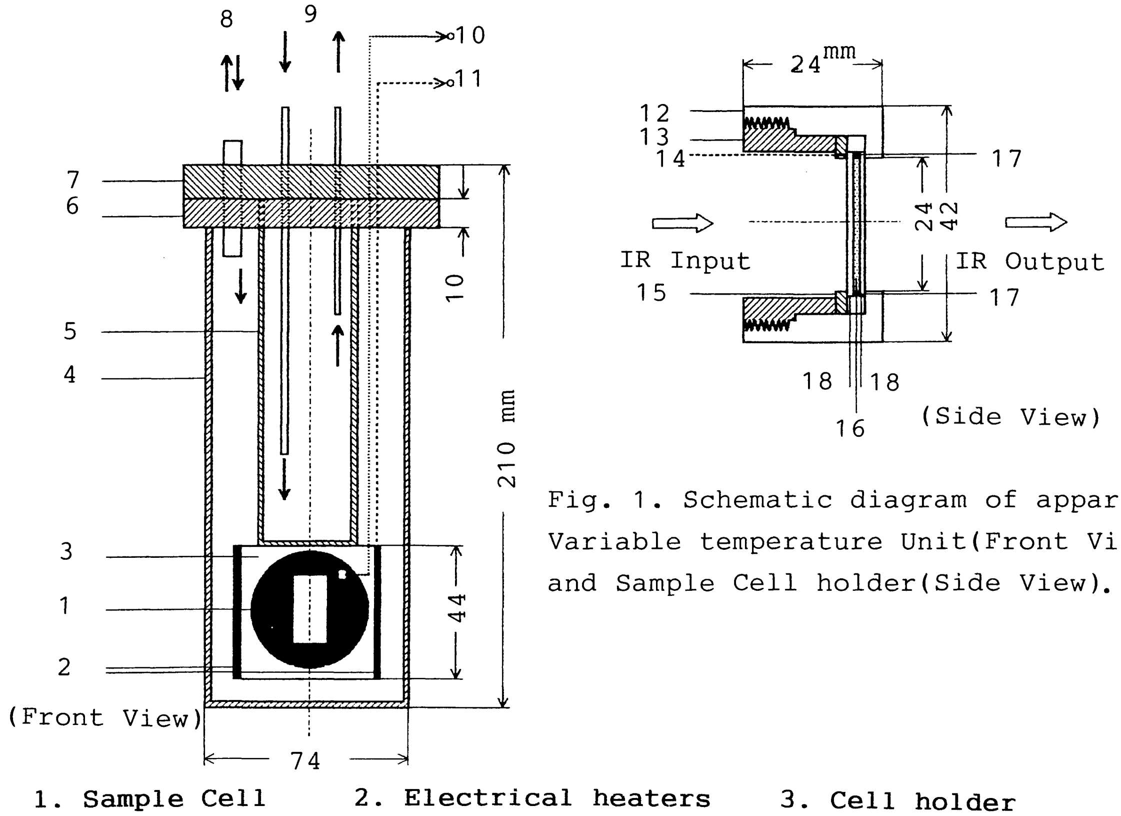

Fig. 1. Schematic diagram of apparatus Variable temperature Unit(Front View) and Sample Cell holder(Side View).

1. Sample Cell 2. Electrical heaters 3. Cell holder
4. Outer stainless steel jacket 5. Refrigerant Vessel
6. Metal cap of outer jacket 7. Metal cap of Refrigerant Vessel
8. Dry air 9. Cooling liquid 10. Thermocouples to Potentiometer
11. To a 12-Volt autotransformer 12. Metal Outer Cell frame with screw
13. Metal Inner Cell frame with screw 14. Thermocouples
15. Metal plate with rectangular aperture 16. Sample
17. 0.06 mm thick copper spacer 18. 1 mm thick IRTRAN-2 window

Eliminating θ_L from Eqs. 4 and 5 gives the volume fraction of ice in the frozen sample:

$$\theta_i = \frac{A_f - A_L}{A_i - A_L} - \left(\frac{A_c - A_L}{A_i - A_L}\right)\theta_c. \qquad (6)$$

The samples used in this experiment were (1) distilled water and (2) NaCl solution which had the concentration of 1 g NaCl per 100 g water, namely 1.0 % by weight. For the measurement of IR spectrum at sub-zero temperature, a specially designed apparatus as shown in Fig. 1, Variable temperature Unit (Beckman VLT-2), was used with a FTIR spectrometer (Perkin Elmer Model 1800). After the sample was frozen with liquid nitrogen, the temperature was upwards in increment, then the IR spectrum was obtained for every 2 cm^{-1} over the range of frequencies between 1600 to 4000 cm^{-1} at each temperature.

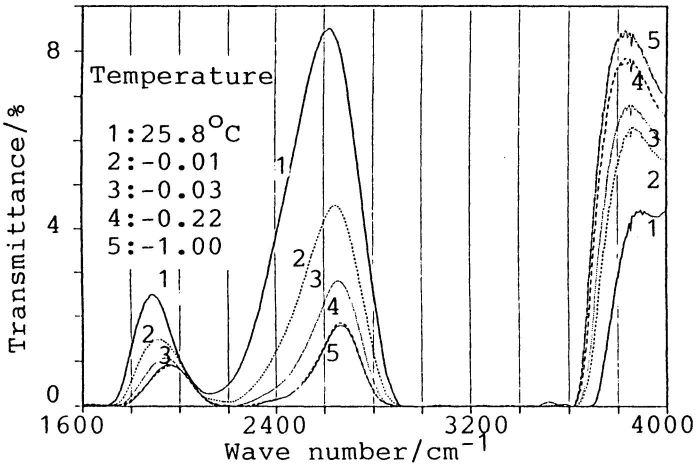

Fig.2. Transmittances of water-window system.

Figure 2 shows the transmittances of water-windows system having the sample thickness of 0.12 mm. The transmittances of the system were high around three frequencies: 1900, 2700, and 3900 cm^{-1}. The transmittances decreased sensitively with decreasing temperature around 1900 and 2700 cm^{-1} and increased around 3900 cm^{-1}. This result means that the transmittances changed with increasing ice content. The sample was so thick, 0.12 mm, that most of infrared energy was absorbed by the vibrational modes of water molecule: OH bending, association, and OH stretching bands[3)] in the ranges of 1600-1700, 2100-2300, and 2900-3600 cm^{-1}.

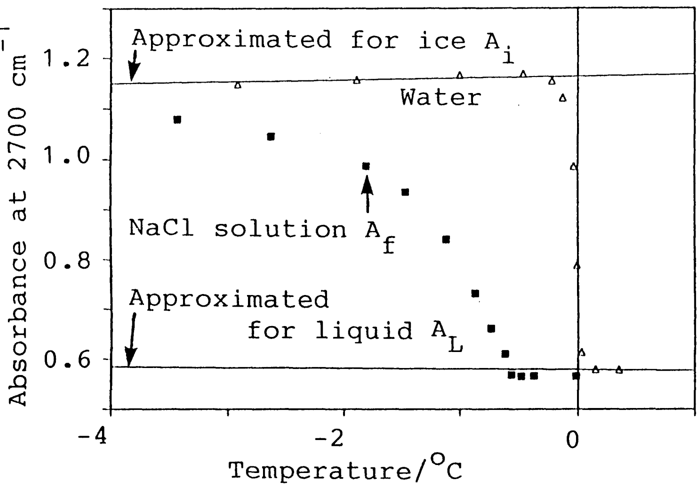

Fig.3. Absorbances of water and NaCl solution at sub-zero temperature.

Figure 3 shows the absorbances in the NaCl solution as a function of sub-zero temperature at 2700 cm^{-1}. The symbols of triangle and solid square are the experimental results, and two solid lines are the values approximated from the results, respectively. The absorbance of the NaCl solution decreased gradually with increasing temperature and became constant at the temperature over -0.57 $^{\circ}$C. These results are attributed to the freezing point depression of solution; as temperature increases, the ice thaws up to the concentration in the residual solution reaches the concentration related to the temperature.

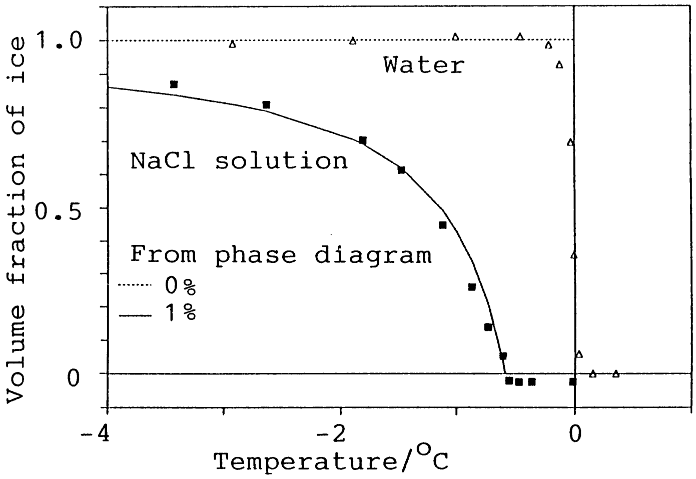

Fig.4. Volume fraction of ice in the NaCl solution.

Since θ_c in Eq. 6 is negligible small for the 1% NaCl solution, the volume fraction of ice, θ_i, is calculated from the absorbance given in Fig.3. Figure 4 shows the relationship between θ_i and temperature. The symbols of triangle and solid square are the calculated values, and a dot and a solid lines are the values predicted from a phase diagram[4)] of the system H_2O-NaCl, respectively. The calculated and predicted values are in excellent agreement. Consequently, it was concluded that the present method of using 2700 cm^{-1} is very promising to determine the volume fraction of ice in frozen samples.

This study was completed during a sabbatical leave at Purdue University. I would like to thank Mie University and Purdue University for supporting during this time.

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(Received August 20, 1992)