DECREASE OF SOLUTE IN THE AQUEOUS SOLUTION IN THE FREEZING PROCESS

Keiichi SATO, Tohru DAIMON, Norimichi TAKENAKA, Hiroshi BANDOW
and Yasuaki MAEDA

*Department of Applied Materials Science, College of Engineering, Osaka Prefecture University,
1–1, Gakuen-cho, Sakai 593*

Abstract: Dilute volatile acidic aqueous solution was frozen by various freezing methods, and concentrations of solutes and pH of the sample were measured after the sample was completely thawed. Concentration of the volatile acid anion in the sample decreased, and pH of the sample increased after freezing. The decrease of solutes in the sample was almost equal to that detected in the gas phase. When dilute salt solution was frozen, solutes were excluded from ice and concentrated into the unfrozen solution. Concentrated anion combines with concentrated proton to form volatile acid such as acetic, formic or nitrous acid without reaction with any other chemicals. These volatile acids are saturated, and evaporation to the gas phase occurs. It is considered that the decrease in concentration of various solutes is mainly due to the freeze-concentration effect.

1. Introduction

Freezing is often used to preserve many substances. Composition of substances in solution is considered not to change in a freezing-thawing process. Some chemical reactions, however, are known to be accelerated by freezing (GRANT and ALBURN, 1965; HATRAY *et al.*, 1986; TAKENAKA *et al.*, 1992, 1993). The following mechanisms for acceleration by freezing have been reported (FENNEMA, 1975; BRONSTEYN and CHERNOV, 1991). (1) Freeze-concentration effect: Solutes are excluded from ice and concentrated into unfrozen solution, and their concentrations increase. (2) Catalytic effect of ice surface: Ice crystal catalyzes the chemical reaction. (3) Hydrolysis: The pH of unfrozen solution is known to be changed by freezing. (4) Dielectric constant change: Reactants approach easily, since the dielectric constant of ice is smaller than that of water. (5) Electrochemical effect: Electrochemical reaction is stimulated by freezing potential which is generated between ice and solution, when a dilute aqueous solution containing electrolytes is frozen. Furthermore, FENNEMA (1975) reported that the freeze-concentration effect is considered to be the most important among the above mentioned mechanisms.

LODGE *et al.* (1956) reported that chloride ion concentration decreased, when dilute sodium chloride aqueous solution was frozen. They explained that this decrease was associated with the freezing potential. FINNEGAN *et al.* (1991) also reported decreases of various solute concentrations associated with electrochemical reaction based on the freezing potential, but the reactions which occurred in freezing process are not well known, because most products of the reaction were not determined. It is not clear why chloride

ion concentration is changed by freezing.

Nitrate and chloride losses from the ice core sample in the Antarctic area have been reported (NAKAMURA et al., 1994). The losses were considered to be caused by nitric acid and hydrochloric acid which escaped from ice.

Losses of solutes have been reported in field measurements and also in laboratory experiments. The mechanism of the losses and the fate of the lost solutes, however, are not understood. The role of freezing in the environment has not been clarified, though freezing is a common process.

It is well known that ice crystal does not incorporate with other substances (FENNEMA, 1975). When dilute acidic solution is frozen, both anions and cations are excluded from ice and concentrated into unfrozen solution. Concentrated anions combine with protons to form acid. If the acid thus formed is volatile, the acid in the unfrozen solution will eventually become saturated and evaporate. In this paper we report the freeze-concentration effect of solutes, decrease in concentration of solutes in the frozen-thawed sample solution and evaporation of solutes to the gas phase, when dilute aqueous solution was frozen by various freezing methods.

2. Experiment

Sample solution of sodium chloride, sodium nitrite, sodium acetate or sodium formate was frozen by various freezing methods. Frozen sample was completely thawed, and then contents of ions in the sample and alkaline solution which was used to collect acid in the gas phase were analyzed. The number of moles of each ion contained in a frozen-thawed sample was compared to that in the original solution. Change of composition in the sample and evaporation to gas phase were investigated.

All Reagent-grade chemicals were obtained from Wako Pure Chemicals Inc. and used without further purification. Sodium nitrite was dried at 120°C for one night. Aqueous solution of sodium chloride, sodium nitrite, sodium acetate or sodium formate was prepared with Milli-Q water (resistance> 18MΩ cm), and the pH of the solution was adjusted with sulfuric acid before freezing. Sample solution was frozen by the following four freezing methods.

(1) An aliquot of the sample solution was put in a Pyrex test tube, and the tube was immersed in a coolant. In this method, the sample was frozen from the outside to the center of the tube, and the sample surface was frozen before the whole sample was frozen.

(2) An aliquot of the sample solution was put in a glass vessel of inner diameter and height 35 mm and 72 mm, respectively, and the bottom of the vessel (5 mm height) was immersed in a coolant. The sample was frozen from bottom to top, and the sample surface was finally frozen. In this method, freezing speed could not be controlled.

(3) In order to control the freezing rate, the sample was frozen at a constant rate with the apparatus shown in Fig. 1. This apparatus consists of three parts: the upper warmer zone, the middle window zone and the lower colder zone. The temperature of the warmer zone was adjusted to 5°C, and the colder zone was adjusted to –5°C or –10°C. The Pyrex test tube containing sample solution was moved down slowly at a constant rate with a microfeeder in order to freeze the sample from the bottom. Inner
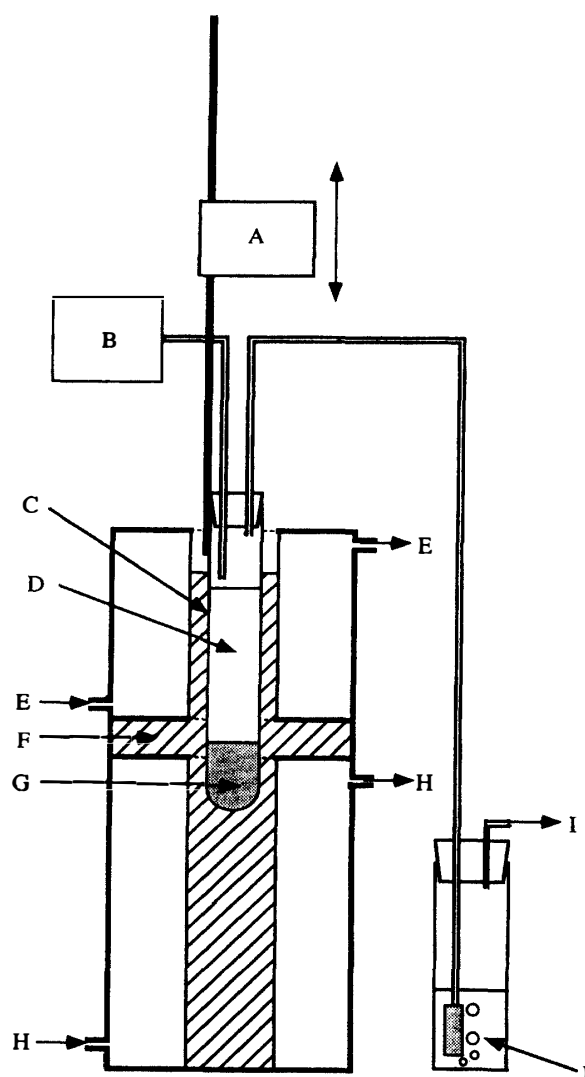
Fig. 1.   The freezing apparatus in freezing methods (3) and (4).   A:
microfeeder, B: N_2 gas bag, C: Pyrex test tube, D: unfrozen
sample, E: warmer water (5 °C), F: water-methanol mixture, G:
frozen sample, H: colder coolant (-5 or -10 °C), I: to suction
pump, J: alkaline solution.

diameter and height of the test tube were 15 mm and 180 mm, respectively. In order to
prevent supercooling, the bottom of the test tube was immersed in liquid nitrogen for
15 s, and a thin ice film was formed before the freezing experiment. When freezing was
carried out in this way, ice crystals grew from the bottom, and the interface of ice and
solution was observed in the middle window zone.

(4) When sodium nitrite solution was frozen by freezing method (3), most nitrite
was oxidized to nitrate. This is due to freeze-concentration in the grain boundary of
polycrystalline ice (TAKENAKA et al., 1996). To prevent the reaction, single crystalline
ice was formed with a freezing tube shown in Fig. 2 and the same freezing apparatus
used in method (3). The detailed method of single crystalline ice preparation is found in
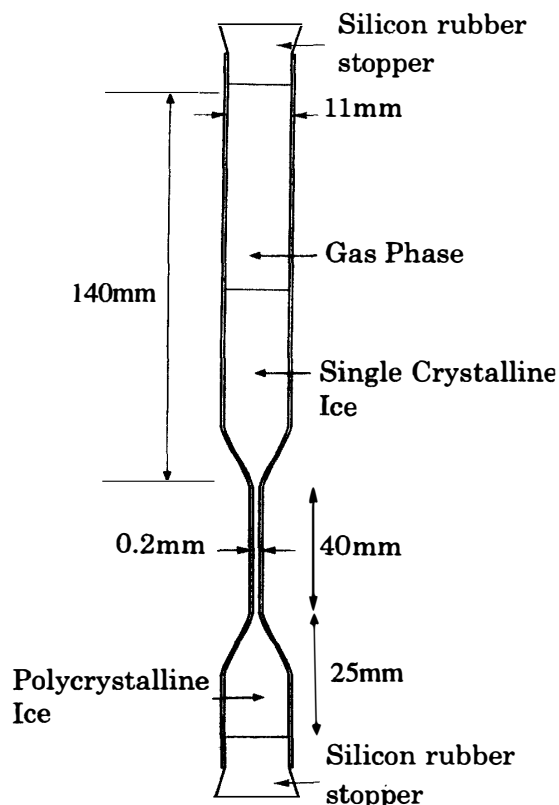the literature (KIM and SINDO, 1989; TAKENAKA et al., 1996).

Fig. 2.   The freezing tube used to form single crystal ice in freez-
ing method (4).

Table 1. Experimental condition in this study.

Solute	pH	Freezing method
NaCl	3.00–5.65	(1) and (2)
CH₃COONa	4.25	(3)
HCOONa	4.00	(3)
NaNO₂	4.00	(4)

In order to investigate the amount of evaporated gas, as shown in Fig. 1, flushing
gas, nitrogen, was introduced to the test tube, and evaporated gas was flushed and then
trapped into an alkaline solution. The experimental condition in this study is shown in
Table 1.

Concentrations of ions were analyzed after the sample was thawed completely. An-
ions were determined by ion chromatography (Yokogawa Analytical Systems Inc. IC-
7000 Ion Chromatographic Analyzer). Sodium ion was determined by flame photometry
(Hitachi Ltd. 208 Atomic Absorption Spectrophotometer), and pH was measured with a
pH meter (CP-1 digital desktop pH meter and SE-1700GC glass electrode). When the
concentrations of ions in ice and solution were analyzed separately, the solution part of
the sample was separated by sucking out with a syringe. We calculated the number of
moles of solute by multiplication of its concentration by its weight.

3. Results

Lodge et al. (1956) reported that chloride ion concentration decreased with repetition of the freezing and thawing operation, when sodium chloride solution was frozen. They reported that chloride ion concentration was changed from 322 μmol dm^{-3} to 230 μmol dm^{-3} by 5 freezing-thawing cycles. They used a polypropylene tube vessel with copper bottom. We found that chloride ion concentration in solution decreased from 100.0 μmol dm^{-3} to 92.8 μmol dm^{-3}, when sodium chloride solution was put in the same kind of vessel used by Lodge et al. On the other hand the same solution was put in a glass vessel, and no change in chloride ion concentration was observed. This suggests that a copper plate adsorbs some chloride ions. Therefore a glass vessel was used in the present study.

Table 2 shows the results obtained in freezing methods (1) and (2). When sample was frozen by freezing method (1), substantial change of chloride ion concentration was not observed. On the other hand, chloride ion concentration decreased in freezing method (2).

Table 2.   Variation of chloride ion concentration when sample
was frozen by freezing method (1) and method (2).

Freezing method	Freezing-thawing cycle	[Cl$^-$] (μmol dm^{-3})
(1)	1	100.7
(1)	6	101.1
(2)	3	93.4
(2)	5	91.8

Initial NaCl concentration was 100.0 μmol dm^{-3}, and the initial pH was 5.65.
Temperature in the coolant was $-10°$C.
All samples were allowed to freeze for 1 hour.

To investigate the time profile of decrease of solute after the sample is completely frozen, 100.0 μmol dm^{-3} sodium chloride solution was frozen by freezing method (2), and the frozen sample was allowed to stand in a freezer at $-18°$C. Figure 3 shows the time profile of chloride ion concentration. From Fig. 3 it is found that chloride ion concentration was decreased with standing time. Standing time in the freezer or coolant affects decrease of solutes, and therefore the frozen sample was allowed to stand in the coolant for the same time (1 hour) in freezing methods (1) and (2).

When an acidic solution containing a salt of volatile acid is frozen, anions combine with protons to form volatile acid, and this acid evaporates. Therefore the evaporation of volatile acid is expected to proceed at low pH. Figure 4 shows the chloride ion concentration after freezing, when 100.0 μmol dm^{-3} sodium chloride solutions adjusted at various initial pH values were frozen by freezing method (2). In this figure, σ means standard deviation for five measurements of 100.0 μmol dm^{-3} chloride ion. Decrease of chloride ion concentration by freezing was observed in acidic solution, but significant pH dependence was not observed. The reason why the difference of chloride decrease was small at various initial pH values is not clear yet.
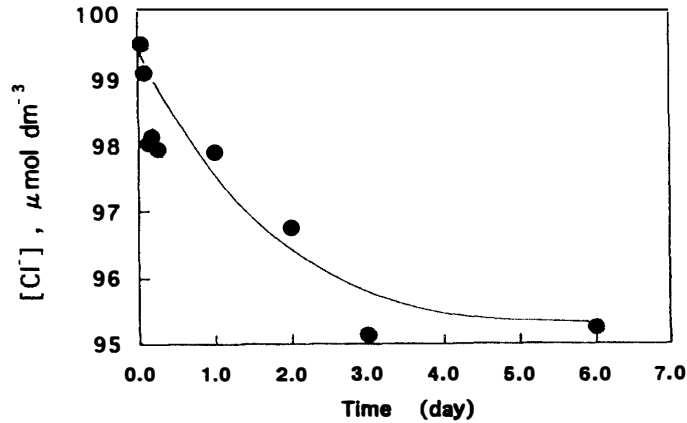
Fig. 3.   Time profile of chloride ion concentration when the sample was frozen
by freezing method (2) and allowed to stand in a freezer. [NaCl]$_0$: 100
$\mu mol\ dm^{-3}$, pH$_0$: 5.65, temperature in the freezer: $-18\,°C$. $t=0$ is defined
as the time when the sample was completely frozen, and each plot shows
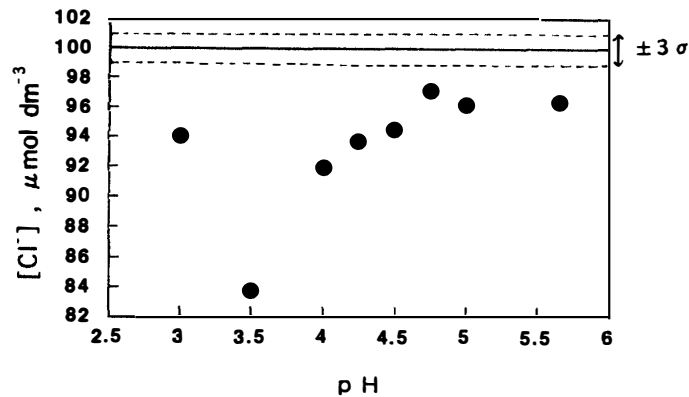the data of an individual sample.

Fig. 4.   Decrease of chloride ion concentration as a function of initial pH of the
sample solution in freezing method (2). [NaCl]$_0$: 100.0 $\mu mol\ dm^{-3}$, tem-
perature in a coolant: $-10\,°C$. All samples were allowed to freeze for 1
hour, and $\pm 3\sigma$ means the error of this study (five measurements).

We investigated the decrease of volatile solute in the case of strong acid salt (such
as sodium chloride) and weak acid salt (such as sodium acetate or formate) in freezing
by freezing method (2). There was no respective difference among these acid salts.

In order to investigate the freeze-concentration effect, the decrease of solute ions in
freezing and evaporation to gas phase, 100.0 $\mu mol\ dm^{-3}$ sodium acetate or sodium for-
mate solution was frozen by freezing method (3), and amounts of acetate or formate ion
in ice, unfrozen solution and gas phase were analyzed. Figures 5a and 5b show varia-
tions of acetate ion concentration and the number of moles of acetate ion, respectively,
in ice, unfrozen solution and gas phase. From Fig. 5a it is observed that acetate ions
were excluded from ice and concentrated into the solution. When 90% of ice was formed,
acetate ion was concentrated by about four times compared to the initial concentration.
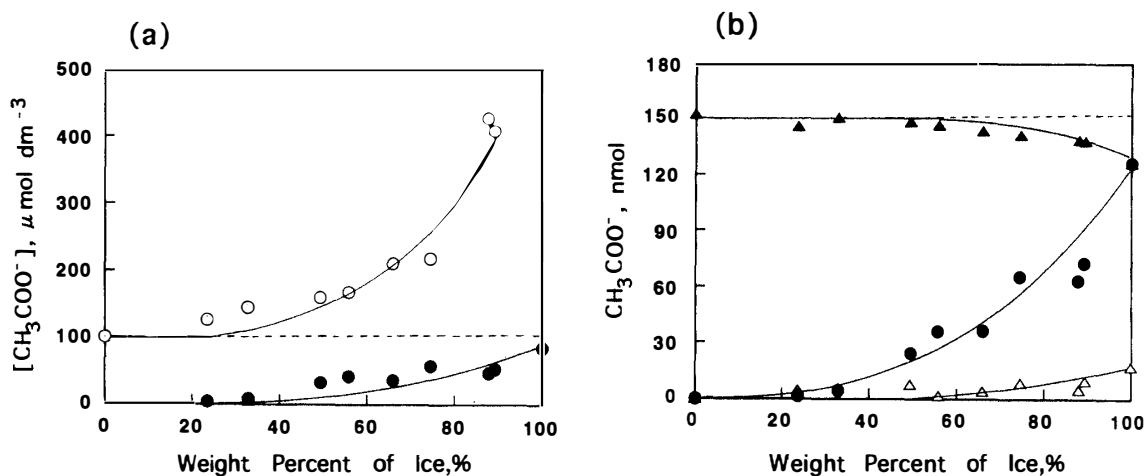From Fig. 5b it is observed that the number of moles of acetate ion in ice plus solution

Fig. 5. Changes in acetate ion concentration (a) and number of moles of acetate ion (b) in ice, unfrozen solution and gas phase, respectively, with the progress of ice formation in freezing method (3). $[CH_3COONa]_0$: 100.0 μmol dm^{-3}, pH_0: 4.25, sample volume: 15.0 cm^3. ●: ice, ○: unfrozen solution, ▲: ice+unfrozen solution, △: gas phase. Each broken line means initial value, and each plot shows the data of an individual sample. No changes of the numbers of moles of sodium and sulfate ions in the sample were observed in this experiment.

decreased, while that in the gas phase increased. When the whole sample was frozen, the decrease of the number of moles of acetate ion in the sample was 22 nmols and almost the same as that detected in the gas phase. In the case of formate, the same results as for acetate were obtained.

We also measured pH values of the ice and the solution part when 100.0 μmol dm^{-3} sodium acetate or formate solution was frozen by freezing method (3). Figure 6 shows pH values of the ice and solution part when sodium acetate solution was frozen. The pH of the solution part was lower than the initial value. In the case of formate, the same results were obtained as in the case of acetate.
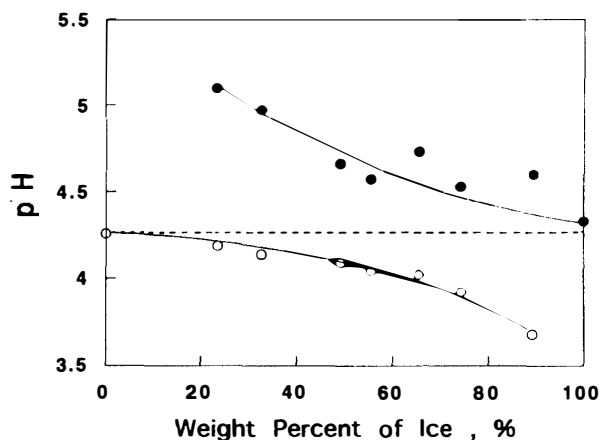

Fig. 6. Changes in pH of the ice part and the unfrozen solution part, respectively, with the progress of ice formation when sodium acetate solution was frozen by the freezing method (3). $[CH_3COONa]_0$: 100.0 μmol dm^{-3}, pH_0: 4.25, sample volume: 15.0 cm^3. ●: ice, ○: unfrozen solution. The broken line shows the initial pH, and each plot shows the data of an individual sample.

Sodium nitrite solution was frozen by freezing method (4). We investigated variations of the concentration and the number of moles of nitrite and sulfate ion in ice, unfrozen solution and gas phase. Sulfate or Sulfuric acid is known to be nonvolatile, and therefore it can be used as an internal standard. Figure 7 shows variations of nitrite and sulfate ion concentrations, respectively, in ice and those in unfrozen solution. From this figure, few nitrite and sulfate ions were incorporated into ice; most of them were excluded from ice and concentrated into the unfrozen solution. We calculated numbers of moles of nitrogen species. Before freezing there were 215 nmols of nitrogen species in the sample, while the total amounts of nitrogen species reduced to 85 nmols after freezing. In order to make this decrease clear, 100.0 μmol dm^{-3} sodium nitrite solution was frozen completely, and numbers of moles of nitrogen species in ice and gas phase were measured. The results are shown in Table 3. As shown in Table 3, considerable amounts of nitrite ions were released from the sample into the gas phase.

Table 4 shows ion concentrations after freezing and comparisons of pH values of the frozen-thawed sample with those of unfrozen sample, when 100.0 μmol dm^{-3} sodium
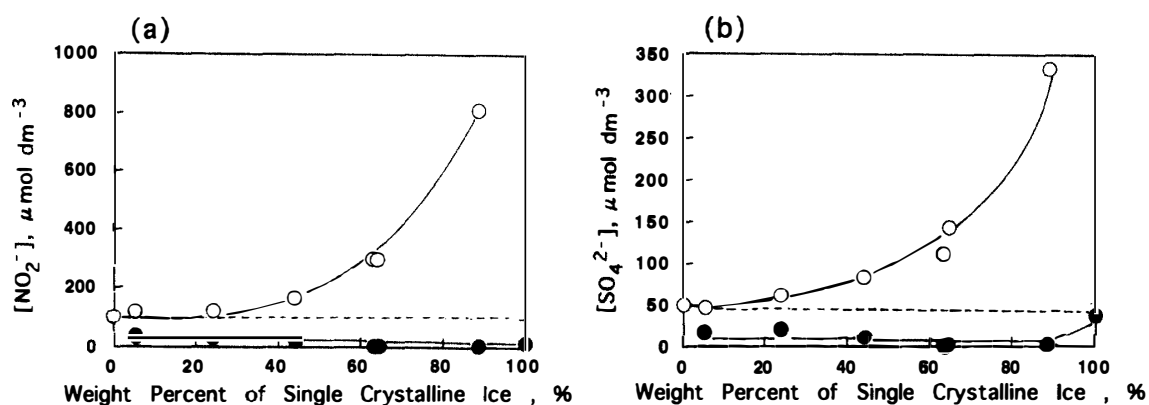

Fig. 7. Changes in concentrations of (a) nitrite and (b) sulfate ions in ice and unfrozen solution, respectively, with the progress of single crystalline ice formation in freezing method (4). $[NaNO_2]_0$: 100.0 μmol dm^{-3}, pH_0: 4.00, $[SO_4^{2-}]_0$: 50.0 μmol dm^{-3}, sample volume: 2.2 cm^3. ●: ice, ○: unfrozen solution. Each broken line means initial value, and each plot shows the data of an individual sample.

Table 3. Compositions of nitrogen species in single crystalline ice and polycrystalline ice, respectively, before freezing and after freezing.

Phase	Species	Before Freezing (nmol)	After Freezing (nmol)
Gas phase	NO_2^-		83.7
Single crystalline	NO_2^-	104.5	9.1
(Upper part)	NO_3^-	0	16.5
Polycrystalline	NO_2^-	153.7	14.7
(Lower part)	NO_3^-	0	133.1
	Total	258.2	257.1

$[NaNO_2]_0$; 100.0 μmol dm^{-3}, pH_0: 4.00, sample volume 2.7 cm^3.

Table 4.   Ion concentrations after freezing and comparisons of pH values of the sample after freezing
with those before freezing.

Solute	Freezing method	Ion concentration after freezing (μ mol dm^{-3})	pH of the sample	
			Before freezing	After freezing
NaCl	(2)	97.2 (Cl$^-$)	4.75	4.88
NaCl	(2)	94.5 (Cl$^-$)	4.50	4.60
NaCl	(2)	93.7 (Cl$^-$)	4.25	4.39
NaCl	(2)	91.9 (Cl$^-$)	4.00	4.12
NaCl	(2)	83.7 (Cl$^-$)	3.50	3.61
NaCl	(2)	94.1 (Cl$^-$)	3.00	3.00
CH$_3$COONa	(3)	84.5 (CH$_3$COO$^-$)	4.25	4.33
HCOONa	(3)	92.6 (HCOO$^-$)	4.00	4.22
NaNO$_2$	(4)	not evaluated	4.00	4.40

Initial NaCl, CH$_3$COONa, HCOONa or NaNO$_2$ concentration was 100.0 μmol dm^{-3}.
pH of the solution: adjusted by H$_2$SO$_4$ addition.
NaCl samples were allowed to freeze for 1 hour.

chloride, sodium acetate, sodium formate or sodium nitrite solution was frozen. Concentrations of chloride, acetate, formate or nitrite ion decreased, and the pH of each sample increased after freezing.

4.   Discussion

When a sample is frozen by freezing method (1), solutes are concentrated to the center of the sample, since the sample was frozen from the outside to the center. As a result, volatile solutes are confined in the sample. On the other hand when a sample is frozen by freezing method (2), solutes are concentrated into the supernatant. It is speculated that volatile solutes could escape from the surface of the sample, since the sample was frozen from bottom to top. As freezing and thawing are repeated in freezing method (2), volatile solutes are further released from the surface of the sample, and their concentrations decrease more (Table 2).

When solution is extremely concentrated by freezing in freezing methods (2), (3) and (4), a very thin unfrozen layer exists on the top surface because of depression of the freezing point. If we assume that all solutes are excluded from ice to the top surface, the sample of sub mm^3 in volume remains as unfrozen solution at $-18°C$, when the sample concentration and volume are 100.0 μmol dm^{-3} and 10.0 cm^3, respectively. Since ion concentration in this unfrozen layer becomes very high (a few mol dm^{-3}), volatilization may occur. Volatilization to the gas phase occurs gradually, and concentration of volatile solutes in the sample decreases with time during standing in the freezer (Fig. 3).

Figures 5a and 7 indicate that each anion in the sample is gradually concentrated to the unfrozen solution with the progress of ice formation. When ice is polycrystalline, some solutes are confined into the grain boundaries. Therefore some ions were observed in the ice phase (Fig. 5a). On the other hand, most other ions were excluded from the ice, so concentrations of solutes in the unfrozen solution increased with the progress of ice formation. When the ice was a single crystal, almost all of the solutes were excluded into the unfrozen solution (Fig. 7). In this case the freezing concentration effect is re-

markable.

Protons are also concentrated into unfrozen solution by the freeze-concentration effect, and the pH of the unfrozen solution decreases compared to the initial value (Fig. 6). Concentrated anions combine with concentrated protons to form volatile acid such as acetic acid, and the amount of volatile acid in the sample increases with the progress of ice formation. At the end of freezing, this volatile acid is saturated, and evaporation occurs (Fig. 5b).

When evaporation occurs, solute in the sample exists as volatile acid. Therefore in acidic solution, evaporation occurs effectively. The pH value of rain, fog or snow is often up to 4.0–4.5 (HARA, 1993). The formation of rain, fog or snow involves freezing. From Fig. 4 the decrease of solute may play an important role in the environment such as the composition of acid rain, fog or snow.

From Fig. 5b, the number of moles of acetate ion which escaped from the sample was almost equal to that detected in the gas phase. In the case of formate ion the same results were obtained. Acetate and formate did not react with any other chemicals. Therefore the decrease of acetate and formate is not associated with chemical reaction. This fact supports the above mentioned mechanism for decrease of solute, that is, volatile acid is formed in the freezing process and evaporates.

From the result of Table 3, in the polycrystalline ice most of the nitrite was changed to nitrate by acceleration of the oxidation reaction in a freezing solution (TAKENAKA et al., 1996). They reported that this reaction was mainly due to the freeze-concentration effect assisted by the freezing potential. In single crystalline ice, some of the nitrite was oxidized to nitrate, just when the sample was frozen completely, because most solutes were excluded from ice and concentrated into the unfrozen solution (TAKENAKA et al., 1996). However, most nitrite in the single crystalline ice was lost and detected in the gas phase. This result is consistent with the above mentioned mechanism.

When acid escapes from a sample, the pH of the sample increases. As shown in Table 4, it is speculated that evaporation of hydrochloric, acetic, formic or nitrous acid which is formed by combining chloride, acetate, formate or nitrite ion with proton causes the increase of pH of the solution after the sample is frozen and thawed.

5. Conclusions

When dilute volatile acidic solution is frozen, solutes are excluded from ice and concentrated unfrozen solution. Concentrated anions combine with concentrated protons to form volatile acid without reaction with other chemicals. Therefore it is considered that the decrease of various solutes is mainly due to the freeze-concentration effect followed by evaporation of acid to the gas phase. It is said that volatilization as hydrochloric acid gas to the gas phase is due to non-sea-salt sulfate incorporated in aerosol, rain, fog water, ice and snow (GUNDEL et al., 1994). The decrease and volatilization by freezing may play an important role in determining the compositions of rain, fog water, ice and snow, because freezing is a normal process. Therefore, it is also required to clarify how this decrease and evaporation occurs in the environment.

References

Bronsteyn, V.L. and Chernov, A.A. (1991): Freezing potentials arising on solidification of dilute aqueous solutions of electrolytes. J. Cryst. Growth, **112**, 129–145.

Fennema, O. (1975): Reaction kinetics in partially frozen aqueous systems. Water Relations of Foods, ed. by R.G. Duckworth. London, Academic Press, 539–556.

Finnegan, W.G., Pitter, R.L. and Young, L.G. (1991): Preliminary study of coupled oxidation-reduction reactions of included ions in growing ice crystals. Atmos. Environ., **25A**, 2531–2534.

Grant, N.H. and Alburn, H.E. (1965): Fast reactions of ascorbic acid and hydrogen peroxide in ice, a presumptive environment. Science, **150**, 1589–1590.

Gundel, L.A, Benner, W.H. and Hansen, A.D.A. (1994): Chemical composition of fog water and interstitial aerosol in Berkeley, California. Atmos. Environ., **28**, 2715–2525.

Hara, H. (1993): Acid deposition chemistry in Japan. Bull. Inst. Public Health, **42**, 426–437.

Hatley, R.H.M., Frank, F., Day, H. and Byth, B. (1986): Subzero-temperature preservation of reactive fluids in the undercooled state. I. The reduction of potassium ferricyanide by potassium cyanide. Biophys. Chem., **24**, 41–46.

Kim, Y. J. and Sindo, K. (1989): Thermocapillary convection in zone-melting crystal growth — An open-boat physical simulation. J. Cryst. Growth, **98**, 637–645.

Lodge, J.P., Baker, M.L. and Pierrard, J.M. (1956): Observations on ion separation in dilute solutions by freezing. J. Chem. Phys., **24**, 716–719.

Nakamura, K., Ageta, Y., Nakao, M. and Azuma, K. (1994): Hyôshô hyôsô (Dome F) ni okeru kagaku busshitsu no kyodô. The 17th Symposium on Polar Meteorology and Glaciology, Programme and Abstracts, Tokyo, Natl Inst Polar Res., 61 (in Japanese).

Takenaka, N., Ueda, A. and Maeda, Y. (1992): Acceleration of the rate of nitrite oxidation by freezing in aqueous solution. Nature, **358**, 736–738.

Takenaka, N., Ueda, A. and Maeda, Y. (1993): Acceleration of oxidation-reduction reactions in freezing solution. Proc. NIPR Symp. Polar Meteorol. Glaciol., **7**, 24–32.

Takenaka, N., Ueda, A., Daimon, T., Bandow, H., Dohmaru, T. and Maeda, Y. (1996): Acceleration mechanism of chemical reaction by freezing; The reaction of nitrous acid with dissolved oxygen. J. Phys. Chem., **100**, 13874–13884.