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Rise in the pH of an Unfrozen Solution in Ice Due to the Presence of NaCl and Promotion of Decomposition of Gallic Acids Owing to a Change in the pH

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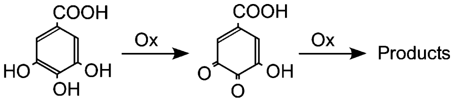
Oxidative decomposition of gallic acid occurs in alkaline solutions but hardly arises in acidic solutions. We have found that the addition of sodium chloride promotes the decomposition of gallic acid caused by freezing even under neutral and acidic conditions. Even at pH 4.5, gallic acid was decomposed by freezing in the presence of NaCl; however, in the absence of NaCl, it was hardly decomposed by freezing at pH lower than 7. Chloride ions are more easily incorporated in ice than sodium ions when the NaCl solution is frozen. The unfrozen solution in ice becomes positively charged, and as a result, protons transfer from the unfrozen solution to the ice. We measured the pH in the unfrozen solution which coexists with single-crystal ice formed from a 5 mmol dm^{-3} NaCl solution and determined the pH to be 8.6 at equilibrium with CO_2 of 380 ppm or 11.3 in the absence of CO_2 compared to pH 5.6 in the original solution. From the model calculation performed for gallic acid solution in the presence of 5 mmol dm^{-3} NaCl, it can be estimated that the amount of OH^- transferred from the ice to the solution corresponds to 1.26×10^{-5} mol dm^{-3}. The amount of OH^- transferred is concentrated into the unfrozen solution and affects the pH of the unfrozen solution. Therefore, the pH in an unfrozen gallic acid solution in ice becomes alkaline, and the decomposition of gallic acid proceeds. It is expected that other base-catalyzed reactions in weakly acidic solutions also proceed by freezing in the presence of NaCl without the need for any alkaline reagents.

Introduction

Some reactions are reported to be accelerated by freezing.[1−16] Most of them are believed to be accelerated due to freeze concentration. Furthermore, it is reported that the acceleration can be observed only in a dilute solution. The effect of freeze concentration is different depending on the kinds of ions and their concentrations. If the effects of freeze concentration for cations and for anions are different, an electric potential is generated between the ice and the unfrozen solution when an electrolyte solution is frozen.[17,18] This is called a freezing potential. The values of freezing potentials are reported to be −90 to +210 V (the sign of the potential refers to the ice).[18] The freezing potential generated is mainly relaxed not by electrochemical reactions but by the transfer of H^+ or OH^- between the ice and the unfrozen solution. Bronshteyn and Chernov reported that potassium ferricyanide at pH 10 was hydrolyzed by freezing in the presence of NaCl[19] despite the fact that potassium ferricyanide is stable at $2 < \mathrm{pH} < 12$.[3] Furthermore, Bronshteyn and Chernov showed the mechanism of pH change by freezing in detail.[19] Takenaka et al. reported that the pH decrease by freezing is an important factor in the acceleration of the reaction of nitrite with dissolved oxygen by freezing.[12] Recently, Heger et al. reported the pH change of the sample containing HF, HCl, HNO_3, H_2SO_4, and *p*-toluenesulfonic acid due to freezing by using cresol red.[20] As described above, the change in pH occurs by freezing in the presence of salts. It is theoretically possible that acidic solutions become alkaline or alkaline solutions become acidic, and the reaction proceeds by the large pH change by freezing.

Oxidative decomposition of gallic acid occurs in alkaline solutions but hardly arises in acidic solutions (eq i).[21] We have found that the addition of NaCl accelerates the decomposition of gallic acid caused by freezing at pH 4.5. We report here that the decomposition of gallic acid under acidic conditions is promoted by freezing in the presence of NaCl. Furthermore, we report the estimated pH value in the unfrozen solution in ice.



(i)

Experimental Section

All reagents, obtained from Wako Pure Chemicals, Inc., were reagent grade and used without further purification. Pure water was prepared by Milli-Q Labo using distilled water. The resistivity of the pure water was higher than 18.2 MΩ cm.

An aqueous solution mixture of gallic acid and sodium chloride in a polyethylene test tube was frozen in a coolant at −5 to −30 °C. Normally, the sample was frozen at −20 °C. The temperature was kept at the preset temperature ±0.5 °C. The pH of the sample solution was adjusted by sodium hydroxide. The pH was measured with an M-13 Horiba Co. Ltd. pH meter with a 6069-10C glass electrode, and the pH meter was calibrated with a phosphate buffer (pH 7) and phthalate buffer (pH 4) or borate buffer (pH 9). After complete freezing, the sample was thoroughly thawed, and the concentration of gallic acid was measured by a UV absorption method. The maximum absorption wavelengths of gallic acid are 212 and 258 nm. The spectrum is different depending on the pH, and therefore, the pH of the sample solution was adjusted at

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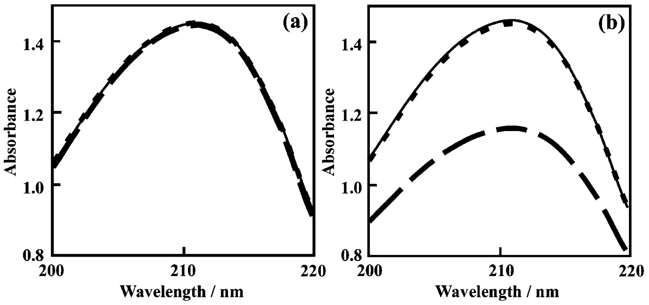

Figure 1. Spectral changes in gallic acid solutions at pH 7: (a) in the absence of NaCl, (b) in the presence of 5 mmol dm^{-3} NaCl, (solid line) initial spectrum, (dotted line) after 3 h of maintaining the solution at 20 °C, (dashed line) after five freeze−thaw cycles. The initial concentration of gallic acid was 50 μmol dm^{-3}. A period of about 12 min was required for freezing at −20 °C, while just a few minutes was required for thawing.

pH 7.5 before measurements by using NaOH or H_2SO_4, and the absorbance was measured at 212 nm. Furthermore, the absorbance of gallic acid at 212 nm does not reach zero even when the spectrum change no longer occurs, but the spectrum is the same as that obtained by the reaction of gallic acid with hydrogen peroxide. Therefore, the concentration of gallic acid was determined by the difference in the initial and final absorbances. The difference between the initial and final absorbances was 1.11 for 50 μmol dm^{-3} gallic acid. The spectrum does not have any isosbestic points, and this means the product gallic acid quinine[21] also decomposes.

Single-crystal ice formed from a 5 mmol dm^{-3} NaCl solution was grown from the bottom up in an hourglass test tube. The design of the test tube, the detailed experimental equipment, and the method have already been reported.[12] Briefly, the test tube was moved very slowly from the upper warmer zone to the lower colder zone. The temperatures of the upper part and the lower part were 282 and 264 K, respectively. The unfrozen solution remaining in the upper part of the single-crystal ice was separated, and the pH was measured at room temperature.

Results and Discussion

Figure 1 shows changes in the UV spectra of gallic acid by the reaction at pH 7. As shown in Figure 1a, without NaCl, it did not decompose in solution even after five freeze−thaw cycles. Some reactions are known to be accelerated by freezing due to freeze concentration. However, the decomposition of gallic acid does not proceed by the simple freeze concentration effect. In the presence of NaCl, gallic acid did not decompose in solution at 20 °C for 3 h as shown in Figure 1b. However, about 30% of the gallic acid decomposed with five freeze−thaw cycles in the presence of 5 mmol dm^{-3} NaCl, as shown in Figure 1b. These results indicate that both the presence of NaCl and the freezing process are the main factors of decomposition.

The decomposition of gallic acid by freezing is also promoted by the concentration of dissolved oxygen, but the decomposition cannot be prevented in the absence of oxygen. The decomposition of gallic acid could be due to oxidation by oxygen and alkaline hydrolysis. Some organic compounds are known to aggregate at higher concentrations.[22] The maximum absorption wavelengths 212 and 258 nm did not change at 10^{-6} to 10^{-2} mol dm^{-3}, and therefore, gallic acid was considered not to aggregate and change the reactivity by freeze concentration or by preceding the decomposition.

Effect of pH and the Concentration of NaCl on the Decomposition. The pH dependence of the decomposition of gallic acid was investigated. Figure 2 shows the effect of the initial pH of the sample on the decomposition of gallic acid in the presence of 5 mmol dm^{-3} NaCl. The black circles indicate the results in the presence of NaCl. At pH higher than 9, most of the gallic acid was decomposed by one freeze−thaw process. At pH lower than 7, it decomposed, and even at pH 4.5, a small amount of gallic acid decomposed. The gallic acid concentration was about 1/3 at pH$_0$ 4.5 (the subscript "0" indicates the initial condition) after 50 freeze−thaw cycles as shown in Figure 3. In the solution, gallic acid was stable for several days at pH 4.5, and furthermore, in the absence of NaCl, gallic acid did

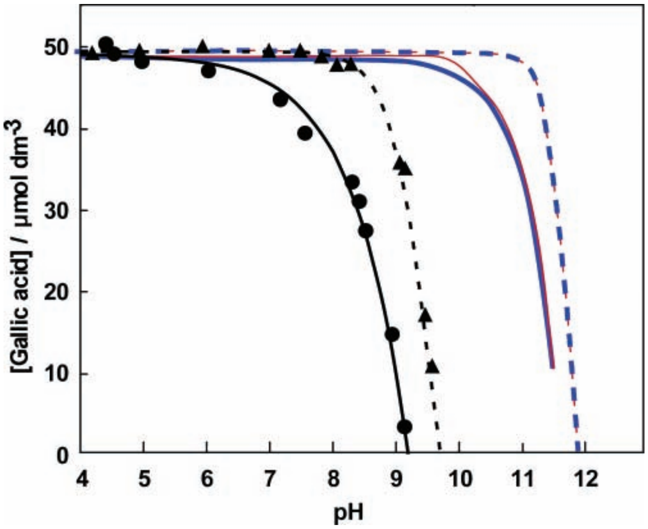

Figure 2. Effect of the initial pH on the decomposition of gallic acid by freezing in the presence of 5 mmol dm^{-3} NaCl and 3.33 mmol dm^{-3} Na_2SO_4. The initial concentration of gallic acid was 50 μmol dm^{-3}. All results were obtained after only one freeze−thaw cycle. The total ion concentration of additional salts was identical to 10 mmol dm^{-3} in both systems to obtain the same freeze concentration. The freezing temperature (−20 °C), time to freezing (ca. 12 min), temperature of the thawing hot water (ca. 60 °C), and time to thawing (ca. a few minutes) were almost the same in each experiment. Black circles and black triangles indicate the measurement results in the cases of NaCl addition and Na_2SO_4 addition, respectively. The black solid and dotted lines are fitting curves in the cases of NaCl addition and Na_2SO_4 addition, respectively. Calculated lines: (red solid narrow line) NaCl addition and a distribution coefficient, $k_{\text{gallic acid}} = 0.1$, (blue solid bold line) NaCl addition and $k_{\text{gallic acid}} = 0.001$, (red dotted narrow line) Na_2SO_4 addition and $k_{\text{gallic acid}} = 0.1$, (blue dotted bold line) Na_2SO_4 addition and $k_{\text{gallic acid}} = 0.001$. See the text for the other conditions of the calculation.

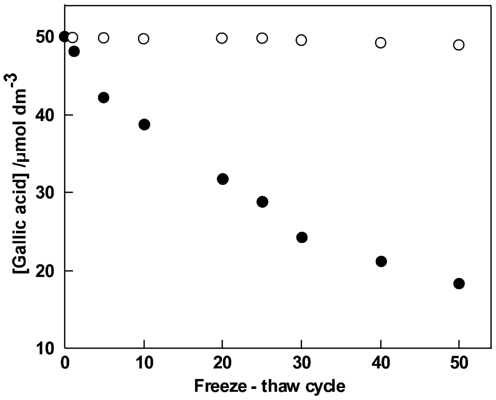

Figure 3. Effects of repeated freeze−thaw cycles: (○) in the absence of NaCl, (●) in the presence of 5 mmol dm^{-3} NaCl. The initial concentration of gallic acid was 50 μmol dm^{-3}. The pH$_0$ was 4.50. A period of about 12 min was required for freezing at −20 °C, and just a few minutes for thawing.

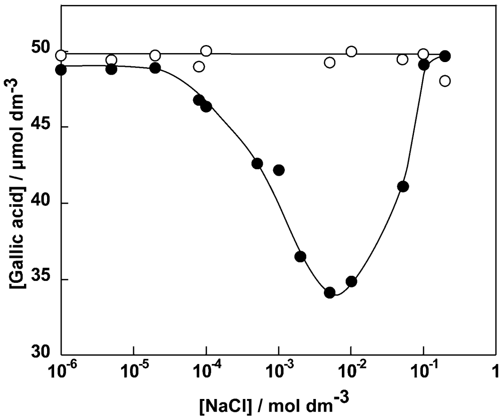

Figure 4. Effect of the NaCl concentration on the decomposition of gallic acid with freezing at pH 7: (○) after 1 h in solution at 20 °C, (●) after five freeze−thaw cycles. The initial concentration of gallic acid was 50 μmol dm^{-3}. A period of about 12 min was required for freezing at −20 °C, while just a few minutes was required for thawing.

not decompose after 50 freeze−thaw cycles. These results also show that the presence of NaCl plays a very important role in the decomposition.

Figure 4 shows the effects of the concentration of NaCl on the decomposition of gallic acid. In the solution, the decomposition of gallic acid does not proceed at any NaCl concentration. It is apparent that only the presence of NaCl has no effect on the decomposition of gallic acid. Both the presence of NaCl and freezing are required for the decomposition of gallic acid. With freezing, it was observed that, in the presence of NaCl, gallic acid decomposed. The maximum decomposition was observed at 5 mmol dm^{-3} NaCl. It was also observed that, even in the presence of several μmol dm^{-3} NaCl, gallic acid decomposed with freezing. The reason the decomposition decreased at higher NaCl concentrations will be explained later.

Change in pH in the Unfrozen Solution by Freezing. The acceleration of the reaction by freezing is mainly due to the freeze concentration, as described above. The pH change can also increase (or decrease) the reaction rates in the unfrozen solution in ice. The pH of the aqueous solution is determined by the simple charge balance relationship

$$[\mathrm{H}^+] + \sum[\text{cation}] = K_\mathrm{w}/[\mathrm{H}^+] + \sum[\text{carbonate ions}] + \sum[\text{anion}] \quad \text{(ii)}$$

The units are equiv dm^{-3}, and K_w denotes the ion product of water. When the pH of the original solution is higher than 7, in other words, when the amounts of the cations except H$^+$ included in the unfrozen solution are more than those of the anion except OH$^-$, the pH of the unfrozen solution in ice becomes very high due to the freeze concentration effect, and vice versa. Actually, at a pH lower than 7, gallic acid does not decompose by freezing in the absence of NaCl, as shown in Figure 2. The black triangles in Figure 2 show the results of the decomposition by freezing in the case of addition of Na_2SO_4. In this case, gallic acid did not decompose at a pH lower than 7.5. The freezing potentials of NaCl are reported as a negative value (the maximum is −43 V for a 250 μmol dm^{-3} NaCl solution).[18] This means that the pH of an unfrozen solution in the presence of NaCl is expected to increase. On the other hand, the freezing potentials of Na_2SO_4 are reported at a slightly positive value (the maximum is +8 V for a 20 μmol dm^{-3} Na_2SO_4 solution).[18] This means that the pH in an unfrozen solution in the presence of Na_2SO_4 is not expected to have a significant change upon freezing. In particular, the concentration of Na_2SO_4 in Figure 2 is much higher than the concentration from which the maximum potential is obtained, and therefore, the pH change due to the freezing potential could be very small. The total ion concentrations of a 5 mmol dm^{-3} NaCl solution and a 3.33 mmol dm^{-3} Na_2SO_4 solution are the same, i.e., 10 mmol dm^{-3}; hence, the effects of freezing point depression can be expected to be almost the same. Therefore, the results for Na_2SO_4 in Figure 2 can be considered as a reference. Furthermore, the pH dependence of the decomposition in the presence of Na_2SO_4 was almost the same as that in the absence of Na_2SO_4. This result suggests that Na_2SO_4 does not effect any pH change by freezing.

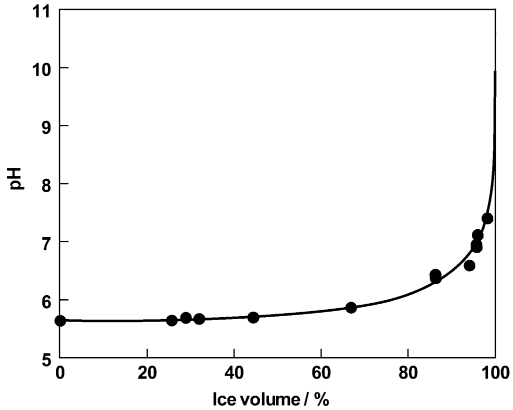

Figure 5. pH values in an unfrozen solution in a single-crystal ice formation: (●) measured pH, (solid line) calculated pH. The concentration of NaCl was 5 mmol dm^{-3}. Single-crystal ice was produced from the bottom up in a test tube. The unfrozen solution, which existed only in the upper part of the sample, was sucked out with a syringe. The temperatures of the upper warmer part and the lower colder part of the setup for single-crystal ice formation were +9 and −9 °C, respectively.

To confirm that an increase in the pH takes place by freezing in the presence of NaCl, single-crystal ice was formed from a 5 mmol dm^{-3} NaCl solution, and the pH of the unfrozen solution was measured (see the Experimental Section). The results are shown in Figure 5. The pH in the unfrozen solution increased as ice formed. This is due to the fact that the chloride ion is more highly incorporated into the crystal than the sodium ion. By using the experimental pH values, the difference between the concentrations of Cl$^-$ and Na$^+$ can be determined. The concentration of carbonate ions is assumed to be in equilibrium with 380 ppm CO_2. The amounts of compounds incorporated in ice are proportional to the concentrations of the compounds. For simplicity, the distribution coefficients, k, ($[\mathrm{X}]_{\mathrm{ice}}/[\mathrm{X}]_{\text{unfrozen solution}}$) of all compounds are independent of the concentration. The concentration in the unfrozen solution, C_t, is expressed as

$$C_\mathrm{t} = C_0(V_0/V_t)^{(1-k)} \quad \text{(iii)}$$

Here, C_t and C_0 indicate the concentrations in the unfrozen solution and initial solution, respectively, and V_t and V_0 indicate the volumes of the unfrozen solution and initial solution, respectively. The unfrozen solution exists in the upper part of the sample, and therefore, the carbonate species are equilibrated with atmospheric CO_2. The pH can be calculated from the following charge balance relationship:

$$[\mathrm{H}^+] + C_\mathrm{t}(\mathrm{Na}) = [\mathrm{OH}^-] + C_\mathrm{t}(\mathrm{Cl}) + [\mathrm{HCO_3}^-] + 2[\mathrm{CO_3}^{2-}] \quad \text{(iv)}$$

Here, C_t(Na) and C_t(Cl) indicate the concentrations of sodium ions and chloride ions, respectively, in the unfrozen solution. In the calculation of the concentrations of bicarbonate and carbonate ions, the Henry's law constant, K_H, and acid dissociation constants, K_{a1} and K_{a2}, have the following values:[23] $K_H = 0.0311 \exp[2423(1/T - 1/298)]$ M atm^{-1}, $K_{a1} = (4.3 \times 10^{-7}) \exp[-913(1/T - 1/298)]$, $K_{a2} = (4.7 \times 10^{-11}) \exp[-1760(1/T - 1/298)]$. The pH measurements were carried out at room temperature, and therefore, we calculate the pH values at 25 °C. If we adopt the reported value of the distribution coefficient of Cl^- of 2.78×10^{-3},[24] the measurement data are best fitted with the calculated curve (bold line) in Figure 5 when the distribution coefficient of the sodium ion is 2.63×10^{-3}. The correlation coefficient r^2 was 0.983. By extrapolation, the pH value of the unfrozen solution is calculated to be 8.60 when the solution is concentrated to a factor of 480, which corresponds to an ice/solution equilibrium of the NaCl aqueous solution at 264 K.[25] Furthermore, in the absence of CO_2, the pH in the unfrozen solution in ice is calculated to be 11.3 under the same conditions. Sola and Corti reported that the pH of the 0.1 mol dm^{-3} NaCl solution changed from 7.5 to 9 when about 50% of the sample was frozen with rapid freezing.[26] The presence of NaCl causes a large pH increase by freezing, and the decomposition of gallic acid by freezing occurs at a high pH.

If we assume that the promotion of the decomposition of gallic acid is due to an increase in the pH, the amounts of OH^- transferred from the ice to the solution can be calculated. From Figure 2, the two curves were best fitted by using a computer, and then, the amount of OH^- was calculated from the difference in the pH at the same amounts of gallic acid decomposed in the case of NaCl addition and that of Na_2SO_4 addition. The average amount of OH^- transferred was $(1.26 \pm 1.10) \times 10^{-5}$ mol dm^{-3}. However, in this value, the changes in the ratios of bicarbonate and carbonate concentrations and gallic acid and gallate ion concentration, etc. with pH change are not included. Then, we calculated the pH in the unfrozen solution with the distribution coefficients of ions and the charge balance relationships. We adopted distribution coefficients of chloride and sodium ions of 2.78×10^{-3} and 2.63×10^{-3} obtained from Figure 5, respectively. The distribution coefficient of sulfate was assumed to be half that of sodium ions since the freezing potential of Na_2SO_4 is nearly zero. The distribution coefficient of gallate, $k_{\text{gallate ion}}$, was altered to be suitable for both the pH values in the unfrozen solutions in ice in the case of NaCl addition and those of Na_2SO_4 addition. The concentration factor and temperature of the solution are assumed to be 785 and −16.7 °C, respectively. The reasons to adopt these values are discussed in the next section. The calculated curves are shown in Figure 2. The bold solid curve and the bold dotted curve indicate the results for $k_{\text{gallate ion}} = 0.1$ in the cases of NaCl addition and Na_2SO_4 addition, respectively. The fine solid curve and the fine dotted curve indicate the results for $k_{\text{gallate ion}} = 0.001$ in the cases of NaCl addition and Na_2SO_4 addition, respectively. An acid dissociation constant, pK_a, of gallic acid of 4.41 (25 °C) was used for the calculation,[27] and the error of the K_a value could be 50−200%. However, the final error in the calculation is considered to be negligibly small. This can be confirmed in Figure 2. The difference between the calculated lines for $k_{\text{gallate ion}} = 0.1$ and 0.001 was very small. This result indicates that the $k_{\text{gallate ion}}$ value cannot be determined from the present experimental methods and calculations. The calculated pH dependencies of the decomposition of gallic acid in the unfrozen solution in NaCl addition and Na_2SO_4 addition are not in complete agreement with each other. There are several possibilities for the inconsistency of the two curves; for example, the distribution coefficient may be concentration-dependent or may depend on the existence of other ions, or the reaction may also take place below the eutectic point of the system. We adopted −16.7 °C (the eutectic point of the sample as shown in the next section) in the calculation, but the experiment was done at −20 °C. Further investigations are required to estimate the more accurate pH value in the unfrozen solution.

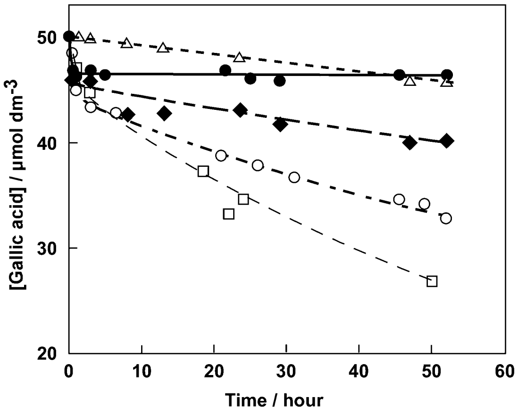

Figure 6. Change in the gallic acid concentration in long-time storage (2 days) at a constant temperature in the presence of 5 mmol dm^{-3} NaCl at pH 7: (△) solution at 20 °C, (□) freezing at −5 °C, (○) freezing at −10 °C, (◆) freezing at −20 °C, (●) freezing at −30 °C. The initial concentration of gallic acid was 50 μmol dm^{-3}. The rapid decreases in the concentration at the beginning at −30, −20, −10, and −5 °C are due to the decomposition that occurred until the whole sample was frozen. After that, the temperatures reached the set temperature.

It has also been reported that the electric potential decreases at a high concentration of electrolytes.[18] The pH change by freezing is expected to be small. This is also confirmed from results by Pincock.[7] When the total concentration is very high, the freeze concentration effect becomes small because the final equilibrium concentration at a certain temperature in the unfrozen solution is the same. This is the reason the decomposition is inhibited at higher NaCl concentrations in Figure 4.

Effect of the Eutectic Point on the Decomposition. The decomposition of gallic acid with freezing in the presence of NaCl was investigated at various temperatures, and the results are shown in Figure 6. At pH 7, gallic acid gradually decomposed in solution. At −5, −10, and −20 °C, it decomposed quickly until the sample was completely frozen, and then it decomposed further and more slowly with time. At −30 °C, rapid decomposition was apparent during freezing, but after complete freezing, the decomposition was inhibited. The eutectic point of the sample was measured to be −16.7 °C as shown in Figure 7. This result implies that the unfrozen solution cannot exist in ice at −30 °C, while it does exist at −5 and −10 °C. At temperatures higher than −16.7 °C, the concentration of gallic acid can become very high by freeze concentration, and the pH values in the unfrozen solution can also become higher by the induced freezing potential in the presence of NaCl. Therefore, gallic acid is expected to decompose continuously at temperatures higher than −16.7 °C in the presence of NaCl. On the contrary, the decomposition can be prevented by lowering the temperature below the eutectic point. However, gallic acid was decomposed slowly at −20 °C after the sample was completely frozen, despite being below the eutectic point. There are several reports about the importance of a quasi-liquid layer (QLL) in the behavior of solutes in the grain boundary.[28,29] The thickness of the QLL of pure ice has been measured by Kuroda and Lacmann.[30] They reported that the thickness of the QLL decreases with decreasing temperature and becomes very

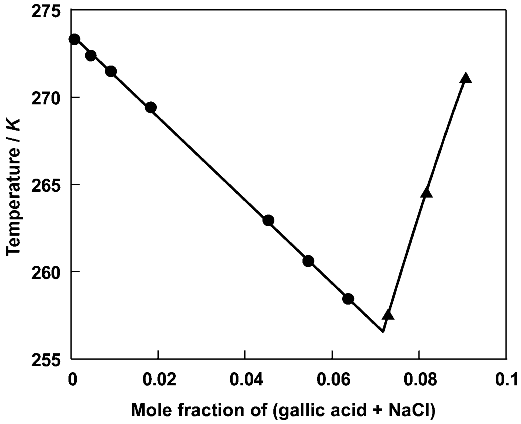

Figure 7. Solid/liquid equilibrium in the gallic acid/NaCl/H_2O system: (●) freezing point of the mixture solution, (▲) solubility. The mole ratio of gallic acid and NaCl was 1:100. The horizontal axis represents the mole fraction of gallic acid + NaCl.

thin and a rough surface of the basal plane appears below −4 °C. Until −10 °C, the QLL exists on the prism plane. Below −10 °C, the basal plane becomes smooth and the prism plane becomes rough. If the QLL plays an important role in the acceleration of the chemical reactions, dramatic changes in the reactivity could be observed. However, we did not observe any dramatic changes in the reactivity of the freeze acceleration reactions.[12] However, diffusion of solutes in ice has been reported recently even below the eutectic point.[28,31,32] It has been reported that the quisi-brine layer still exists below the eutectic point. The results of long-term preservation at −20 °C may be due to the existence of the quasi-brine layer. Therefore, the existence of the quasi-brine layer has to be considered when the decomposition of gallic acid in long-term preservation in the frozen sample is investigated. In the present study (except the results in Figures 5−7), the sample has been thawed immediately after complete freezing, and therefore, more than 90% of the gallic acid must be incorporated into the grain boundary during freezing. This can be confirmed from the result of the NaCl addition in Figure 2, because more than 90% of the gallic acid was decomposed. Most experiments were carried out at −20 °C. Even if some gallic acid that is incorporated into ice migrates from the ice to the quasi-brine layer at the grain boundary, the amounts are very small compared to that of gallic acid already decomposed into the unfrozen solution. Therefore, the contribution to the results of the short-term decomposition could be negligibly small.

In Figure 6, the reaction rate at −5 °C was faster than that at −10 °C. The pH at −10 °C could be higher than that at −5 °C, but the reaction rate at −5 °C is faster than that at −10 °C. This phenomenon has also been mentioned by Pincock,[7] and this is due to the balance between the freeze concentration effect (in this case, the effect of pH change) and the temperature effect.

Conclusion and Environmental Significance. The results reported in this paper suggest that compounds that are stable in acidic solutions but unstable in alkaline solutions can be reacted by freezing in the presence of NaCl, even if the initial solution is acidic. As shown in this paper, the freezing can be a unique method of base-catalyzed reaction under neutral or acidic conditions without addition of any alkaline reagents.

Gallic acid is sometimes used as a model compound for humic acid. Humic acid or humic substances are the main sink of organic compounds in soil and exist in river water[33] and also in rain.[34] Freezing occurs on a large percentage of the earth's surface, and NaCl exists everywhere. As shown in Figure 2, even in the presence of several μmol dm^{-3} NaCl, gallic acid decomposed with freezing. The concentration of NaCl ranges from several μmol dm^{-3} in clean rain in urban areas to several hundred μmol dm^{-3} in fog, dew, and rivers.[35,36] Hence, NaCl would have a great influence on the behavior of humic acids in the environment. Furthermore, it decomposes at pH higher than 4.5. The pH value of natural water, such as that in lakes, rivers, rain, and dew, is generally between 4 and 8; therefore, the decomposition of gallic acid as a result of freezing ordinarily takes place in the presence of NaCl. Even with a small degree of decomposition, in nature the total is significant considering that the freezing and thawing processes have been repeated a number of times.

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