Enhanced Dissolution of SO_2 into Dewwater by Forming Hydroxyalkanesulfonate

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Hydroxymethanesulfonate ion (HMSA) is an important species in dewwater and the formation of HMSA enhances the dissolution of SO_2. The HMSA stability constant calculated from the measured concentrations of free formaldehyde and S(IV) in dewwater agreed in the order with the reported value, which suggested the formation of HMSA and other S(IV) complexes.

In dewwater, various air pollutant species are dissolved and it has been reported that the concentrations of major inorganic ions are much higher than those in rainwater.[1-3] The aldehydes are important species in a polluted environment but the behavior of aldehydes in dewwater had not been studied in detail. Aldehydes are known to form S(IV) adducts in aqueous phase and the kinetics has been studied by Hoffmann and co-workers.[4-7] Munger et al.[8] reported the concentrations of S(IV), formaldehyde, and HMSA in fogwater collected in Los Angeles, in which S(IV) was in excess with respect to the Henry's law equilibrium for SO_2 and gaseous formaldehyde. This paper will provide the HMSA formation in dewwater and the effect of the formation on the SO_2 dissolution into dewwater.

Dewwater was collected from January to December in 1994 on the rooftop of a fourth-floor building in Kanagawa University in Yokohama. The collector was 100-μm-thick Teflon sheet (90 x 90 cm) mounted with double-stick tape on a 10-cm-thick slab of Styrofoam. The dewwater formed on the sheet (10 - 200 g; average value, 58 g) was collected in early morning and analyzed after the filtration of 0.45 μm membrane filter immediately. pH and S(IV) concentration of the solution were determined by a pH meter and an ion chromatograph, respectively. Five species of aldehyde (formaldehyde, acetaldehyde, glyoxal, 2-oxopropanal, and hydroxyacetaldehyde) were determined after the derivatization with 2,4-dinitrophenylhydrazine (DNPH) by a high performance liquid chromatograph (HPLC).[9] In the analysis, free aldehydes were determined with the DNPH method, while total S(IV) was determined with ion chromatography because of the HMSA decomposition in the basic eluent.

The volume-weighted mean concentrations of S(IV) and free aldehydes in dewwater were as follows: S(IV), 221 μM (1M = 1mol dm^{-3}); formaldehyde, 10 μM; acetaldehyde, 5.1 μM; glyoxal, 3.1 μM; 2-oxopropanal, 4.8 μM; hydroxyacetaldehyde, 3.7 μM, respectively. Figure 1 shows the relationship between pH and S(IV) concentrations defined as follows.

$$[S(IV)] = [H_2SO_3]_F + [HSO_3^-]_F + [SO_3^{2-}]_F + \Sigma[HASA] \quad (1)$$

where HASA is hydroxyalkanesulfonate and subscript F represents free species. The solid and dashed lines show the concentrations of S(IV) calculated from the Henry's law constants of SO_2 and the dissociation constants of sulfurous acid, when the concentration of SO_2 in the ambient air was 1 ppb and 10 ppb (1 ppb is 10^{-9} atm). The measured concentrations of S(IV) were much higher than the calculated values in the pH range 5 to 6. The concentrations of S(IV) were, however, in the level of the estimated values shown in dotted and chain lines in Figure 1, which was obtained by assuming 10 μM free formaldehyde present in dewwater. The assumed concentration of 10 μM for free formaldehyde is reasonable comparing with the measured values. It suggests that HMSA is formed in dewwater and its formation enhances the dissolution of SO_2.

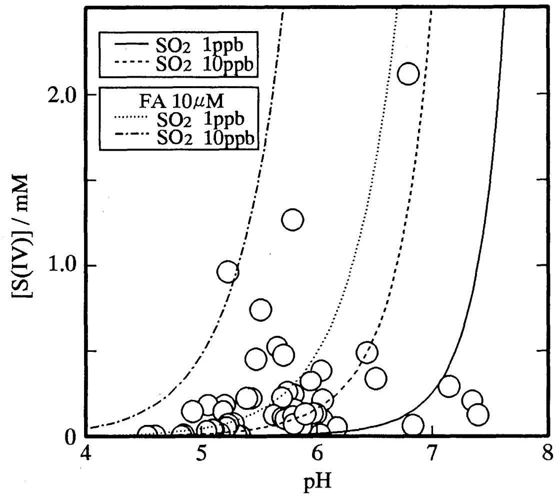

Figure 1. Relationship between pH and S(IV) concentration in dewwater. FA; formaldehyde.

HMSA was decomposed to formaldehyde and free S(IV) by the addition of 10 μL of 0.3% H_2O_2 and 10 μL of 2 M NaOH solution to 1 mL sample solution. This method was modified from that reported by Dong and Dasgupta.[10] The difference in formaldehyde concentrations before and after the decomposition corresponds to HMSA concentration. HPLC chromatograms of hydrazone derivatives of aldehydes were shown in Figure 2. The peak 2 in the chromatograms (A) and (B) corresponds to the free and total formaldehydes, respectively, and the peak height increased by the decomposition. When the standard solution of hydroxyalkanesulfonate ions was analyzed by the decomposition, the determined value was 97% for HMSA. Acetaldehyde-S(IV) adduct was also decomposed but other adducts were not fully decomposed under the condition. The volume-weighted mean concentration of HMSA in dewwater was 65 μM, ranging from 0.9 μM to 580 μM. HMSA was the third most abundant anion and its content was 14.6% of the total anions on the annual basis.

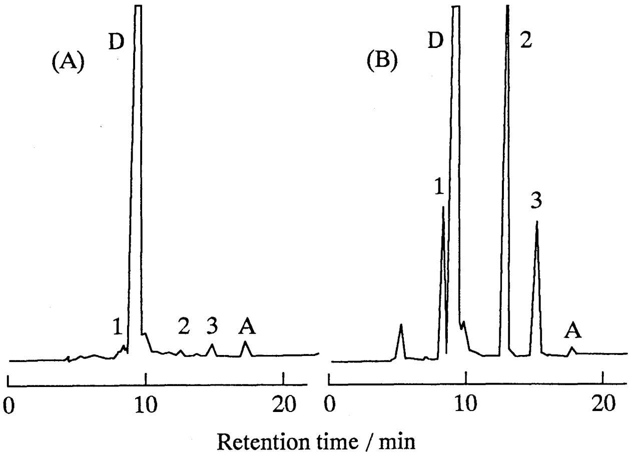

Figure 2. HPLC chromatograms for aldehydes analysis.
The chromatograms (A) and (B) were before and after decomposition of HASA. The numbers and symbols were as follows: 1; hydroxyacetaldehyde, 2; formaldehyde, 3; acetaldehyde, D; 2,4-dinitrophenylhydrazine, and A; acetone.

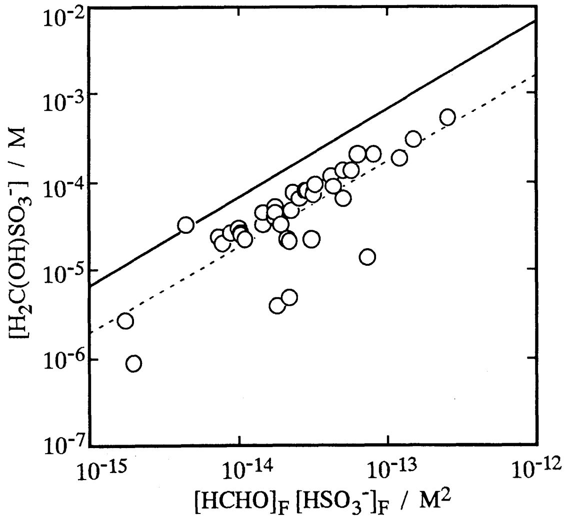

Figure 3. Formation of HMSA in dewwater.
———— , the formation constant reported.[11]
- - - - - - - , regression line for measured values.

Bisulfite ion concentration in dewwater was estimated by Eq. (1) and the following equilibrium and mass balance equations,

$$K_f = [RHC(OH)SO_3^-] / [RCHO]_F [HSO_3^-]_F \quad (2)$$

$$K_h = [RHC(OH)_2] / [RCHO]_F \quad (3)$$

$$[RCHO] = [RCHO]_F + [RHC(OH)_2] \quad (4)$$

where K_f is the formation constant of HASA and K_h is the hydration constant of aldehyde. The relationship between the product of free formaldehyde and S(IV) concentrations and HMSA concentration in dewwater was shown in Figure 3. Free S(IV) concentration in Figure 3 was obtained by calculation on the assumption that there were not only formaldehyde but also acetaldehyde, 2–oxopropanal, and hydroxyacetaldehyde, whose both formation and hydration constants were reported already,[5,6] and the adducts were formed from the aldehydes. The solid line is the calculated values from the formation constant reported by Deister et al.[11] and the dashed line is the regression line for the values measured in this study. The formation constant of HMSA was estimated to be $10^{9.31}$ (dm^3 mol^{-1}) from the regression line, while the constant reported was $10^{9.82}$ (dm^3 mol^{-1}). These constants agreed in the order but the former was 30% of the latter. The difference may be caused by the formation of S(IV) complexes of HASA other than four aldehyde adducts and the complex of metal ion, including iron and manganese, and S(IV) concentration in dewwater is much lower than the value used in the calculation. From the comparison of these constants, the free S(IV) concentration was estimated to be 12 μM, which was 5.4% of total S(IV).

The aldehydes in dewwater enhance the SO_2 dissolution by the formation of HASA. The dewwater formed on plants and structures may contain some chemical species leached from their surfaces as is distict from that formed on an inert surface, Teflon sheet. The content of sulfuric acid may increase in dewwater when the oxidation potential rises in the ambient air, because sulfuric acid is readily formed from HASA by oxidizing agents.

References

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