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# Reactive processing of formaldehyde and acetaldehyde in aqueous aerosol mimics: surface tension depression and secondary organic products

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## Abstract

The reactive uptake of carbonyl-containing volatile organic compounds (cVOCs) by aqueous atmospheric aerosols is a likely source of particulate organic material. The aqueous-phase secondary organic products of some cVOCs are surface-active. Therefore, cVOC uptake can lead to organic film formation at the gas-aerosol interface and changes in aerosol surface tension. We examined the chemical reactions of two abundant cVOCs, formaldehyde and acetaldehyde, in water and aqueous ammonium sulfate (AS) solutions mimicking tropospheric aerosols. Secondary organic products were identified using Aerosol Chemical Ionization Mass Spectrometry (Aerosol-CIMS), and changes in surface tension were monitored using pendant drop tensiometry. Hemiacetal oligomers and aldol condensation products were identified using Aerosol-CIMS. A hemiacetal sulfate ester was tentatively identified in the formaldehyde-AS system. Acetaldehyde depresses surface tension to  $65(\pm 2)$  dyn cm<sup>-1</sup> in pure water and  $62(\pm 1)$  dyn cm<sup>-1</sup> in AS solutions. Surface tension depression by formaldehyde in pure water is negligible; in AS solutions, a 9% reduction in surface tension is observed. Mixtures of these species were also studied in combination with methylglyoxal in order to evaluate the influence of cross-reactions on surface tension depression and product formation in these systems. We find that surface tension depression in the solutions containing mixed cVOCs exceeds that predicted by an additive model based on the single-species isotherms.

## 1 Introduction

Organic material is a ubiquitous component of atmospheric aerosols, making up a major fraction of fine aerosol mass, but its sources and influence on aerosol properties are still poorly constrained (Kanakidou et al., 2005; Jimenez et al., 2009). Many common organic aerosol species are surface-active (Shulman et al., 1996; Fachini et al., 1999). Surface-active molecules in aqueous solution form structures that allow

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where  $\sigma$  is surface tension,  $\Delta\rho$  is the difference in density between the solution and the gas phase, and  $g$  is acceleration due to gravity (Adamson and Gast, 1997). Solution density was measured using an analytical balance (Denver Instruments). The drops were allowed to equilibrate for 2 min before image capture. Each measurement was repeated 7 times.

Aerosol-CIMS was used to detect the organic composition of the product mixtures as described in detail previously (Sareen et al., 2010; Schwier et al., 2010). Mixtures of formaldehyde, acetaldehyde-MG, and formaldehyde-MG in water and 3.1 M AS were prepared. Total organic concentration ranged from 0.2–2 M. All the AS solutions were diluted at 24 h with Millipore water until the salt concentration was 0.2 M. The solutions were aerosolized in a stream of  $N_2$  using a constant output atomizer (TSI) and flowed through a heated 23 cm long, 1.25 cm ID PTFE tube (maintained at 135 °C) at RH > 50 % before entering the CIMS, in order to volatilize the organic species into the gas phase for detection. The time between atomization and volatilization ( $\leq 3.5$  s) is too short for detectable quantities of the expected reaction products to form, therefore the detected molecules are most likely formed in the bulk aqueous solutions. The solutions were tested in both positive and negative ion mode, using  $H_3O^+ \cdot (H_2O)_n$  and  $I^-$  as reagent ions, respectively. The applicability of this approach to the detection of acetal oligomers and aldol condensation products formed by dicarbonyls in aqueous aerosol mimics has been demonstrated previously (Sareen et al., 2010; Schwier et al., 2010). The average particle concentration was  $\sim 4 \times 10^4 \text{ cm}^{-3}$  and the volume weighted geometric mean diameter was  $414(\pm 14)$  nm.

The Pyrex vessels shielded the reaction mixtures from UV light with wavelengths <280 nm (Corning, Inc.), but the samples were not further protected from visible light. We previously showed that exposure to visible light in identical vessels does not impact chemistry in the glyoxal-AS or MG-AS reactive systems (Sareen et al., 2010; Shapiro et al., 2009).

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### 3 Results

#### 3.1 Surface tension measurements

##### 3.1.1 Single-organic mixtures

Results of the PDT experiments (Fig. 1) show that both formaldehyde and acetaldehyde depress surface tension in 3.1 M AS solution, but the formaldehyde mixture is less surface-active than that of acetaldehyde. The formaldehyde-AS solutions reach a minimum surface tension of  $71.4 \pm 0.4 \text{ dyn cm}^{-1}$  at  $0.082 \text{ mol C (kg H}_2\text{O)}^{-1}$ . This represents a 9 % reduction in surface tension from that of a 3.1 M AS solution ( $78.5 \pm 0.3 \text{ dyn cm}^{-1}$ ). The acetaldehyde-AS solutions showed more significant surface tension depression. The surface tension of the solutions reached a minimum of  $62 \pm 1 \text{ dyn cm}^{-1}$  when the acetaldehyde concentration exceeded  $0.527 \text{ mol C kg (H}_2\text{O)}^{-1}$  (20.6 % reduction compared to 3.1 M AS solution). Compared to the surface tension of the acetaldehyde in 3.1 M AS, the surface tension depression of acetaldehyde in water is less significant. The surface tension of acetaldehyde in water decreases rapidly and reaches a minimum value of  $65 \pm 2 \text{ dyn cm}^{-1}$  at  $0.89 \text{ mol C kg (H}_2\text{O)}^{-1}$ . Formaldehyde does not show any detectable surface tension depression in water in the absence of AS.

The surface tension data can be fit using the Szyszkowski-Langmuir equation:

$$\sigma = \sigma_0 - aT \ln(1 + bC) \quad (2)$$

where  $\sigma$  and  $\sigma_0$  are surface tension of the solution with and without organics,  $T$  is ambient temperature (298 K),  $C$  is total organic concentration (moles carbon per kg  $H_2O$ ), and  $a$  and  $b$  are fit parameters (Adamson and Gast, 1997). The parameters from the fits to the data in Fig. 1 are listed in Table 1.

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### 3.1.2 Binary mixtures

Surface tension results for aqueous solutions containing a mixture of two organic compounds (MG and formaldehyde or acetaldehyde) and 3.1 M AS are shown in Fig. 2. For a given total organic concentration (0.5 or 0.05 M), the surface tension decreased with increasing MG concentration. Re-plotting the data from Fig. 2 as a function of MG concentration, it is apparent that the surface tension was very similar for mixtures with the same MG concentration, regardless of the identity or amount of the other species present in the mixture (Fig. 3).

Henning and coworkers developed the following model based on the Szyszkowski-Langmuir equation to predict the surface tension of complex, nonreacting mixtures of organics (Henning et al., 2005):

$$\sigma = \sigma_0(T) - \sum_i \chi_i a_i T \ln(1 + b_i C_i) \quad (3)$$

Here,  $C_i$  is the concentration of each organic species (moles carbon per kg H<sub>2</sub>O),  $\chi_i$  is the concentration (moles carbon per kg H<sub>2</sub>O) of compound  $i$  divided by the total soluble carbon concentration in solution, and  $a_i$  and  $b_i$  are the fit parameters from the Szyszkowski-Langmuir equation for compound  $i$ . The Henning model has been shown to describe mixtures of nonreactive organics, such as succinic acid-adipic acid in inorganic salt solution, well (Henning et al., 2005). We also found that it was capable of describing surface tension depression in reactive aqueous mixtures containing MG, glyoxal, and AS (Schwier et al., 2010).

The predicted surface tension depression for the binary mixtures as calculated with the Henning model is shown in Fig. 2 as a black line, and the confidence intervals based on uncertainty in the Szyszkowski-Langmuir parameters are shown in grey. The experimentally measured surface tensions are, in general, lower than the Henning model prediction, indicating a synergistic effect between MG and acetaldehyde/formaldehyde. The error of the prediction for the mixtures of MG and acetaldehyde is between 8–24%. The error tends to increase with the concentration of MG. However, the error is less than 10% for formaldehyde-MG mixtures.

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### 3.1.3 Ternary mixtures

As shown in Fig. 4, 3.1 M AS solutions containing ternary mixtures of MG, acetaldehyde and formaldehyde also exhibit surface tension depression lower than that predicted by the Henning model. For the ternary mixture experiments, the molar ratio of acetaldehyde to formaldehyde was either 1:3 (Fig. 4a and b) or 1:1 (Fig. 4c and d) and the MG concentration was varied. The total organic concentration remained constant at 0.05 M. Recasting the data of Fig. 4 as a function of MG concentration shows a similar trend as what was observed for the binary mixtures; for a constant total organic concentration, MG content largely determines the surface tension, regardless of the relative amounts of acetaldehyde and formaldehyde present (Fig. 3).

## 3.2 Aerosol-CIMS characterization

The CIMS data show products of self- and cross-reactions of formaldehyde, acetaldehyde and MG in pure water and 3.1 M AS. We did not perform Aerosol-CIMS analysis on acetaldehyde-AS or acetaldehyde-H<sub>2</sub>O solutions because these systems have been characterized extensively by others (Nozière et al., 2010a; Casale et al., 2007).

### 3.2.1 Formaldehyde

The mass spectra for formaldehyde in H<sub>2</sub>O and in 3.1 M AS obtained using negative ion detection with I<sup>-</sup> as the reagent ion is shown in Fig. 5. Possible structures are shown in Table 2. The spectrum shows peaks with mass-to-charge ratios corresponding to formic acid at 81.7 (CHO<sub>2</sub><sup>-</sup>·2H<sub>2</sub>O) and 208.7 amu (I<sup>-</sup>·CH<sub>2</sub>O<sub>2</sub>·2H<sub>2</sub>O) and several peaks consistent with hemiacetal oligomers. 223.3, 291.1, and 323.5 amu are consistent with clusters of hemiacetals with I<sup>-</sup>. A small amount of formic acid impurity exists in the 37% formaldehyde aqueous stock solution (Sigma Aldrich). The peaks at 95.6, 110.4, 273.8 and 304.7 amu are consistent with clusters of ionized hemiacetals with H<sub>2</sub>O. While ionization of alcohols by I<sup>-</sup> is normally not favorable, ionized

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following ion formulas,  $C_6H_9O_6^-$  and  $C_2H_7O_6S^- \cdot H_2O$ , but the mechanisms and structures are unknown.

Note that several peaks appear at similar mass-to-charge ratios in the negative mode mass spectra of both the formaldehyde-MG and acetaldehyde-MG mixtures. MG self-reaction products are expected to be present in both systems. Beyond this, formaldehyde and acetaldehyde are structurally similar small molecules which follow similar oligomerization mechanisms alone and with MG. In several cases, peaks in the mass spectra corresponding to structurally distinct expected reaction products for each system have similar mass-to-charge ratios. For example, the formaldehyde hemiacetal 4-mer ( $I^- \cdot C_4H_{10}O_5$ ) and the acetaldehyde dimer ( $I^- \cdot C_4H_6O_3 \cdot 2H_2O$ ) are both apparent at 264 amu.

#### 4 Discussion

Both formaldehyde and acetaldehyde, and their aqueous-phase reaction products, were found to depress surface tension in AS solutions. However, surface tension depression was not observed in aqueous formaldehyde solutions containing no salt. Net surface tension depression by acetaldehyde was greater in the AS solutions than in pure water. These differences are likely due to chemical and physical effects of the salt. The salt promotes the formation of surface-active species: several of the reaction products in the AS systems identified using Aerosol-CIMS are known or expected to be surface-active, such as organosulfates (Nozière et al., 2010b) and organic acids. Salts can also alter the partitioning of these volatile yet water-soluble organic species between the gas phase and aqueous solution. Formaldehyde has a small Henry's Law constant of  $2.5 \text{ Matm}^{-1}$ , although hydration in the aqueous phase leads to an effective Henry's Law constant of  $3 \times 10^3 \text{ Matm}^{-1}$ , similar to that of MG (Seinfeld and Pandis, 1998; Betterton and Hoffmann, 1988). The effective Henry's Law constant for acetaldehyde in water at  $25^\circ\text{C}$  was measured by Betterton and Hoffmann (1988) to be  $11.4 \text{ Matm}^{-1}$ . The Henry's Law constant of formaldehyde was shown by Zhou and

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Mopper to increase slightly in aqueous solutions containing an increasing proportion of seawater (up to 100 %), but the opposite is true for acetaldehyde (Zhou and Mopper, 1990). The reaction mixtures studied here equilibrated with the gas phase for 24 h before the surface tension measurements were performed. Each pendant drop equilibrated for 2 min before image capture, after which time there was no detectable change in drop shape. Some of the organics may be lost to the gas phase during equilibration. However, the lower volatility of the aqueous-phase reaction products, especially those formed through oligomerization, leads to significant organic material remaining in the condensed phase (enough to cause surface tension depression and be detected via Aerosol-CIMS).

When formaldehyde and acetaldehyde are present in combination with MG, as would likely happen in the atmosphere, there is a synergistic effect: surface tension depression in the solutions containing mixed organics exceeds that predicted by an additive model based on the single-species isotherms. This effect could be due to the formation of more surface-active reaction products in the mixed systems. The deviation from the Henning model prediction was less than 10 % except in the case of the acetaldehyde-MG-AS mixtures. Between 21–30 % of the detected product mass was identified as cross products in the Aerosol-CIMS positive mode analysis of the acetaldehyde-MG mixtures following Schwier et al. (2010). Most of the oligomers identified in this system were aldol condensation products, which have fewer hydroxyl groups than acetal oligomers and are therefore expected to be more hydrophobic. A number of organic acid products, likely to be surface-active, were also identified in the acetaldehyde-MG-AS system.

In contrast to the MG-glyoxal system (Schwier et al., 2010), the presence of formaldehyde and/or acetaldehyde in aqueous MG-AS solutions does influence surface tension depression, in fact, to a greater extent than predicted by the Henning model. However, the results of the binary and ternary mixture experiments suggest that MG still plays a dominant role in these systems since the measured surface tension was remarkably similar in each mixture for a given MG concentration.

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The formaldehyde hemiacetal dimer ( $C_2H_6O_6S$ ) may form via the reaction of  $C_2H_6O_3$  with  $H_2SO_4$  (Deno and Newman, 1950). The equilibrium concentration of  $H_2SO_4$  in our bulk solutions (3.1 M AS, pH = 3) is small ( $2.8 \times 10^{-7}$  M). Minerath and coworkers showed that alcohol sulfate ester formation is slow under tropospheric aerosol conditions (Minerath et al., 2008). Based on our observations, assuming a maximum Aerosol-CIMS sensitivity of  $100 \text{ Hz ppt}^{-1}$  to this species (Sareen et al., 2010) we infer a concentration of  $\geq 2 \times 10^{-4}$  M in the bulk solution after 24 h of reaction. Using our experimental conditions and the kinetics of ethylene glycol sulfate esterification from Minerath et al., we predict a maximum concentration of  $7 \times 10^{-8}$  M. This suggests that either (a) the kinetics of sulfate esterification for paraformaldehyde are significantly faster than for alcohols (b)  $SO_4^{2-}$  or  $HSO_4^-$  is the active reactant, contrary to the conclusions of Deno and Newman, or (c) sulfate esterification is enhanced by atomization. See the Supplement for details of these calculations. Photochemical production of organosulfates has also been observed (Galloway et al., 2009; Nozière et al., 2010b; Perri et al., 2010). Our samples were protected from UV light by the Pyrex reaction vessels, and no significant OH source was present, so we don't expect photochemical organosulfate production to be efficient in this system.

Nitrogen-containing compounds could also be formed in these reaction mixtures due to the presence of the ammonium ion (Sareen et al., 2010; Nozière et al., 2009; Galloway et al., 2009). No unambiguous identifications of C-N containing products were made in this study, but analysis using a mass spectrometry technique with higher mass resolution could reveal their presence.

The relatively low solubility of formaldehyde and acetaldehyde in water suggests that their potential to contribute to total SOA mass is low as compared to highly soluble species such as glyoxal. This is supported by the observations of Kroll et al. (2005) that AS aerosols exposed to formaldehyde in an aerosol reaction chamber did not result in significant particle volume growth. However, formaldehyde and acetaldehyde in the gas phase could adsorb at the aerosol surface (vs. bulk aqueous absorption), and this may also impact aerosol surface tension (Donaldson and Vaida, 2006). Furthermore,

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Romakkaniemi and coworkers recently showed significant enhancement of aqueous-phase SOA production by surface-active species beyond what would be predicted based on Henry's Law due to surface-bulk partitioning (Romakkaniemi et al., 2011).

## 5 Conclusions

Two highly volatile organic compounds, formaldehyde and acetaldehyde, were found to form secondary organic products in aqueous ammonium sulfate (AS) solutions mimicking tropospheric aerosols. These species, and their aqueous-phase reaction products, lead to depressed surface tension in the aqueous solutions. This adds to the growing body of evidence that VOCs are a secondary source of surface-active organic material in aerosols.

**Supplementary material related to this article is available online at:**  
**<http://www.atmos-chem-phys-discuss.net/11/19477/2011/acpd-11-19477-2011-supplement.pdf>**

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**Table 1.** Szyszkowski-Langmuir Fit Parameters according to Eq. (2).

Mixture	$\sigma_0$ (dyn cm <sup>-1</sup> )	$a$ (dyn cm <sup>-1</sup> K <sup>-1</sup> )	$b$ (kg H <sub>2</sub> O (mol C) <sup>-1</sup> )
Methylglyoxal + 3.1 M (NH <sub>4</sub> ) <sub>2</sub> SO <sub>4</sub> (Sareen et al., 2010)	78.5	0.0185 ± 0.0008	140 ± 34
Acetaldehyde + 3.1 M (NH <sub>4</sub> ) <sub>2</sub> SO <sub>4</sub>	78.5	0.0008 ± 0.0046	9.53 ± 3.86
Formaldehyde + 3.1 M (NH <sub>4</sub> ) <sub>2</sub> SO <sub>4</sub>	78.5	0.0119 ± 0.0043	50.23 ± 44.8
Acetaldehyde + H <sub>2</sub> O	72.0	0.0037 ± 0.0011	491.64 ± 689

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**Table 2.** Proposed peak assignments for Aerosol-CIMS mass spectra with I<sup>-</sup> of atomized solutions of 0.2 M formaldehyde in 3.1 M AS.

m/z (amu) ± 1.0 amu	Ion Formula	Molecular Formula	Possible Structures	Mechanism
81.7	CHO <sub>2</sub> <sup>-</sup> ·2H <sub>2</sub> O	CH <sub>2</sub> O <sub>2</sub>		Formic Acid
95.6	C <sub>2</sub> H <sub>3</sub> O <sub>3</sub> <sup>-</sup> ·H <sub>2</sub> O	C <sub>2</sub> H <sub>6</sub> O <sub>3</sub>		n=2 hemiacetal
110.4	C <sub>2</sub> H <sub>3</sub> O <sub>3</sub> <sup>-</sup> ·2H <sub>2</sub> O	C <sub>2</sub> H <sub>4</sub> O <sub>3</sub>		n=2 hemiacetal
176.7	C <sub>6</sub> H <sub>9</sub> O <sub>6</sub> <sup>-</sup> C <sub>2</sub> H <sub>7</sub> O <sub>6</sub> S <sup>-</sup> ·H <sub>2</sub> O	C <sub>6</sub> H <sub>10</sub> O <sub>6</sub> C <sub>2</sub> H <sub>8</sub> O <sub>6</sub> S	Unknown	Unknown
193.8	C <sub>2</sub> H <sub>3</sub> O <sub>6</sub> S <sup>-</sup> ·2H <sub>2</sub> O	C <sub>2</sub> H <sub>6</sub> O <sub>6</sub> S		Hemiacetal sulfate
208.7	I <sup>-</sup> ·CH <sub>2</sub> O <sub>2</sub> ·2H <sub>2</sub> O	CH <sub>2</sub> O <sub>2</sub>		Formic Acid
223.3	I <sup>-</sup> ·C <sub>2</sub> H <sub>6</sub> O <sub>3</sub> ·H <sub>2</sub> O	C <sub>2</sub> H <sub>6</sub> O <sub>3</sub>		n=2 hemiacetal
273.8	C <sub>8</sub> H <sub>15</sub> O <sub>9</sub> <sup>-</sup> ·H <sub>2</sub> O C <sub>8</sub> H <sub>17</sub> O <sub>10</sub> <sup>-</sup>	C <sub>8</sub> H <sub>16</sub> O <sub>9</sub> C <sub>8</sub> H <sub>18</sub> O <sub>10</sub>		n=8 hemiacetal
291.1	I <sup>-</sup> ·C <sub>5</sub> H <sub>8</sub> O <sub>6</sub>	C <sub>5</sub> H <sub>8</sub> O <sub>6</sub>		n=5 hemiacetal
304.7	C <sub>9</sub> H <sub>19</sub> O <sub>10</sub> <sup>-</sup> ·H <sub>2</sub> O	C <sub>9</sub> H <sub>20</sub> O <sub>10</sub>		n=9 hemiacetal
323.5	I <sup>-</sup> ·C <sub>6</sub> H <sub>14</sub> O <sub>7</sub>	C <sub>6</sub> H <sub>14</sub> O <sub>7</sub>		n=6 hemiacetal

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**Table 3.** Proposed peak assignments 446 for Aerosol-CIMS mass spectra with I<sup>-</sup> of atomized solutions of 2 M formaldehyde/MG (1:1) in 3.1 M AS.

m/z (amu) ± 1.0 amu	Ion Formula	Molecular Formula	Possible Structures	Mechanism
172.8	I <sup>-</sup> ·CH <sub>2</sub> O <sub>2</sub>	CH <sub>2</sub> O <sub>2</sub>		Formic Acid
186.7	I <sup>-</sup> ·C <sub>3</sub> H <sub>4</sub> O <sub>2</sub>	C <sub>3</sub> H <sub>4</sub> O <sub>2</sub>		cyclic F acetal
203.5	C <sub>3</sub> H <sub>11</sub> O <sub>6</sub> <sup>-</sup> ·2H <sub>2</sub> O	C <sub>3</sub> H <sub>12</sub> O <sub>6</sub>		n=5 F hemiacetal
208.7	I <sup>-</sup> ·CH <sub>2</sub> O <sub>2</sub> ·2H <sub>2</sub> O	CH <sub>2</sub> O <sub>2</sub>		Formic Acid
216.5	I <sup>-</sup> ·C <sub>3</sub> H <sub>6</sub> O <sub>3</sub>	C <sub>3</sub> H <sub>6</sub> O <sub>3</sub>		Hydrated MG or cyclic F acetal
230.3	I <sup>-</sup> ·C <sub>3</sub> H <sub>4</sub> O <sub>4</sub>	C <sub>3</sub> H <sub>4</sub> O <sub>4</sub>		n=3 F hemiacetal
252.4	I <sup>-</sup> ·C <sub>6</sub> H <sub>6</sub> O <sub>3</sub> I <sup>-</sup> ·C <sub>3</sub> H <sub>6</sub> O <sub>7</sub> ·H <sub>2</sub> O I <sup>-</sup> ·C <sub>3</sub> H <sub>6</sub> O <sub>5</sub> ·2H <sub>2</sub> O	C <sub>6</sub> H <sub>6</sub> O <sub>3</sub> C <sub>3</sub> H <sub>6</sub> O <sub>4</sub> C <sub>3</sub> H <sub>6</sub> O <sub>5</sub>		MG aldol, n=3 F hemiacetal, Hydrated MG, or cyclic F acetal
257.4	C <sub>8</sub> H <sub>17</sub> O <sub>7</sub> <sup>-</sup>	C <sub>8</sub> H <sub>18</sub> O <sub>8</sub>		n=8 F hemiacetal
264.5	I <sup>-</sup> ·C <sub>4</sub> H <sub>10</sub> O <sub>2</sub>	C <sub>4</sub> H <sub>10</sub> O <sub>2</sub>		n=4 F hemiacetal
272.2	I <sup>-</sup> ·C <sub>6</sub> H <sub>10</sub> O <sub>4</sub> I <sup>-</sup> ·C <sub>3</sub> H <sub>6</sub> O <sub>3</sub>	C <sub>6</sub> H <sub>10</sub> O <sub>4</sub> C <sub>3</sub> H <sub>6</sub> O <sub>3</sub>		MG aldol and hemiacetal MG + 2F hemiacetal
288.1	I <sup>-</sup> ·C <sub>6</sub> H <sub>10</sub> O <sub>5</sub> I <sup>-</sup> ·C <sub>6</sub> H <sub>8</sub> O <sub>7</sub> ·H <sub>2</sub> O I <sup>-</sup> ·C <sub>6</sub> H <sub>6</sub> O <sub>5</sub> ·2H <sub>2</sub> O	C <sub>6</sub> H <sub>10</sub> O <sub>5</sub> C <sub>6</sub> H <sub>8</sub> O <sub>4</sub> C <sub>6</sub> H <sub>6</sub> O <sub>5</sub>		MG aldol and hemiacetal
314.3	I <sup>-</sup> ·C <sub>3</sub> H <sub>12</sub> O <sub>3</sub> ·2H <sub>2</sub> O	C <sub>3</sub> H <sub>12</sub> O <sub>3</sub>		MG + 2F hemiacetal
324.5	I <sup>-</sup> ·C <sub>6</sub> H <sub>14</sub> O <sub>7</sub> I <sup>-</sup> ·C <sub>6</sub> H <sub>12</sub> O <sub>9</sub> ·H <sub>2</sub> O I <sup>-</sup> ·C <sub>6</sub> H <sub>10</sub> O <sub>7</sub> ·2H <sub>2</sub> O	C <sub>6</sub> H <sub>14</sub> O <sub>7</sub> C <sub>6</sub> H <sub>12</sub> O <sub>8</sub> C <sub>6</sub> H <sub>10</sub> O <sub>9</sub>		n=6 F hemiacetal, MG hemiacetal
342.6	I <sup>-</sup> ·C <sub>6</sub> H <sub>14</sub> O <sub>7</sub> ·H <sub>2</sub> O I <sup>-</sup> ·C <sub>6</sub> H <sub>12</sub> O <sub>9</sub> ·2H <sub>2</sub> O	C <sub>6</sub> H <sub>14</sub> O <sub>7</sub> C <sub>6</sub> H <sub>12</sub> O <sub>8</sub>		n=6 F hemiacetal, MG hemiacetal

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**Table 4.** Proposed peak assignments for Aerosol-CIMS mass spectra with  $\text{H}_3\text{O}^+$  of atomized solutions of 0.5 M acetaldehyde/MG (1:1) in 3.1 M AS.

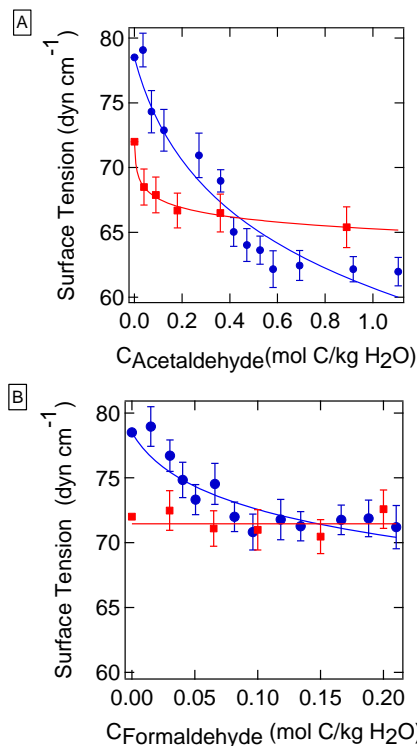
m/z (amu) $\pm$ 1.0 amu	Ion Formula	Molecular Formula	Possible Structures	Mechanism
84.4	$\text{CH}_2\text{O}_2 \cdot 2\text{H}_2\text{O}$	$\text{CH}_2\text{O}_2$		Formic Acid
88.9	$\text{C}_3\text{H}_5\text{O}_3^-$	$\text{C}_3\text{H}_5\text{O}_3$		Pyruvic Acid
	$\text{C}_3\text{H}_5\text{O}^+ \cdot \text{H}_2\text{O}$ $\text{C}_3\text{H}_6\text{O}_2^+$	$\text{C}_3\text{H}_6\text{O}$ $\text{C}_3\text{H}_6\text{O}_2$		A aldol
93.5	$\text{C}_2\text{H}_3\text{O}_3^+ \cdot \text{H}_2\text{O}$	$\text{C}_2\text{H}_3\text{O}_3$		Glyoxylic Acid
95.5	$\text{C}_2\text{H}_3\text{O}_3^+ \cdot \text{H}_2\text{O}$	$\text{C}_2\text{H}_4\text{O}_3$		Glycolic Acid
98.4	$\text{C}_2\text{H}_3\text{O}_2^+ \cdot 2\text{H}_2\text{O}$	$\text{C}_2\text{H}_4\text{O}_2$		Hydrated A
107.2	$\text{C}_3\text{H}_5\text{O}_3^+ \cdot \text{H}_2\text{O}$	$\text{C}_3\text{H}_5\text{O}_3$		Pyruvic Acid
	$\text{C}_3\text{H}_6\text{O}_2^+ \cdot \text{H}_2\text{O}$	$\text{C}_3\text{H}_6\text{O}_2$		A aldol
126.0	$\text{C}_7\text{H}_{10}\text{O}_2^+$	$\text{C}_7\text{H}_{10}\text{O}_2$		MG + 2 A aldol
134.0	$\text{C}_8\text{H}_{11}\text{O}_4^+ \cdot \text{H}_2\text{O}$	$\text{C}_8\text{H}_{10}\text{O}_4$		MG + A aldol
137.3	$\text{C}_8\text{H}_{11}\text{O}_3^+ \cdot \text{H}_2\text{O}$	$\text{C}_8\text{H}_{10}\text{O}_3$		Unknown
145.1	$\text{C}_9\text{H}_{12}\text{O}_4^+$ $\text{C}_9\text{H}_{13}\text{O}_5^+ \cdot \text{H}_2\text{O}$	$\text{C}_9\text{H}_{12}\text{O}_4$ $\text{C}_9\text{H}_{13}\text{O}_5$		MG aldol
162.9	$\text{C}_9\text{H}_{11}\text{O}_3^+$ $\text{C}_9\text{H}_{12}\text{O}_4^+ \cdot \text{H}_2\text{O}$	$\text{C}_9\text{H}_{10}\text{O}_3$ $\text{C}_9\text{H}_{10}\text{O}_4$		MG hemiacetal and aldol
164.7	$\text{C}_8\text{H}_{11}\text{O}_5^+$	$\text{C}_8\text{H}_{12}\text{O}_5$		MG aldol
	$\text{C}_8\text{H}_{11}\text{O}_4^+ \cdot \text{H}_2\text{O}$	$\text{C}_8\text{H}_{10}\text{O}_4$		MG hemiacetal and aldol
192.9	$\text{C}_{12}\text{H}_{19}\text{O}^+ \cdot \text{H}_2\text{O}$	$\text{C}_{12}\text{H}_{18}\text{O}$		6 A aldol
206.7	$\text{C}_{11}\text{H}_{17}\text{O}_4^+$	$\text{C}_{11}\text{H}_{16}\text{O}_4$		A + 3 MG aldol
235	$\text{C}_8\text{H}_{13}\text{O}_7^+$	$\text{C}_8\text{H}_{12}\text{O}_7$		MG hemiacetal
248.9	$\text{C}_{10}\text{H}_{17}\text{O}_2^+ \cdot \text{H}_2\text{O}$	$\text{C}_{10}\text{H}_{16}\text{O}_2$		IMG + 6 A aldol
289.6	$\text{C}_{10}\text{H}_{17}\text{O}^+ \cdot 2\text{H}_2\text{O}$	$\text{C}_{10}\text{H}_{16}\text{O}$		9 A aldol
297	$\text{C}_{10}\text{H}_{17}\text{O}^+ \cdot \text{H}_2\text{O}$	$\text{C}_{10}\text{H}_{16}\text{O}$		10 A Aldol

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**Table 5.** Proposed peak assignments 454 for Aerosol-CIMS mass spectra with  $\text{I}^-$  of atomized solutions of 2 M acetaldehyde/MG (1:1) in 3.1 M AS.

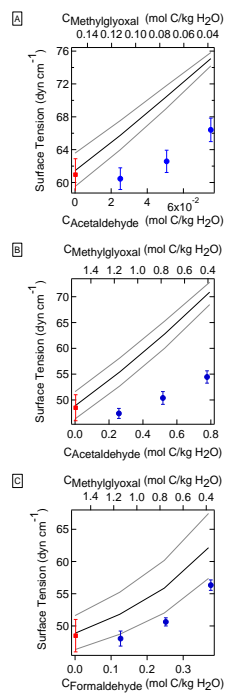
n/z (amu) $\pm$ 1.0 amu	Ion Formula	Molecular Formula	Possible Structures	Mechanism
172.7	$\text{I}^- \cdot \text{CH}_2\text{O}_2$ $\text{I}^- \cdot \text{C}_2\text{H}_4\text{O}$	$\text{CH}_2\text{O}_2$ $\text{C}_2\text{H}_4\text{O}$		Formic Acid
186.4	$\text{I}^- \cdot \text{C}_2\text{H}_4\text{O}_2$	$\text{C}_2\text{H}_4\text{O}_2$		Acetic Acid
189.6	$\text{I}^- \cdot \text{C}_2\text{H}_6\text{O}_2$	$\text{C}_2\text{H}_6\text{O}_2$		Hydrated A
194.6	$\text{C}_8\text{H}_{10}\text{O}_6^-$ $\text{C}_2\text{H}_3\text{O}_6\text{S}^- \cdot \text{H}_2\text{O}$	$\text{C}_8\text{H}_{10}\text{O}_6$ $\text{C}_2\text{H}_3\text{O}_6\text{S}$	Unknown	Unknown
208.4	$\text{I}^- \cdot \text{CH}_2\text{O}_2 \cdot 2\text{H}_2\text{O}$	$\text{CH}_2\text{O}_2$		Formic Acid
216.3	$\text{I}^- \cdot \text{C}_3\text{H}_6\text{O}_3$	$\text{C}_3\text{H}_6\text{O}_3$		Hydrated MG
224.1	$\text{I}^- \cdot \text{C}_2\text{H}_6\text{O}_2 \cdot 2\text{H}_2\text{O}$	$\text{C}_2\text{H}_6\text{O}_2$		Hydrated A
230.7	$\text{I}^- \cdot \text{C}_4\text{H}_8\text{O}_3$	$\text{C}_4\text{H}_8\text{O}_3$		A hemiacetal
	$\text{I}^- \cdot \text{C}_4\text{H}_8\text{O}_2 \cdot \text{H}_2\text{O}$	$\text{C}_4\text{H}_8\text{O}_2$		Crotonic acid
242.9	$\text{I}^- \cdot \text{C}_3\text{H}_8\text{O}_3$	$\text{C}_3\text{H}_8\text{O}_3$		MG + A aldol
256.4	$\text{I}^- \cdot \text{C}_6\text{H}_{10}\text{O}_3$	$\text{C}_6\text{H}_{10}\text{O}_3$		MG aldol
264.4	$\text{I}^- \cdot \text{C}_4\text{H}_8\text{O}_2 \cdot 2\text{H}_2\text{O}$	$\text{C}_4\text{H}_8\text{O}_2$		A hemiacetal
269.5	$\text{I}^- \cdot \text{C}_4\text{H}_{10}\text{O}_3 \cdot 2\text{H}_2\text{O}$	$\text{C}_4\text{H}_{10}\text{O}_3$		A hemiacetal
272.2	$\text{I}^- \cdot \text{C}_6\text{H}_{10}\text{O}_4$	$\text{C}_6\text{H}_{10}\text{O}_4$		MG aldol and hemiacetal
342.3	$\text{I}^- \cdot \text{C}_8\text{H}_{12}\text{O}_6 \cdot 2\text{H}_2\text{O}$	$\text{C}_8\text{H}_{12}\text{O}_6$		MG hemiacetal

19498



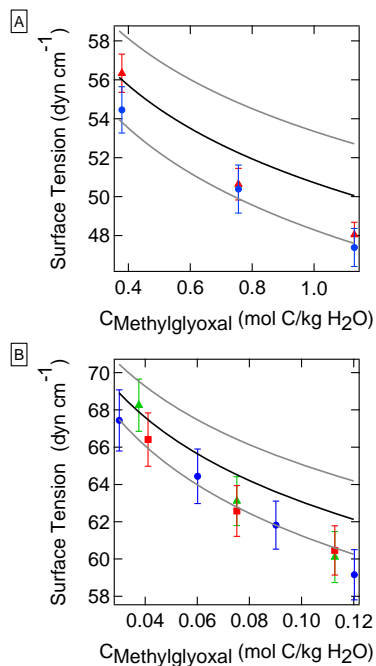
**Fig. 1.** Surface tension of solutions containing **(A)** acetaldehyde and **(B)** formaldehyde in 3.1 M AS (●) and in water (■). The curves shown are fits to the data using the Szyszkowski-Langmuir equation (Eq. 2). A linear fit is shown for the formaldehyde-water data as a guide to the eye.

19499



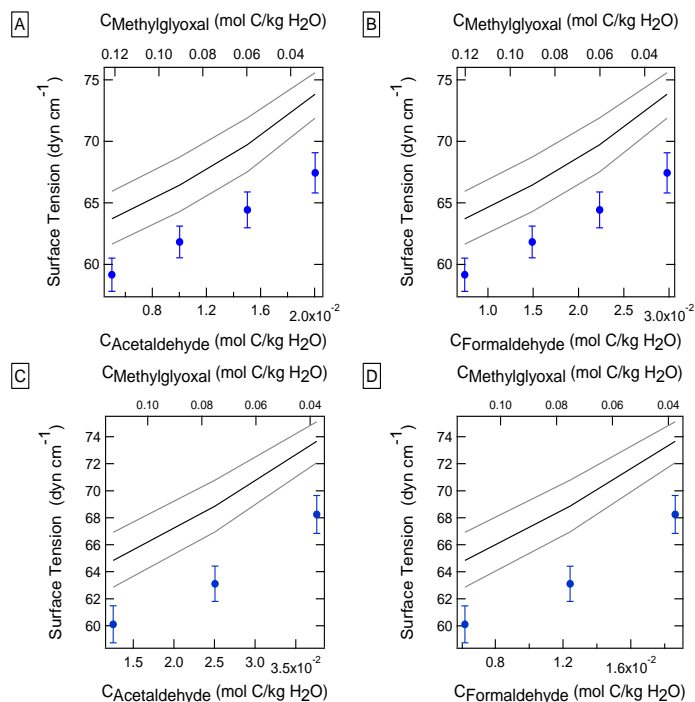
**Fig. 2.** Surface tension of binary mixtures of acetaldehyde or formaldehyde with MG in 3.1 M AS solutions. The total organic concentration was 0.05 M **(A)** or 0.5 M **(B, C)**. The black line shows Henning model predictions (Eq. 3) using the parameters listed in Table 1. The grey lines show the confidence interval of the model predictions. ■: MG in AS (based on the Szyszkowski-Langmuir equation (Eq. 2), using the parameters in Table 1). ●: Acetaldehyde **(A and B)** or Formaldehyde **(C)** with MG in 3.1 M AS solutions.

19500



**Fig. 3.** Surface tension in binary and ternary organic mixtures (Figs. 2 and 3) as a function of MG concentration. **(A)** Binary mixtures (0.5 M total organic concentration) ▲: acetaldehyde-MG, ●: formaldehyde-MG **(B)** 0.05 M total organic concentration. ▲: ternary mixture (acetaldehyde:formaldehyde = 1:1 by mole, varying MG); ●: ternary mixture (acetaldehyde:formaldehyde = 1:3 by mole, varying MG); ■: binary mixture (acetaldehyde-MG). Black curves indicate the Szyszkowski-Langmuir curve for MG in AS using the parameters in Table 1. Grey curves show the confidence intervals.

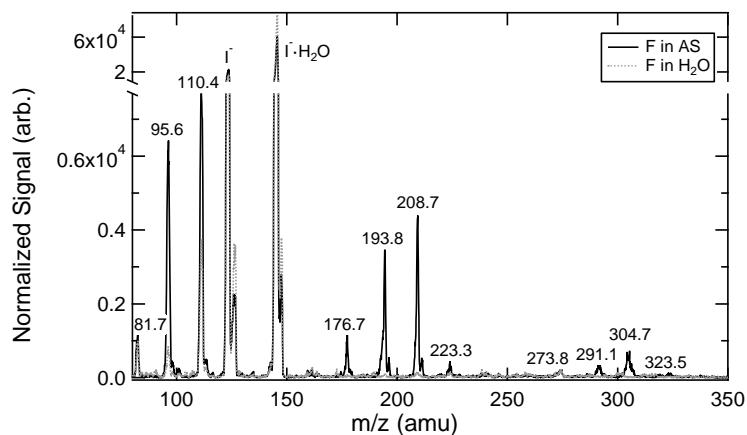
19501



**Fig. 4.** Surface tension data for ternary (acetaldehyde, formaldehyde and MG) mixtures in 3.1 M AS solutions. The molar ratios of acetaldehyde to formaldehyde are 1:3 **(A and B)** and 1:1 **(C and D)**. The total organic concentration was constant at 0.05 M. The black line shows Henning model predictions using the parameters listed in Table 1. The grey lines show the confidence interval of the predicted data.

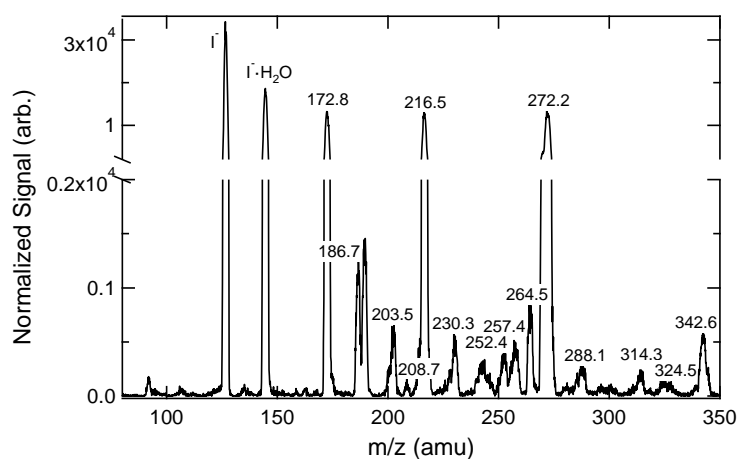
19502





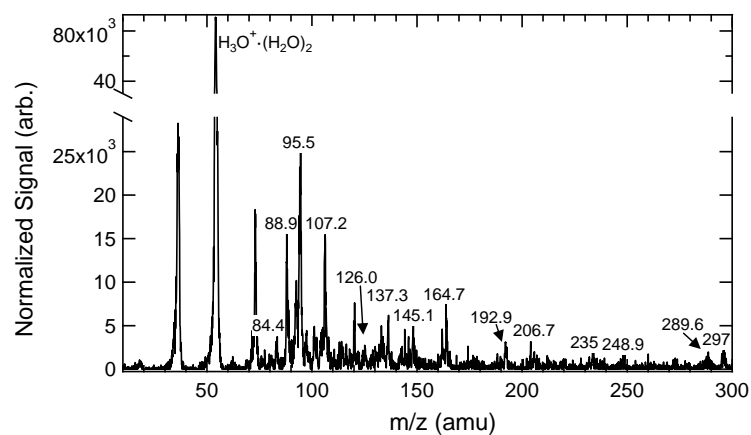
**Fig. 5.** Aerosol-CIMS spectra of atomized solutions of 0.2 M formaldehyde in 3.1 M AS and H<sub>2</sub>O. See the text for details of sample preparation and analysis. Negative-ion mass spectrum obtained using I<sup>-</sup> as the reagent ion.

19503



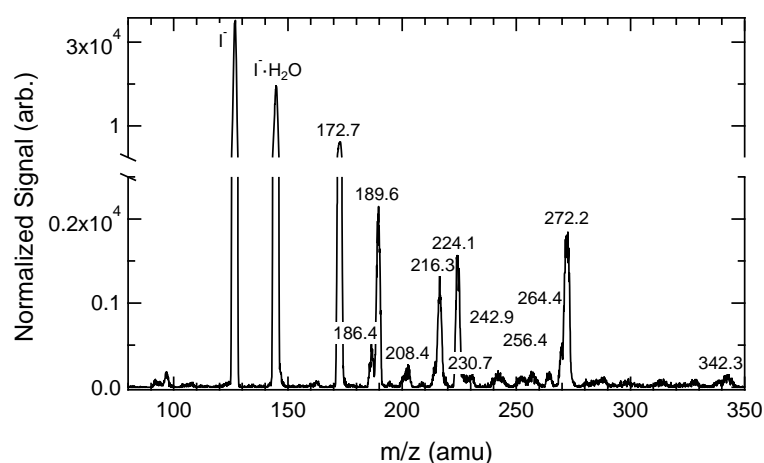
**Fig. 6.** Aerosol-CIMS spectra of atomized solutions of 2 M formaldehyde/MG (1:1) in 3.1 M AS. See the text for details of sample preparation and analysis. Negative-ion mass spectrum obtained using I<sup>-</sup> as the reagent ion.

19504



**Fig. 7.** Aerosol-CIMS spectra of atomized solutions of 0.5 M acetaldehyde/MG (1:1) in 3.1 M AS. See the text for details of sample preparation and analysis. Positive-ion mass spectrum using  $\text{H}_3\text{O}^+(\text{H}_2\text{O})_n$  as the reagent ion.

19505



**Fig. 8.** Aerosol-CIMS spectra of atomized solutions of 2 M acetaldehyde/MG (1:1) in 3.1 M AS. See the text for details of sample preparation and analysis. Negative-ion mass spectrum was obtained using  $\text{I}^-$  as the reagent ion.

19506