Supplemental Information to "Modeling the surface tension of complex, reactive organic-inorganic mixtures"

A. N. Schwier, G. A. Viglione, Z. Li, V. Faye McNeill*

Department of Chemical Engineering, Columbia University, New York, NY 10027

† Now at Laboratoire de Météorologie Physique CNRS, UMR6016, Observatoire de Physique du Globe de Clermont-Ferrand, Université Blaise Pascal,

‡ Now at University of Florida, Department of Chemical Engineering

* To whom correspondence should be addressed.

Email: vfm2103@columbia.edu; phone: (212) 854-2869; fax: (212) 854-3054

Information for determining the confidence intervals for complex mixtures

The confidence intervals for the complex mixtures were found by combining the known confidence regions for each individual organic (in either ionic or aqueous solution) at the concentrations relevant to the complex mixtures, following error propagation methods.

The Schwier2010 model confidence intervals are described by,

$$\Delta^{CI}_{Schwier\,2010} = \sqrt{\sum_{i=1}^{n} (\Delta^{CI}_{i}(C_i))^2} \qquad \text{(S1)}$$

where $\Delta^{CI}_{Schwier}$ is the confidence interval of the complex mixture and $\Delta^{CI}_{i}(C_i)$ is the confidence interval of the individual species *i* at the given species' carbon concentration.

The Henning model confidence intervals are described by,

$$\Delta^{CI}_{Henning} = \sqrt{\sum_{i=1}^{n} (\psi_i \Delta^{CI}_{i}(C))^2} \qquad \text{(S2)}$$

where $\Delta^{CI}_{Henning}$ is the confidence interval of the complex mixture, $\psi_i = (C_i\ C^{-1})$ and $\Delta^{CI}_{i}(C)$ is the confidence interval of the individual species *i* at the total organic carbon concentration.

Table S1. Fit parameters for all species in Millipore H_2O and in 3.1 M $(NH_4)_2SO_4$ at 25°C. These values were found using Eq. (1).

Solution	σ_o [+]	a (dyn cm^{-1} K^{-1})	b (kg H_2O (mol C)$^{-1}$)
[*]Acetaldehyde	72.5	$0.003 \pm 2.1\times10^{-3}$	1281 ± 4450
[*]Acetaldehyde in 3.1 M $(NH_4)_2SO_4$	78.5	$0.025 \pm 4.6\times10^{-3}$	9.51 ± 3.86
[*]Formaldehyde	72.5	$0.0007 \pm 3.6\times10^{-3}$	$2626 \pm 7.9\times10^{4}$
[*]Formaldehyde in 3.1 M $(NH_4)_2SO_4$	78.5	$0.012 \pm 4.8\times10^{-3}$	51.2 ± 45.8
Glyoxal	72.5	$0.001 \pm 4.8\times10^{-3}$	$753 \pm 2.7\times10^{4}$
Glyoxal in 3.1 M $(NH_4)_2SO_4$	78.5	0.009 ± 14	-0.012 ± 19
Methylglyoxal	72.5	$0.025 \pm 3.6\times10^{-3}$	2.99 ± 1.25
[**]Methylglyoxal in 3.1 M $(NH_4)_2SO_4$	78.5	$0.018 \pm 8\times10^{-4}$	140 ± 34
Alanine	72.5	$0.014 \pm 2.7\times10^{-2}$	5.99 ± 17.4
Alanine in 3.1 M $(NH_4)_2SO_4$	78.5	$0.0004 \pm 2.4\times10^{-2}$	3.5 ± 273
Serine	72.5	$0.004 \pm 5.6\times10^{-3}$	$294 \pm 1.58\times10^{3}$
Serine in 3.1 M $(NH_4)_2SO_4$	78.5	$0.002 \pm 1.7\times10^{-3}$	$1393 \pm 8.01\times10^{3}$
Glycine	72.5	0.045 ± 0.11	2.97 ± 9.09
Glycine in 3.1 M $(NH_4)_2SO_4$	78.5	$-0.002 \pm 7.1\times10^{-2}$	0.83 ± 47
Leucine	72.5	$0.013 \pm 9\times10^{-3}$	13.72 ± 18.5
Leucine in 3.1 M $(NH_4)_2SO_4$	78.5	$0.033 \pm 8.5\times10^{-3}$	32.71 ± 14.8
‡Oxalic Acid	72.5	$0.003 \pm 5\times10^{-4}$	6.91 ± 2.82
Oxalic Acid in 3.1 M $(NH_4)_2SO_4$	78.5	$0.013 \pm 2.4\times10^{-2}$	1.06 ± 2.91
‡Succinic Acid	72.5	$0.010 \pm 7.4\times10^{-4}$	2.51 ± 0.39
Succinic Acid in 3.1 M $(NH_4)_2SO_4$	78.5	$0.035 \pm 2.2\times10^{-2}$	0.75 ± 0.75

[+] The surface tension of $(NH_4)_2SO_4$ was taken from the International Critical Tables (Washburn, 2003).
[*]Previously published in Li et al. (2011); [**]Previously published in Sareen et al. (2010)
‡Calculated from surface tension data from Hyvärinen et al. (2006)

Table S2. k values calculated for all organics in 3.1 M $(NH_4)_2SO_4$ using Eqn. (5).

Organic	k
Acetaldehyde	-0.36 ± 0.02
Methylglyoxal	-2.34 ± 0.05
Alanine	1.04 ± 0.18
Serine	0.06 ± 0.06
Glycine	3.98 ± 0.26
Leucine	-4.63 ± 0.13
Oxalic Acid	-0.29 ± 0.09
Succinic Acid	-0.92 ± 0.10
Formaldehyde	-0.31 ± 0.02
Glyoxal	0.07 ± 0.04

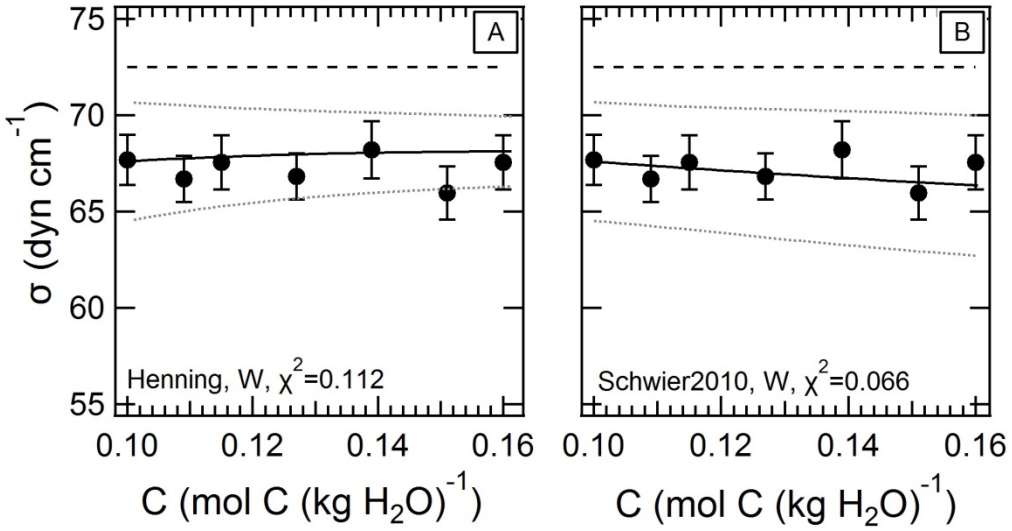

Figure S1. 0.05 M acetaldehyde with varying amounts of alanine in Millipore H_2O. (A) and (B) are the Henning semi-empirical model (Eq. 3) and the Schwier2010 semi-empirical model (Eq. 4) with water fit parameters (W), respectively. In all figures, the black dots represent the experimental data, the black line is the semi-empirical model result, and the gray lines show the 95% confidence interval of the model result.

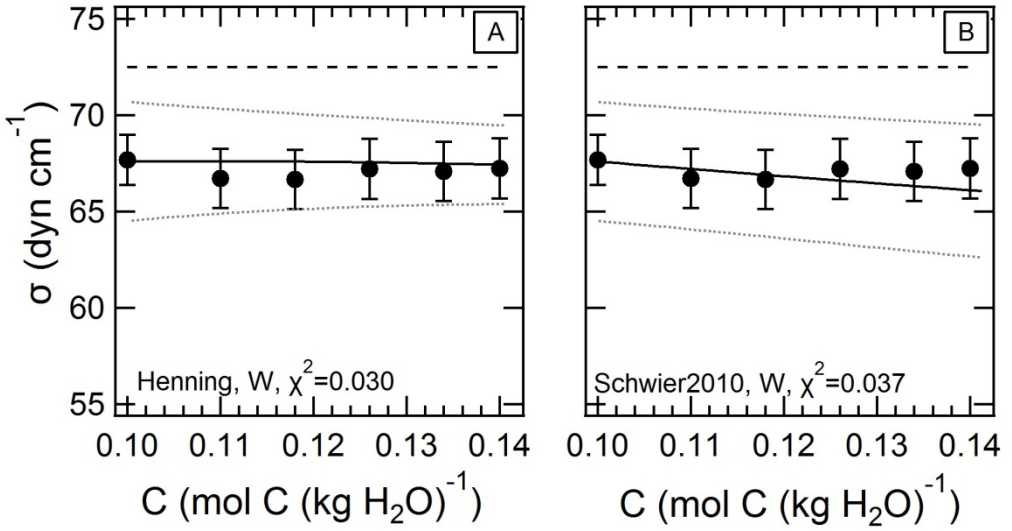

Figure S2. 0.05 M acetaldehyde with varying amounts of glycine in Millipore H_2O. (A) and (B) are the Henning semi-empirical model (Eq. 3) and the Schwier2010 semi-empirical model (Eq. 4) with water fit parameters (W), respectively.

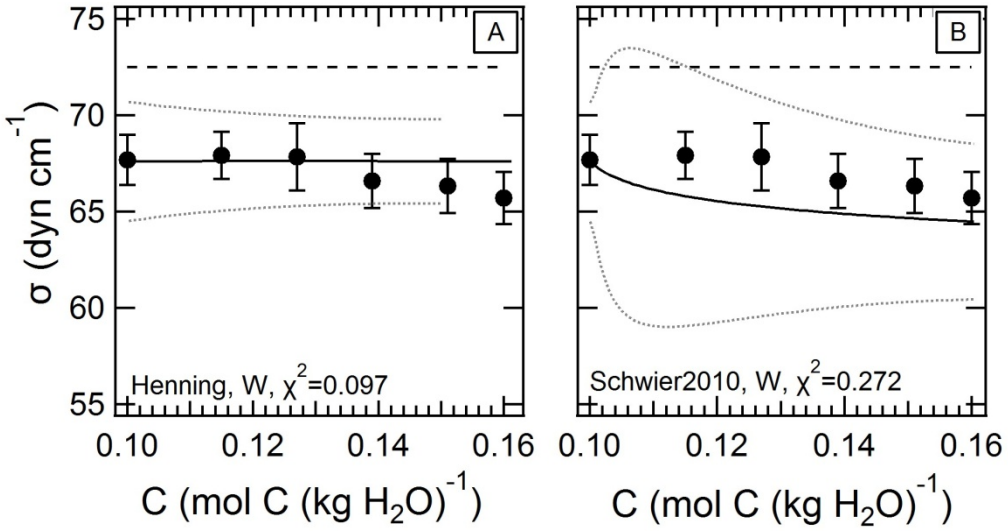

Figure S3. 0.05 M acetaldehyde and varying amounts of serine in Millipore H_2O. (A) and (B) are the Henning semi-empirical model (Eq. 3) and the Schwier2010 semi-empirical model (Eq. 4) with water fit parameters (W), respectively. The abbreviated confidence interval in (A) is due to the lack of serine surface tension data at high enough organic concentrations (>0.15m).

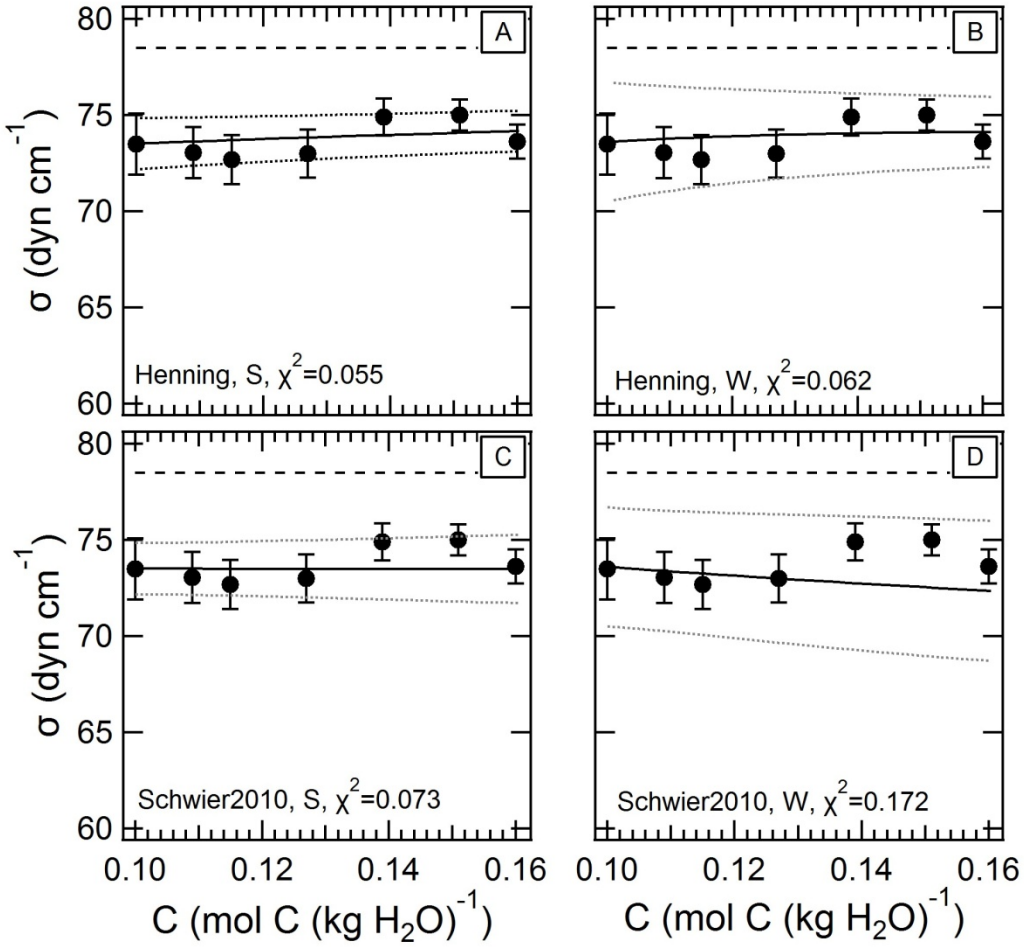

Figure S4. 0.05 M acetaldehyde with varying amounts of alanine in 3.1 M $(NH_4)_2SO_4$. (A) and (C) are the Henning semi-empirical model and Schwier2010 semi-empirical model with $(NH_4)_2SO_4$ fit parameters (S), respectively; (B) and (D) are the same with water fit parameters (W), respectively.

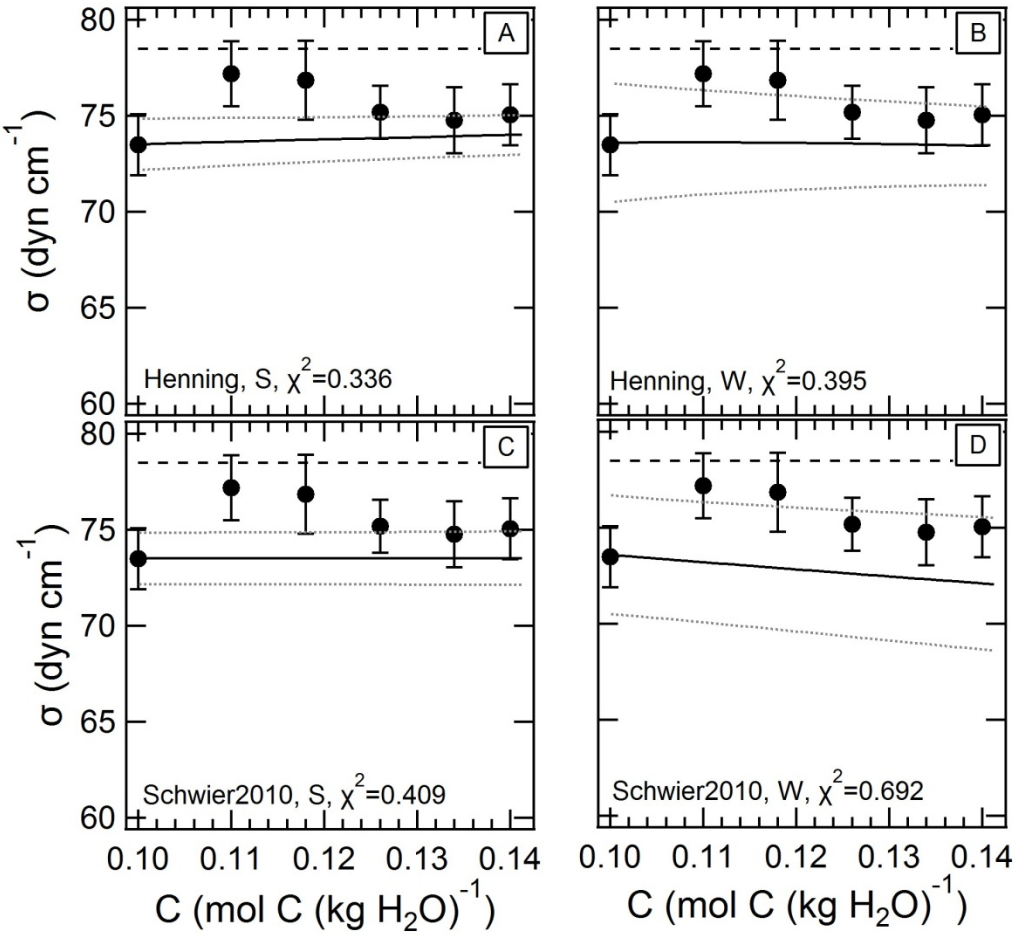

Figure S5. 0.05 M acetaldehyde with varying amounts of glycine in 3.1 M $(NH_4)_2SO_4$. (A) and (C) are the Henning semi-empirical model and Schwier2010 semi-empirical model with $(NH_4)_2SO_4$ fit parameters (S), respectively; (B) and (D) are the same with water fit parameters (W), respectively.

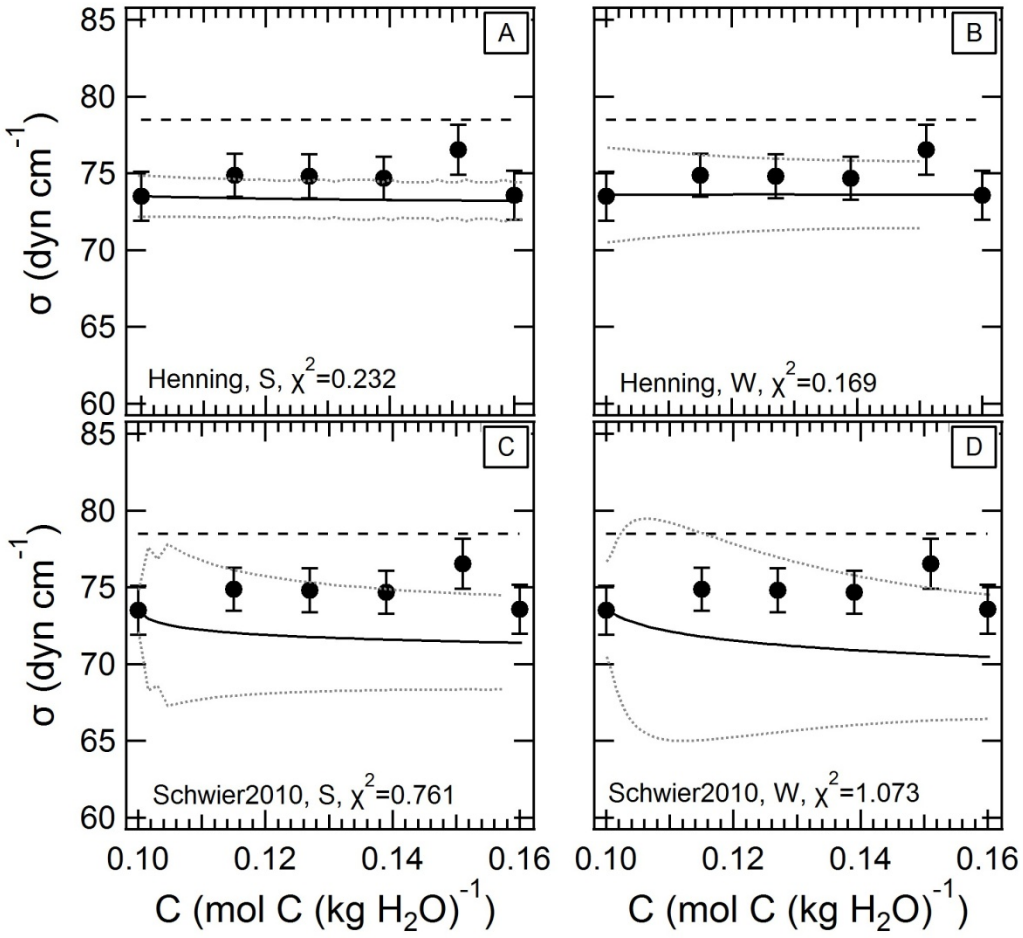

Figure S6. 0.05 M acetaldehyde and varying amounts of serine in 3.1 M $(NH_4)_2SO_4$. (A) and (C) are the Henning semi-empirical model and Schwier2010 semi-empirical model with $(NH_4)_2SO_4$ fit parameters (S), respectively; (B) and (D) are the same with water fit parameters (W), respectively. The abbreviated confidence interval in (B) is due to the lack of serine surface tension data at high enough organic concentrations (>0.15m).

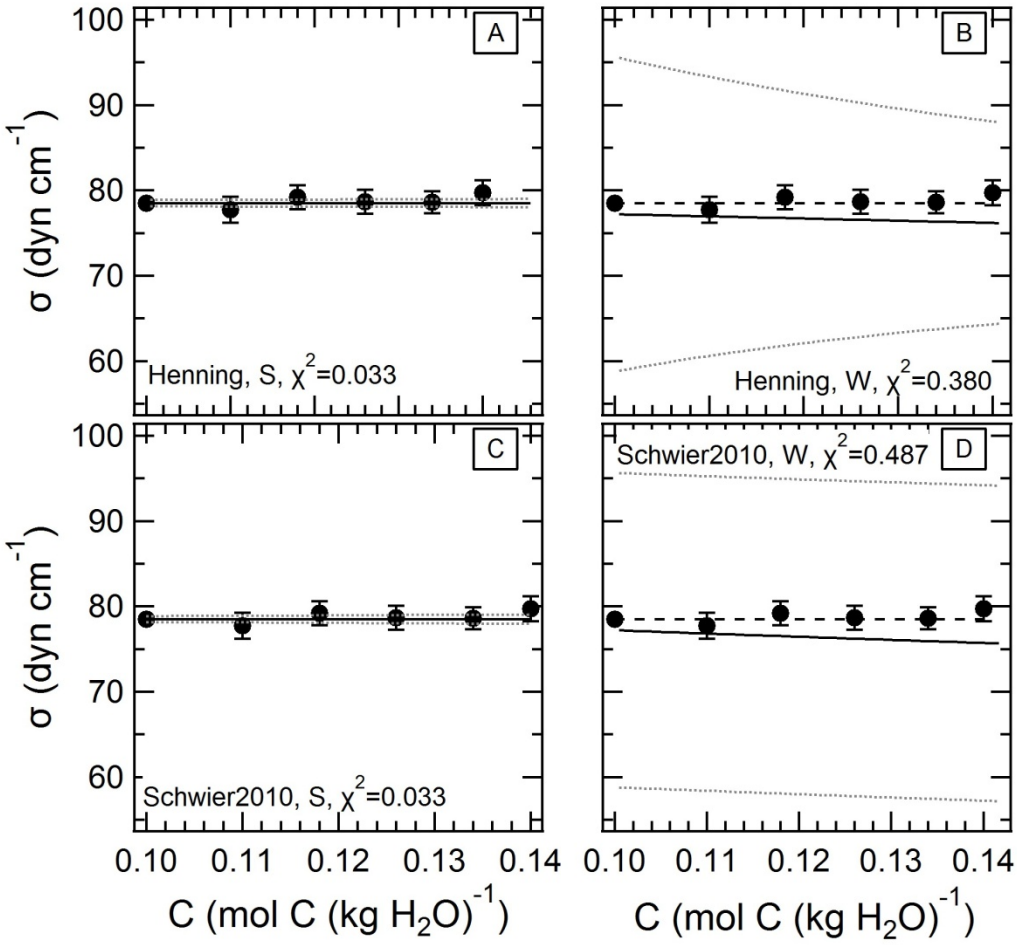

Figure S7. 0.05 M glyoxal and varying amounts of glycine in 3.1 M $(NH_4)_2SO_4$. (A) and (C) are the Henning semi-empirical model and Schwier2010 semi-empirical model with $(NH_4)_2SO_4$ fit parameters (S), respectively; (B) and (D) are the same with water fit parameters (W), respectively.

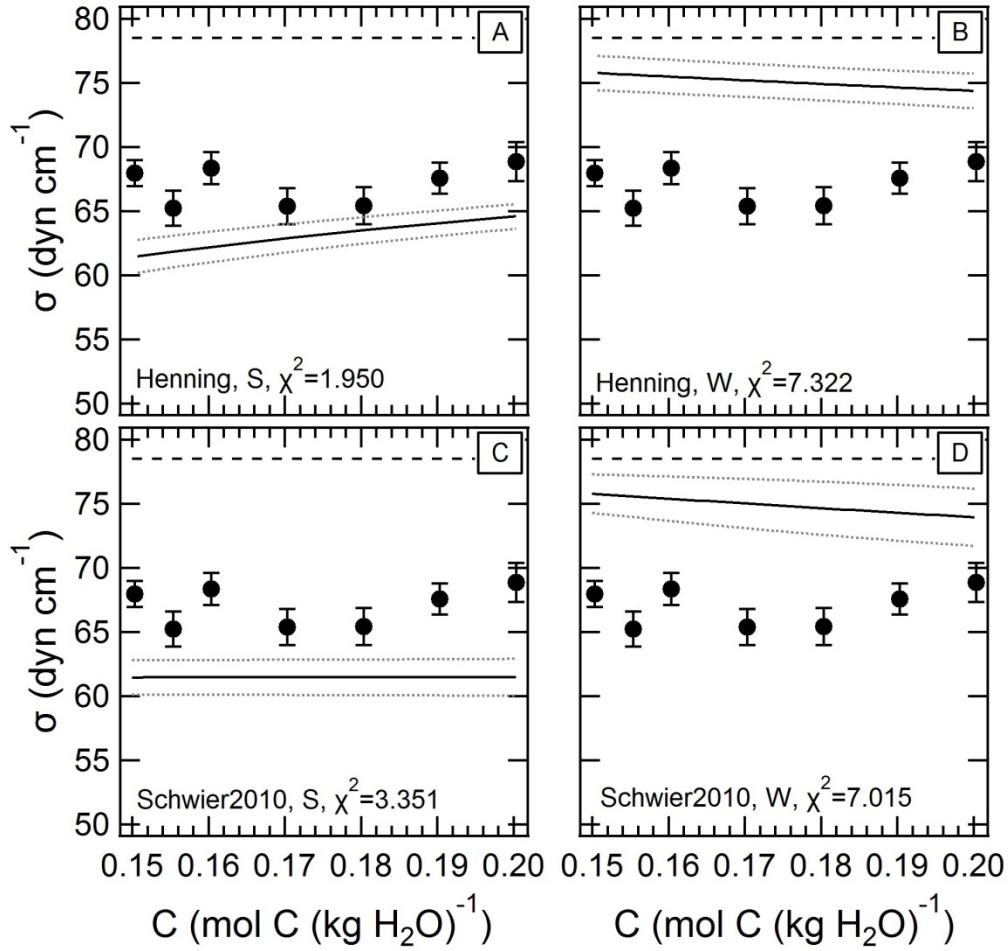

Figure S8. 0.05 M methylglyoxal and varying amounts of glycine in 3.1 M $(NH_4)_2SO_4$. (A) and (C) are the Henning semi-empirical model and Schwier2010 semi-empirical model with $(NH_4)_2SO_4$ fit parameters (S), respectively; (B) and (D) are the same with water fit parameters (W), respectively.

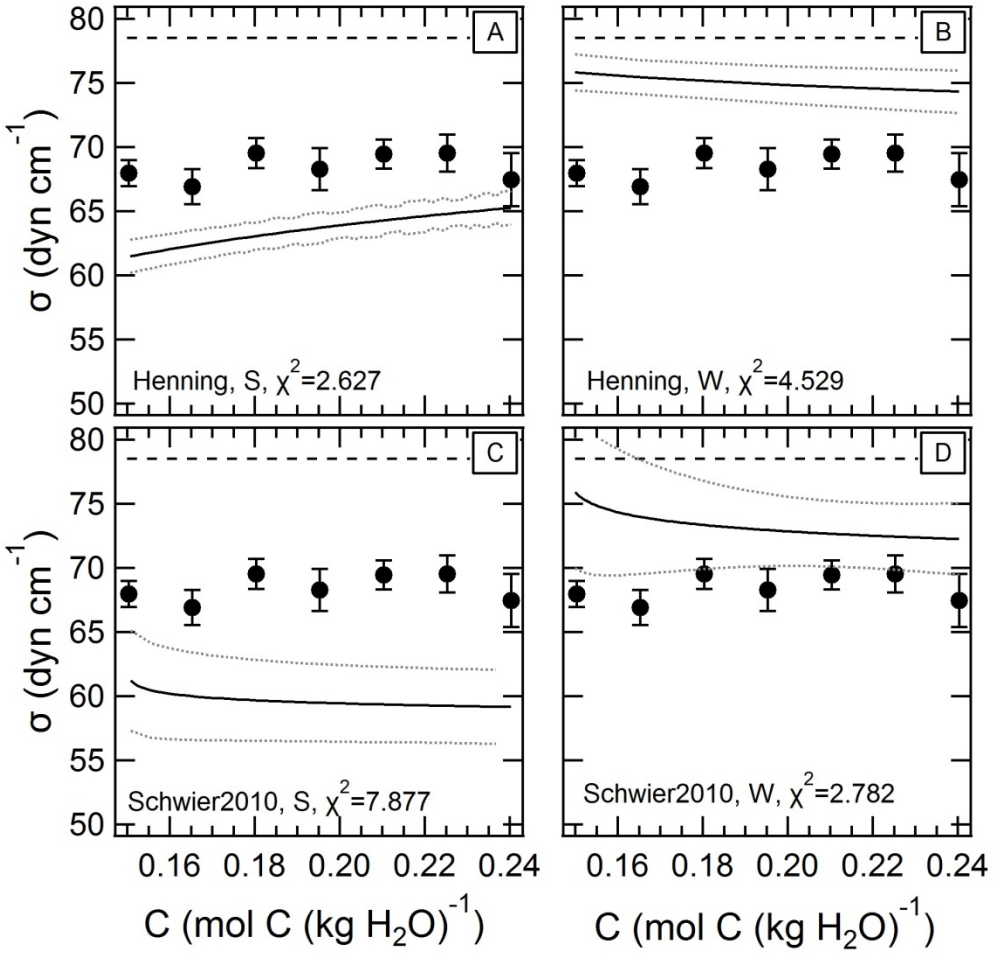

Figure S9. 0.05 M methylglyoxal and varying amounts of serine in 3.1 M $(NH_4)_2SO_4$. (A) and (C) are the Henning semi-empirical model and Schwier2010 semi-empirical model with $(NH_4)_2SO_4$ fit parameters (S), respectively; (B) and (D) are the same with water fit parameters (W), respectively. The average confidence interval value of serine at lower concentrations (0-0.15 m) was used for the confidence interval contribution from serine in (B) due to a lack of experimental data at high serine concentrations (>0.15m).

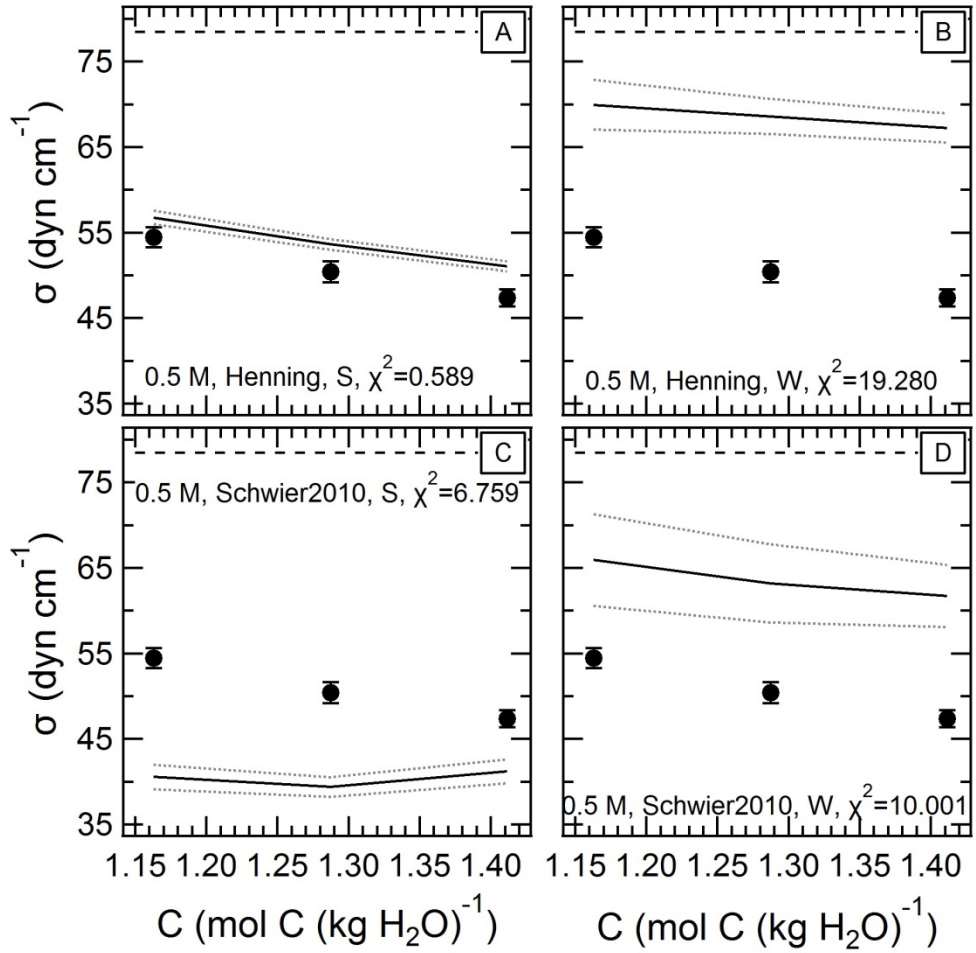

Figure S10. 0.5 M total organic, varying ratio of acetaldehyde and methylglyoxal in 3.1 M $(NH_4)_2SO_4$. (A) and (C) are the Henning semi-empirical model and Schwier2010 semi-empirical model with $(NH_4)_2SO_4$ fit parameters (S), respectively; (B) and (D) are the same with water fit parameters (W), respectively. The average confidence interval value of acetaldehyde at lower concentrations (0-1.1 m) was used for the confidence interval contribution from acetaldehyde in (A) and (B) due to a lack of experimental data at high acetaldehyde concentrations (1.14-1.42 m).

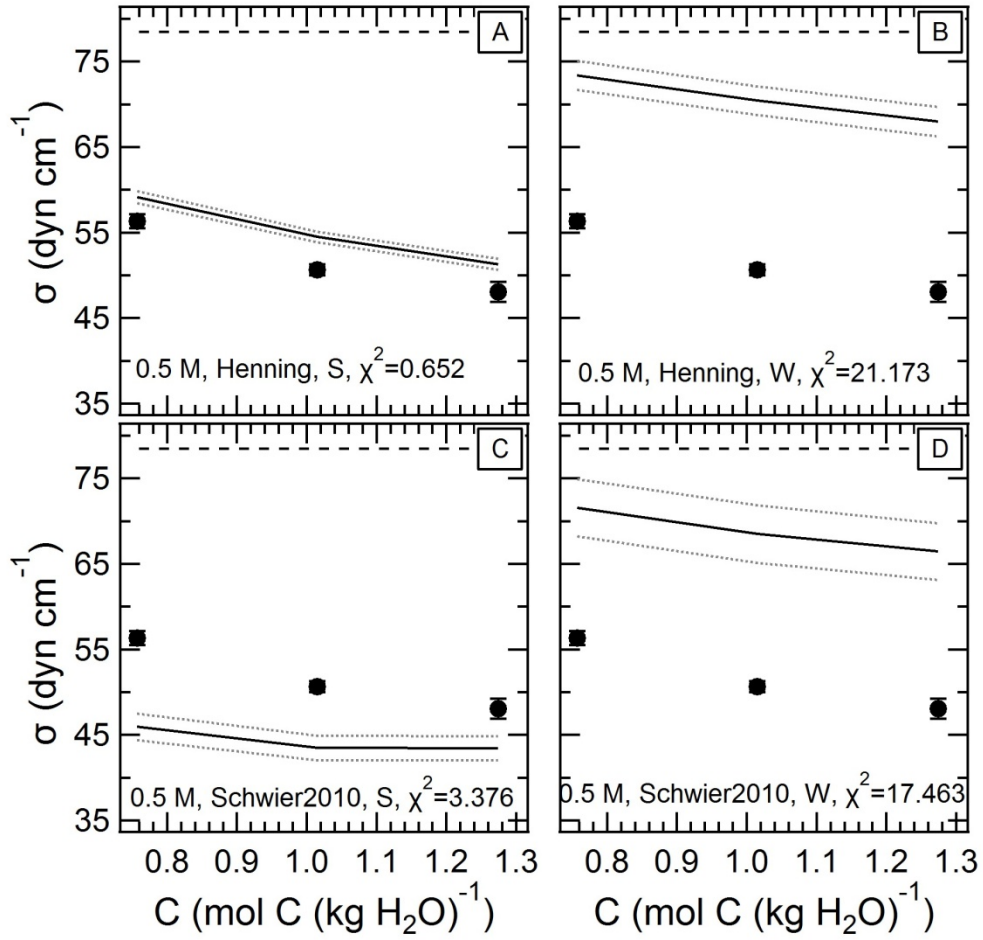

Figure S11. 0.5 M total organic, varying ratio of formaldehyde and methylglyoxal in 3.1 M $(NH_4)_2SO_4$. (A) and (C) are the Henning semi-empirical model and Schwier2010 semi-empirical model with $(NH_4)_2SO_4$ fit parameters (S), respectively; (B) and (D) are the same with water fit parameters (W), respectively. The average confidence interval value of formaldehyde at lower concentrations (0-0.2 m) was used for the confidence interval contribution from formaldehyde in all subplots due to a lack of experimental data at high formaldehyde concentrations (0.78-1.3 m m).

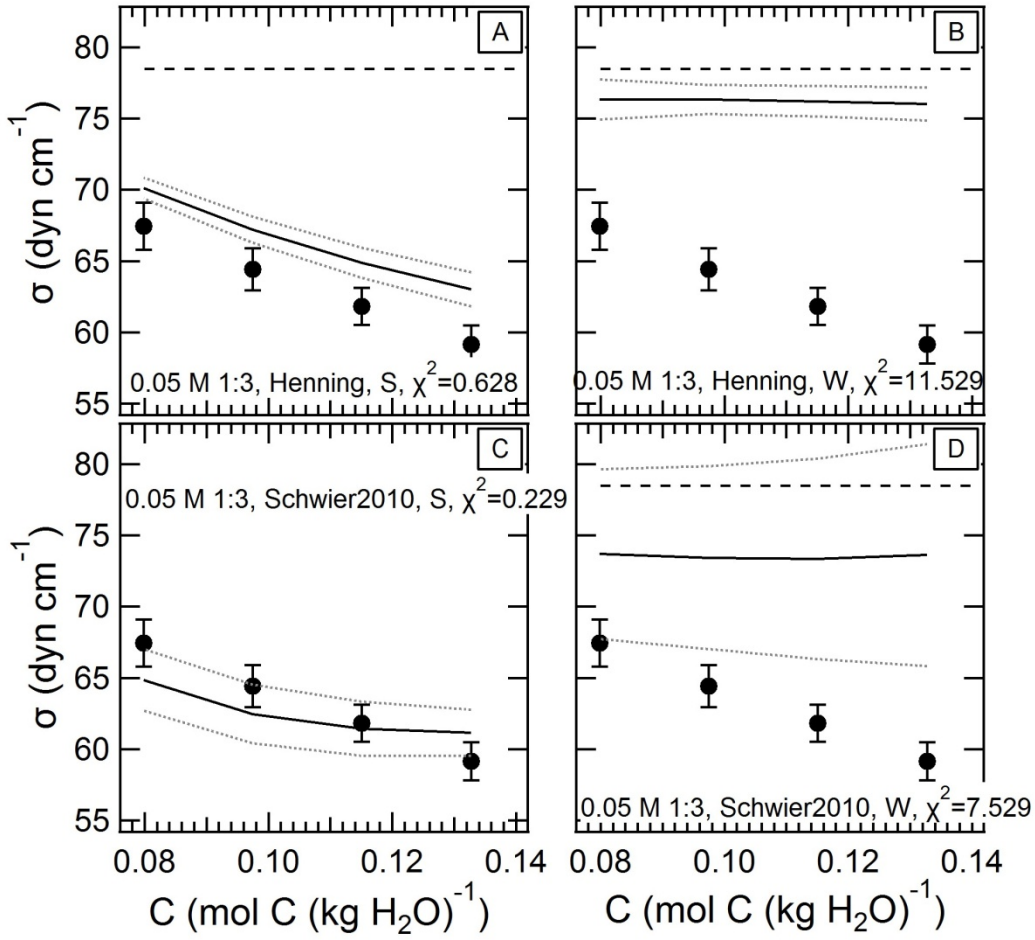

Figure S12. 0.05 M total organic with varying amounts of acetaldehyde:formaldehyde (3:1) and methylglyoxal in 3.1 M $(NH_4)_2SO_4$. (A) and (C) are the Henning semi-empirical model and Schwier2010 semi-empirical model with $(NH_4)_2SO_4$ fit parameters (S), respectively; (B) and (D) are the same with water fit parameters (W), respectively.

References:

Hyvärinen, A. R., Lihavainen, H., Gaman, A., Vairila, L., Ojala, H., Kulmala, M., and Viisanen, Y.: Surface tensions and densities of oxalic, malonic, succinic, maleic, malic, and cis-pinonic acids, *Journal of Chemical and Engineering Data*, *51* (1), 255-260, doi:10.1021/je050366x, 2006.

Li, Z., Schwier, A. N., Sareen, N., and McNeill, V. F.: Reactive processing of formaldehyde and acetaldehyde in aqueous aerosol mimics: Surface tension depression and secondary organic products, *Atmospheric Chemistry & Physics*, *11,* 19477-19506, doi:10.5194/acpd-11-19477-2011, 2011.

Sareen, N., Schwier, A. N., Shapiro, E. L., Mitroo, D., and McNeill, V. F.: Secondary organic material formed by methylglyoxal in aqueous aerosol mimics, *Atmospheric Chemistry and Physics*, *10,* 997-1016, doi:10.5194/acp-10-997-2010, 2010.

Washburn, E. W., International Critical Tables Of Numerical Data, Physics, Chemistry and Technology (1st Electronic Edition), 1926-1930; 2003.