

1 **Effects of molecular weight and temperature on liquid-liquid phase separation in particles**  
2 **containing organic species and inorganic salts**

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8 **Abstract**

9 Atmospheric particles containing organic species and inorganic salts may undergo liquid-liquid  
10 phase separation when the relative humidity varies between high and low values. To better  
11 understand the parameters that affect liquid-liquid phase separation in atmospheric particles, we  
12 studied the effects of molecular weight and temperature on liquid-liquid phase separation in  
13 particles containing one organic species mixed with either ammonium sulfate or ammonium  
14 bisulfate. In the molecular weight dependent studies, we measured liquid-liquid phase separation  
15 relative humidity (SRH) in particles containing ammonium sulfate and organic species with large  
16 molecular weights (up to 1153 Da). These results were combined with recent studies of liquid-  
17 liquid phase separation in the literature to assess if molecular weight is a useful parameter for  
18 predicting SRH. The combined results, which include results from 33 different particle types,  
19 illustrate that SRH does not depend strongly on molecular weight (i.e. a clear relationship  
20 between molecular weight and SRH was not observed). In the temperature dependent studies, we  
21 measured liquid-liquid phase separation in particles containing ammonium sulfate mixed with 20  
22 different organic species at  $244 \pm 1$  K,  $263 \pm 1$  K, and  $278 \pm 1$  K, as well as  $290 \pm 1$  K for a few  
23 of these particle types. These new results were combined with previous measurements of the  
24 same particle types at  $290 \pm 1$  K. The combined SRH data illustrate that for the organic-  
25 ammonium sulfate particles studied the SRH does not depend strongly on temperature. At most  
26 the SRH varied by 9.7 % as the temperature varied from 290 to 244 K. The high SRH values (>  
27 65%) in these experiments may explain the lack of temperature dependence. Since water is a  
28 plasticizer, high relative humidities can lead to high water contents, low viscosities and high  
29 diffusion rates in the particles. For these cases, unless the temperature is very low, liquid-liquid  
30 phase separation is not expected to be kinetically inhibited. The occurrence of liquid-liquid phase  
31 separation and SRH did depend strongly on temperature over the range of 290-244 K for  
32 particles containing  $\alpha$ ,4-dihydroxy-3-methoxybenzeneacetic acid mixed with ammonium  
33 bisulfate. For this particle type, a combination of low temperatures and low water content likely  
34 favored kinetic inhibition of the liquid-liquid phase separation by slow diffusion rates in highly  
35 viscous particles. The combined results suggest that liquid-liquid phase separation is likely a  
36 common occurrence in atmospheric particles at temperatures from 244-290 K, although particles  
37 that do not undergo liquid-liquid phase separation are also likely common.

## 38 **1 Introduction**

39 A large fraction of particles in the atmosphere contains both organic species and inorganic salts  
40 (Murphy and Thomson, 1997; Murphy et al., 1998; Middlebrook et al., 1998; Buzorius et al.,  
41 2002; Murphy, 2005; Murphy et al., 2006; Tolocka et al., 2005; Chen et al., 2009; Pratt and  
42 Prather, 2010). Ammonium sulfate and ammonium bisulfate are both common inorganic salts in  
43 these particles (Dibb et al., 1996; Huebert et al., 1998; Talbot et al., 1998; Dibb et al., 2000; Lee  
44 et al., 2003). The types of organic species in these particles are numerous with only around 10%  
45 by mass of these organic species identified at the molecular level (Hamilton et al., 2004;  
46 Goldstein and Galbally, 2007; Decesari et al., 2006; Hallquist et al., 2009). Organic functional  
47 groups found in mixed organic-inorganic salt particles include carboxylic acids, alcohols,  
48 oxidized aromatic compounds, ethers, and esters (Finlayson-Pitts and Pitts, 2000; Seinfeld and  
49 Pandis, 2006; Decesari et al., 2006; Hallquist et al., 2009; Takahama et al., 2011; Rogge et al.,  
50 1993; Saxena and Hildemann, 1996; Finlayson-Pitts and Pitts, 1997; Day et al., 2009; Gilardoni  
51 et al., 2009; Liu et al., 2009; Russell et al., 2009; Russell et al., 2011; Fu et al., 2011; Fuzzi et al.,  
52 2001). The molecular weight of organic molecules in these mixed particles is thought to range  
53 from less than 100 Da to as high as 1000 Da (Gao et al., 2004; Tolocka et al., 2004; Kalberer et  
54 al., 2004; Nguyen et al., 2010). In addition, the average oxygen-to-carbon elemental ratios (O:C)  
55 of the organic material in ambient particles generally range from 0.1 to 1.0 (Chen et al., 2009;  
56 Aiken et al., 2008; DeCarlo et al., 2008; Jimenez et al., 2009; Hawkins et al., 2010; Heald et al.,  
57 2010; Ng et al., 2010; Takahama et al., 2011), while the average organic-to-inorganic mass ratios  
58 (OIR) of atmospheric particles generally range from 0.2 to 3.5 (Chen et al., 2009; Zhang et al.,  
59 2007; Jimenez et al., 2009).

60 When the relative humidity varies in the atmosphere, mixed organic-inorganic salt particles can  
61 undergo different phase transitions, including efflorescence and deliquescence (Martin, 2000;  
62 Brooks et al., 2002; Choi and Chan, 2002; Brooks et al., 2003; Chan and Chan, 2003; Wise et al.,  
63 2003; Braban and Abbatt, 2004; Pant et al., 2004; Parsons et al., 2004a; Badger et al., 2006;  
64 Chang and Pankow, 2006; Erdakos et al., 2006; Parsons et al., 2006; Salcedo, 2006; Ling and  
65 Chan, 2008; Treuel et al., 2009; Bodsworth et al., 2010). More recent laboratory measurements  
66 and calculations have focused on liquid-liquid phase separation (Clegg et al., 2001; Pankow,  
67 2003; Marcolli and Krieger, 2006; Anttila et al., 2007; Buajjarern et al., 2007; Zuend et al., 2008;  
68 Ciobanu et al., 2009; Kwamena et al., 2010; Prisle et al., 2010; Zuend et al., 2010; Bertram et al.,  
69 2011; Reid et al., 2011; Smith et al., 2011; Zuend et al., 2011; Krieger et al., 2012; Pöhlker et al.,  
70 2012; Smith et al., 2012; Song et al., 2012a, b; You et al., 2012; Zuend and Seinfeld, 2012;  
71 Drozd et al., 2013; Shiraiwa et al., 2013; Song et al., 2013; Veghte et al., 2013; You et al., 2013;  
72 Zuend and Seinfeld, 2013; Veghte et al., 2014). Liquid-liquid phase separation in the  
73 atmospheric particles can influence the partitioning of organic molecules between the gas and the  
74 particle phase (Seinfeld et al., 2001; Chang and Pankow, 2006; Zuend et al., 2010; Shiraiwa et  
75 al., 2013) and influence the reactive uptake of important gas-phase molecules, such as N<sub>2</sub>O<sub>5</sub>, into  
76 atmospheric particles (Anttila et al., 2006; Folkers et al., 2003; Escoreia et al., 2010; Cosman and

77 Bertram, 2008; Park et al., 2007; Thornton and Abbatt, 2005; McNeill et al., 2006; Gaston et al.,  
78 2014). Liquid-liquid phase separation can also influence the deliquescence and efflorescence  
79 relative humidity in mixed organic-inorganic salt particles (Bertram et al., 2011; Smith et al.,  
80 2012; Song et al., 2013). In addition, liquid-liquid phase separation can alter the ice nucleation  
81 properties of particles (Schill and Tolbert, 2013).

82 Recent work has investigated different parameters that influence liquid-liquid phase separation in  
83 particles containing mixtures of organic species and inorganic salts (You et al., 2014).  
84 Understanding the parameters that affect these transitions is necessary for predicting these phase  
85 transitions in atmospheric particles. Studies have shown that O:C is an important parameter for  
86 predicting liquid-liquid phase separation in these particles, with this phase transition always  
87 observed for O:C less than 0.5, frequently observed for O:C values between 0.5 and 0.8, and  
88 never observed for O:C values greater than 0.8 (Bertram et al., 2011; Song et al., 2012a, b; You  
89 et al., 2013). Measurements have also illustrated that the type of functional groups can also  
90 influence the relative humidity required for liquid-liquid phase separation when the O:C of the  
91 organic material is in the range of approximately 0.5 to 0.8 (Song et al., 2012b). On the other  
92 hand, the occurrence of liquid-liquid phase separation is not a strong function of the OIR or the  
93 number of organic species (Marcolli and Krieger, 2006; Ciobanu et al., 2009; Bertram et al.,  
94 2011; Song et al., 2012a, b; Schill and Tolbert, 2013). In addition, the occurrence of liquid-liquid  
95 phase separation may not be a strong function of the type of inorganic salt for  $O:C \geq 0.8$  and  $\leq$   
96 0.5, but, in the range of 0.5 to 0.8, the occurrence of liquid-liquid phase separation can depend on  
97 the salt type (You et al. 2013).

98 In the following paper, we investigate if molecular weight of the organic material and  
99 temperature of the particles influence liquid-liquid phase separation in particles containing  
100 organic species and inorganic salts. Molecular weight of the organic molecules is of interest  
101 because viscosity of organic-inorganic salt mixtures can depend roughly on the molecular weight  
102 of the organic species, and at high molecular weights, liquid-liquid phase separation may become  
103 kinetically inhibited in highly viscous solutions. The effect of molecular weight of the organic  
104 material on the occurrence of liquid-liquid phase separation in mixed organic-inorganic salt  
105 particles has not been explored.

106 Temperature is of interest since temperature ranges from approximately 220 to 300 K in the  
107 troposphere, and temperature can influence the thermodynamics and kinetics of liquid-liquid  
108 phase separation. As an example of the effect of temperature on the thermodynamics of liquid-  
109 liquid phase transitions consider the binary mixture of water and butanol. At room temperature  
110 the binary mixture is partially immiscible. But as the temperature increases the region of  
111 immiscibility decreases until the upper critical solution temperature is reached. At higher  
112 temperatures the binary mixture is completely miscible. Certain mixtures can also have lower  
113 critical solution temperatures due to an increase in hydrogen bonding as the solution temperature  
114 decreases (Levine. 2009). Temperature may also influence the kinetics of liquid-liquid phase  
115 transitions. Some mixtures of organic species and inorganic salts can become highly viscous at

116 lower temperatures and low relative humidities (Tong et al., 2011; Zobrist et al., 2008; Koop et  
117 al., 2011; Zobrist et al., 2011; Murray, 2008; Mikhailov et al., 2009; Saukko et al., 2012). At  
118 these low temperatures and relative humidities, liquid-liquid phase separation may be kinetically  
119 inhibited due to diffusion limitations. Only two studies have investigated liquid-liquid phase  
120 separation in mixed organic-inorganic salt particles at temperatures below 290 K. Bertram et al.  
121 reported that SRH results were similar at 273 K and 290 K for particles containing ammonium  
122 sulfate and 1,2,6-hexanetriol (Bertram et al., 2011). Schill and Tolbert reported that SRH results  
123 were similar for temperatures from 240 to 265 K for particles containing ammonium sulfate  
124 mixed with 1,2,6-hexanetriol and particles containing ammonium sulfate, 1,2,6-hexanetriol, and  
125 2,2,6,6-tetrakis(hydroxymethyl)cyclohexanol (Schill and Tolbert, 2013).

126 Here we carried out a systematic study of the effect of molecular weight of the organic material  
127 on liquid-liquid phase separation at  $290 \pm 1$  K. We first studied liquid-liquid phase separation in  
128 particles containing ammonium sulfate mixed with one of ten organic species, with molecular  
129 weights up to 1153 Da. The data from these studies were then combined with recent studies of  
130 liquid-liquid phase separation in particles reported in the literature (You et al., 2013) to assess if  
131 molecular weight is a useful parameter to predict the occurrence of liquid-liquid phase separation  
132 and the liquid-liquid phase separation relative humidity (SRH).

133 To gain a better understanding of the effect of temperature on liquid-liquid phase separation in  
134 mixed organic-inorganic salt particles, we investigated liquid-liquid phase separation in particles  
135 containing ammonium sulfate mixed with one of twenty organic species at  $244 \pm 1$  K,  $263 \pm 1$  K,  
136 and  $278 \pm 1$  K, respectively. Some of these particle types were also studied at  $290 \pm 1$  K. These  
137 new data were combined with previous measurements of liquid-liquid phase separation at  $290 \pm$   
138  $1$  K by You et al. (You et al., 2013) to assess the effect of temperature on liquid-liquid phase  
139 separation in mixed organic-ammonium sulfate particles.

140 We also investigated liquid-liquid phase separation in particles containing ammonium bisulfate  
141 mixed with  $\alpha$ ,4-dihydroxy-3-methoxybenzeneacetic acid at temperatures of  $244 \pm 1$  K,  $263 \pm 1$   
142 K, and  $278 \pm 1$  K. This system was studied since it has a relatively low SRH-value (38%) at  $290$   
143  $\pm 1$  K and, hence, has relatively low water content at the onset of liquid-liquid phase separation.  
144 In addition to temperature and molecular weight, water content is likely important for the  
145 kinetics of liquid-liquid phase separations, as the viscosity and diffusion rates within the particles  
146 are expected to be sensitive to water content (Koop et al. 2011; Renbaum-Wolff et al. 2013;  
147 Power et al. 2013; Kidd et al. 2014).

## 148 **2 Experimental**

### 149 **2.1 Sample preparation and apparatus.**

150 Solutions of ammonium sulfate or ammonium bisulfate and one organic species were prepared in  
151 high purity water (Millipore, 18.2 M $\Omega$  cm) with OIR of  $2.0 \pm 0.1$ . The solutions were then  
152 nebulized to produce submicron particles, which impacted onto a hydrophobic glass slide

153 (Hampton Research) and coagulated into super-micron droplets. Water was then evaporated to  
154 generate mixed organic-inorganic salt particles with lateral dimensions ranging from 10 to 35  
155  $\mu\text{m}$ .

156 The glass slide supporting the mixed organic-inorganic salt particles was mounted to a  
157 temperature and relative humidity controlled flow cell, which was coupled to an optical  
158 reflectance microscope (Zeiss Axiotech; 50 $\times$  objective) (Koop et al., 2000; Parsons et al., 2004b;  
159 Pant et al., 2006; Bodsworth et al., 2010). To control the relative humidity in the flow cell, dry  
160 and humidified nitrogen gas flows were combined and continuously passed through the cell. The  
161 total flow rate was approximately 1.5 L  $\text{min}^{-1}$ . While the RH was decreased, liquid-liquid phase  
162 separation was identified by monitoring the change in morphology of the particles. The relative  
163 humidity of the gas was determined with a chilled mirror hygrometer (General Eastern, Model  
164 1311DR). The hygrometer was calibrated prior to experiments at each temperature ( $244 \pm 1$  K,  
165  $263 \pm 1$  K,  $278 \pm 1$  K, and  $290 \pm 1$  K) by measuring the deliquescence relative humidity (DRH)  
166 of ammonium sulfate particles, and comparing the measured DRH value to the DRH value  
167 predicted with the Extended Aerosol Inorganic Model (E-AIM model) (Clegg et al. 1998). The  
168 uncertainty ( $2\sigma$ ) of the hygrometer was  $\pm 2.5$  % RH after calibration based on reproducibility of  
169 the DRH measurements.

## 170 **2.2 Molecular weight dependent studies.**

171 Particles containing ammonium sulfate mixed with one of ten organic species were studied at  
172  $290 \pm 1$  K (see Table 1). Most of previous laboratory studies of liquid-liquid phase separation in  
173 particles containing organic species mixed with ammonium sulfate used organic species with  
174 molecular weight less than 200 Da (Bertram et al., 2011; Song et al., 2012a, b; You et al., 2013).  
175 To complement these previous studies, in the current study we investigated particles containing  
176 ammonium sulfate and organic species with molecular weight ranging from 180 to 1153 Da (see  
177 Table 1). The specific organic species selected for these studies (Table 1) also had a relatively  
178 wide range of O:C values. The glass transition temperatures of the organics studied covered at  
179 least the range of 223 K to 412 K (see Table 1). In all the studies, the organic-to-inorganic mass  
180 ratio (OIR) was  $2.0 \pm 0.1$ . This value was chosen so that the current studies could be compared  
181 with the previous studies by You et al. (2013), who also used an OIR =  $2.0 \pm 0.1$ . In addition,  
182 this OIR value is in the range of OIR values observed in many field studies (Zhang et al., 2007;  
183 Jimenez et al., 2009).

184  
185 In a typical experiment, the RH in the cell was ramped down at a rate of 0.4-0.6% RH  $\text{min}^{-1}$ ,  
186 while the temperature of the cell was held at  $290 \pm 1$  K. At the same time, images of the particles  
187 were captured continuously until one of the following conditions occurred: liquid-liquid phase  
188 separation was observed, the particles effloresced, or the RH reached  $\leq 0.5\%$ . For each type of  
189 particle, experiments were repeated at least three times. All of the organic species were  
190 purchased from Sigma-Aldrich and had purities  $\geq 95\%$ , except for maltoheptaose, which had a  
191 purity  $\geq 90\%$ .

192

### 193 **2.3 Temperature dependent studies.**

194 Particles consisting of ammonium sulfate mixed with one of twenty organic species were studied  
195 (see Table 2) at  $244 \pm 1$  K,  $263 \pm 1$  K, and  $278 \pm 1$  K, as well as  $290 \pm 1$  K for a few of these  
196 particle types. For these studies, we chose the same particle types previously studied by You et  
197 al. (2013) at  $290 \pm 1$  K. These particle types cover a wide range of O:C values and included  
198 functional groups found in atmospheric particles. Also, ammonium sulfate is one of the most  
199 common inorganic salts found in the atmosphere. In addition to picking the particles types  
200 previously studied by You et al. (2013), we also studied two additional organic species mixed  
201 with ammonium sulfate. These two organic species were raffinose and poly(ethylene glycol)  
202 diacrylate. These two species were chosen since they had relatively high molecular weights. An  
203 OIR value of  $2.0 \pm 0.1$  was used in all the studies, consistent with You et al. (2013). The glass  
204 transition temperatures of the organic species studied cover the range of at least 192 K to 396 K.

205 In addition to studying particles consisting of ammonium sulfate mixed with one of twenty  
206 organic species, we also studied particles containing ammonium bisulfate mixed with  $\alpha$ ,4-  
207 dihydroxy-3-methoxybenzeneacetic acid at temperatures of  $244 \pm 1$  K,  $263 \pm 1$  K, and  $278 \pm 1$   
208 K. As mentioned in the introduction, this system was studied since it has a low SRH-value (38%)  
209 at  $290 \pm 1$  K and hence has relatively low water content at the onset of liquid-liquid phase  
210 separation.

211 The organic species studied were purchased from Sigma-Aldrich with purities  $\geq 98\%$ . All  
212 organics were used without further purification. In a typical temperature dependent experiment,  
213 the RH was ramped down at a rate of around 0.1- 0.5 % RH  $\text{min}^{-1}$ . Images were recorded in the  
214 same way as the molecular weight dependent studies.

## 215 **3 Results and Discussion**

### 216 **3.1 Effect of molecular weight on liquid-liquid phase separation**

217 Particles containing ammonium sulfate mixed with one of ten organic species were studied at  
218  $290 \pm 1$  K. In these studies organic species with large molecular weights (180 to 1153 Da) were  
219 used. The organic-to-inorganic mass ratio (OIR) was  $2.0 \pm 0.1$  in all the studies. The results from  
220 these studies are listed in Table 3 as well as the data from You et al., who also studied particles  
221 with an OIR of  $2.0 \pm 0.1$  at  $290 \pm 1$  K (You et al., 2013). The combined data set in Table 3,  
222 which includes results of liquid-liquid phase separation for 33 different particle types, was used  
223 to determine the importance of molecular weight of the organic species on liquid-liquid phase  
224 separation.

225 In Figure 1, the data from Table 3 were plotted as a function of O:C and molecular weight. Open  
226 circles indicate liquid-liquid phase separation was observed and stars indicate liquid-liquid phase  
227 separation was not observed. No clear relationship between molecular weight and the occurrence

228 of liquid-liquid phase separation was observed, however a relationship between occurrence of  
229 liquid-liquid phase separation and O:C was clear: liquid-liquid phase separation was always  
230 observed when  $O:C < 0.57$  (orange hatched region), was never observed when  $O:C > 0.83$  (green  
231 hatched region), and was frequently observed when  $O:C$  ranged from 0.57 to 0.83. This range is  
232 slightly different than the range previously measured (0.5 to 0.8) (Bertram et al. 2011; Song et al.  
233 2012a, b; You et al. 2013), which is not surprising since this range is expected to change slightly  
234 with the type of organic molecules studied. As such, there is a small uncertainty in this range. In  
235 Figure 2, the SRH data from Table 3 were plotted as a function of molecular weight of the  
236 organic species. The colors of the symbols indicate the O:C of organic species in the mixed  
237 particles. Data at SRH = 0 % indicate liquid-liquid phase separation was not observed even at the  
238 lowest relative humidity studied. Similar to Figure 1, no correlation with molecular weight was  
239 apparent. For contrast, in Figure 3, we show the same SRH data plotted as a function of O:C of  
240 organic species with the color of the symbols representing the molecular weight of organic  
241 species. Consistent with previous results (Bertram et al., 2011; Song et al., 2012b), a correlation  
242 between SRH and O:C is apparent. These results suggest that O:C is more important for  
243 predicting the occurrence of liquid-liquid phase separation in atmospherically relevant mixed  
244 organic-ammonium sulfate particles compared with molecular weight.

### 245 **3.2 Effect of temperature on liquid-liquid phase separation**

246 In the temperature dependent experiments, particles containing ammonium sulfate mixed with  
247 one of twenty organic species were studied at  $244 \pm 1$  K,  $263 \pm 1$  K, and  $278 \pm 1$  K. Some of the  
248 particle types were also studied at  $290 \pm 1$  K. The temperature dependent results are included in  
249 Table 4 as well as results from You et al., who studied most of the same types of particles but  
250 only at  $290 \pm 1$  K (You et al., 2013). The combined SRH data from Table 4, which cover the  
251 temperature range of 290-244 K, were plotted in Figure 4A as a function of O:C of the organic  
252 species. The temperature dependent results show that for all the particle types studied and at all  
253 the temperatures studied liquid-liquid phase separation was always observed when  $O:C < 0.57$ ,  
254 frequently observed when  $0.57 \leq O:C < 0.8$ , and never observed when  $O:C \geq 0.8$ . We conclude  
255 that the O:C range at which liquid-liquid phase separation was observed at 290-293 K in  
256 previous studies (Ciobanu et al., 2009; Bertram et al., 2011; Song et al., 2012b; You et al., 2013),  
257 is reasonably consistent with the range observed at temperatures down to  $244 \pm 1$  K.

258 Figure 5 shows the same data as in Figure 4A, but displayed in a slightly different way. The SRH  
259 results for the twelve types of mixed organic-ammonium sulfate particles that underwent liquid-  
260 liquid phase separation in Figure 4A, are shown as a function of temperature, with the colors of  
261 the symbols representing the O:C values of the organic species in the particles. For all the  
262 particle types included in Figure 5, the SRH varied by less than 9.7 % RH as the temperature  
263 varied from 244 to 290 K. Figure 4A and 5 illustrate that SRH is not a strong function of  
264 temperature for the particle types investigated. These results are consistent with earlier studies by  
265 Bertram et al. and Schill and Tolbert discussed in the Introduction. In the Supplementary  
266 Material we carried out a linear regression analysis to determine the level of significance of the

267 temperature dependent trends observed in Figure 5. In short, five out of the twelve systems  
268 studied had a high correlation coefficient ( $r \geq 0.94$ ) between temperature and SRH and an  
269 associated low p-value ( $\leq 0.06$ ). A decrease in SRH with a decrease in temperature may be  
270 expected if there is a closed loop miscibility gap and the measurements are probing the lower  
271 temperature region of the closed loop.

272 Based on our results, particles containing poly(propylene glycol) and ammonium sulfate had  
273 SRH values ranging from 87.7 to 94.1 % as the temperature ranged from 244 to 290 K. Solutions  
274 of water and poly(propylene glycol) show a lower critical solution temperature of approximately  
275 50 °C (Malcom and Rowlinson, 1957). A comparison between this result and our current results  
276 indicate that the lower critical solution temperature is decreased significantly when ammonium  
277 sulfate is added to mixtures of poly(propylene glycol) and water.

278 As mentioned in the introduction, some mixtures of organic species and inorganic salts can  
279 become highly viscous at lower temperatures and low relative humidities, and at these low  
280 temperatures and relative humidities, liquid-liquid phase separation may be kinetically inhibited  
281 due to diffusion limitations. A possible reason that a stronger dependence on temperature was  
282 not observed in the studies discussed above may be because for the systems studied the particles  
283 either didn't undergo liquid-liquid phase separation or the SRH was relatively high ( $> 65\%$  RH).  
284 For the cases where liquid-liquid phase separation did not occur, an increase in viscosity from a  
285 decrease in temperature is not expected to change the results. For cases where the SRH was  
286 relatively high ( $> 65\%$  RH), the water content in the particles was also likely relatively high.  
287 Since water is a plasticizer, high water contents can lead to low viscosities and high diffusion  
288 rates. In this case, unless the temperature is very low, liquid-liquid phase separation is not  
289 expected to be kinetically inhibited.

290 Although SRH does not appear to be a strong function of the temperature for the organic-  
291 ammonium sulfate particle types studied over the temperature range of 244 to 290 K, SRH may  
292 be a strong function of temperature for these particles at temperatures lower than 244 K due to  
293 kinetic limitations or thermodynamic reasons. Additional studies of SRH at temperatures lower  
294 than 244 K are still needed for these particle types.

295 In Figure 6, SRH as a function of temperature is plotted for particles containing  $\alpha,4$ -dihydroxy-3-  
296 methoxybenzeneacetic acid mixed with ammonium bisulfate. At  $263 \pm 1$  K and warmer no  
297 strong dependence on temperature is observed, with an average SRH value of approximately  
298 37.6 %. At 244 K, however, liquid-liquid phase separation was not observed. A likely  
299 explanation for this drastic decrease in the SRH is likely kinetic inhibition of the liquid-liquid  
300 phase separation. Related, previous research has shown that efflorescence is inhibited in particles  
301 containing organic species and inorganic salts at low temperatures and low relative humidities  
302 likely due to diffusion limitations (Bodsworth et al., 2010). The studies with particles containing  
303 ammonium bisulfate and  $\alpha,4$ -dihydroxy-3-methoxybenzeneacetic acid suggests that a



304 combination of low temperatures (e.g. 244 K) and low relative humidities (e.g. approximately  
305 38% RH) can lead to kinetic inhibition of liquid-liquid phase separation.

306 The average O:C of organic material in atmospheric particles has been measured at many  
307 locations in the Northern Hemisphere and in the Amazon and has been shown to range from 0.1  
308 to 1.0 (Chen et al., 2009; Aiken et al., 2008; DeCarlo et al., 2008; Jimenez et al., 2009; Hawkins  
309 et al., 2010; Heald et al., 2010; Ng et al., 2010; Takahama et al., 2011). This range of O:C values  
310 is indicated in Figure 4B. The range of average O:C values measured in the atmosphere overlaps  
311 with the range of O:C values where liquid-liquid phase separation was observed at temperatures  
312 ranging from 244 to 290 K (Figure 4 B). This overlap suggests that liquid-liquid phase separation  
313 is likely a common occurrence in the atmosphere over this temperature range. Particles that do  
314 not undergo liquid-liquid phase separation are also expected to be common based on a  
315 comparison between our data and the range of O:C values found in the atmosphere.

#### 316 **4 Conclusions**

317 The occurrence of liquid-liquid phase separation and SRH did not depend strongly on the  
318 molecular weight of the organic species at  $290 \pm 1$  K, at least for the particle types studied. The  
319 occurrence of liquid-liquid phase separation and SRH also did not depend strongly on  
320 temperature over the range of 290- 244 K for particles containing ammonium sulfate mixed with  
321 one organic species. The SRH varied by at most 9.7 % RH as the temperature varied from  $290 \pm$   
322  $1$  K to  $244 \pm 1$  K for the particle types studied. The high SRH values ( $> 65\%$ ) in these  
323 experiments may explain the lack of temperature dependence. Since water is a plasticizer, high  
324 relative humidities can lead to high water contents, low viscosities and high diffusion rates. For  
325 these cases, unless the temperature is very low, liquid-liquid phase separation is not expected to  
326 be kinetically inhibited. The occurrence of liquid-liquid phase separation and SRH did depend  
327 strongly on temperature over the range of 290-244 K for particles containing  $\alpha$ ,4-dihydroxy-3-  
328 methoxybenzeneacetic acid mixed with ammonium bisulfate. For this particle type, a  
329 combination of low temperatures and low water content likely favored kinetic inhibition of the  
330 liquid-liquid phase separation by slow diffusion rates in highly viscous particles.

331 The combined results suggest that liquid-liquid phase separation is likely a common occurrence  
332 in the atmospheric particles at 290-244 K, although particles that do not undergo liquid-liquid  
333 phase separation are also likely common.

334

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338

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695 **Tables**

696 **Table 1.** List of the ten organic species used in molecular weight dependent measurements. Each  
 697 organic species was separately mixed with ammonium sulfate to make particles, and liquid-  
 698 liquid phase separation was studied in these particles at  $290 \pm 1$  K.

Compounds	Formula	Molecular weight (Da)	O:C	Functional group(s)	Glass transition temperature, $T_g$ (K)	References for $T_g$
Glucose	$C_6H_{12}O_6$	180.2	1	alcohol, ether	$296.1 \pm 3.1$	Zobrist et al. 2008
Poly(ethylene glycol) bis(carboxymethyl) ether	$C_{2n+4}H_{4n+6}O_{n+5}$	250	0.83	alcohol, ether	-	-
Sucrose	$C_{12}H_{22}O_{11}$	342.3	0.92	alcohol, ether	$335.7 \pm 3.6$	Zobrist et al. 2008
Poly(ethylene glycol)	$C_{2n}H_{4n+2}O_{n+1}$	400	0.56	alcohol, ether	223	Faucher et al. 1966
Ouabain	$C_{29}H_{44}O_{12}$	584	0.41	alcohol, ether, ester, C-C double bonds	$373^a$	Koop et al. 2011
Raffinose	$C_{18}H_{32}O_{16}$	594.5	0.89	alcohol, ether	$395.7 \pm 21.6$	Zobrist et al. 2008
Poly(ethylene glycol)	$C_{2n}H_{4n+2}O_{n+1}$	600	0.54	alcohol, ether	231	Faucher et al. 1966
Maltopentaose	$C_{30}H_{52}O_{26}$	829	0.87	alcohol, ether	398	Slade and Levine 1994
Poly(ethylene glycol)	$C_{2n}H_{4n+2}O_{n+1}$	900	0.53	alcohol, ether	231-245	Faucher et al. 1966
Maltoheptaose	$C_{42}H_{72}O_{36}$	1153	0.86	alcohol, ether	412	Slade and Levine 1994

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700 <sup>a</sup>  $T_g$  values are estimates based on the melting points of those organic compounds using the results from  
 701 Koop et al. 2011.

702 - Literature data not available

703

704 **Table 2.** Summary of the twenty organic species used in temperature dependent experiments.  
 705 Each organic species was separately mixed with ammonium sulfate to make particles, and liquid-  
 706 liquid phase separation was studied in these particles at  $244 \pm 1$  K,  $263 \pm 1$  K and  $278 \pm 1$  K.  
 707 Two of the organic species (poly(ethylene glycol) diacrylate and raffinose) mixed with  
 708 ammonium sulfate were also studied at  $290 \pm 1$  K.

Compounds	Formula	O:C	Molecular weight (Da)	Functional group(s)	Glass transition temperature $T_g$ (K)	References for $T_g$
2,5-hexanediol	$C_6H_{14}O_2$	0.33	118.2	alcohol	$192.4 \pm 1.3$	Zobrist et al. 2008
Poly(propylene glycol)	$C_{3n}H_{6n+2}O_{n+1}$	0.38	425	alcohol, ether	-	-
Poly(ethylene glycol) diacrylate	$C_{2n+6}H_{4n+6}O_{n+3}$	0.5	575	ester, ether, C-C double bond	-	-
Poly(ethylene glycol) 900	$C_{2n}H_{4n+2}O_{n+1}$	0.53	900	alcohol, ether	$231-245^a$	Faucher et al. 1966
$\alpha$ ,4-dihydroxy-3-methoxybenzoic acid	$C_9H_{10}O_5$	0.56	198.2	alcohol, aromatic, carboxylic acid, ether	$293.6 \pm 6.6$	Zobrist et al. 2008
Diethylmalonic acid	$C_7H_{12}O_4$	0.57	160.2	carboxylic acid	$282^b$	Koop et al. 2011
3,3-dimethylglutaric acid	$C_7H_{12}O_4$	0.57	160.2	carboxylic acid	$261^b$	Koop et al. 2011
2,5-hydroxybenzoic acid	$C_7H_6O_4$	0.57	154.2	carboxylic acid, aromatic	$225^b$	Koop et al. 2011
Poly(ethylene glycol) 300	$C_{2n}H_{4n+2}O_{n+1}$	0.58	300	alcohol, ether	203-223	Faucher et al. 1966
Poly(ethylene glycol) 200	$C_{2n}H_{4n+2}O_{n+1}$	0.63	200	alcohol, ether	203	Faucher et al. 1966
Poly(ethylene glycol) bis(carboxymethyl) ether	$C_{2n+4}H_{4n+6}O_{n+5}$	0.63	600	alcohol, ether	-	-
2-methylglutaric acid	$C_6H_{10}O_4$	0.67	146.1	carboxylic acid	$247^b$	Koop et al. 2011
2,2-dimethylsuccinic acid	$C_6H_{10}O_4$	0.67	146.2	carboxylic acid	$289^b$	Koop et al. 2011
Diethyl-L-tartrate	$C_8H_{14}O_6$	0.75	206.2	alcohol, ether	-	-
Glycerol	$C_3H_8O_3$	1.00	92.1	alcohol	$193.3 \pm 1.1$	Zobrist et al. 2008
Glutaric acid	$C_5H_8O_4$	0.8	132.1	carboxylic acid	$258^b$	Koop et al. 2011

Levoglucozan	C <sub>6</sub> H <sub>10</sub> O <sub>5</sub>	0.83	162.1	alcohol, ester	319 <sup>b</sup>	Koop et al. 2011
Raffinose	C <sub>18</sub> H <sub>32</sub> O <sub>16</sub>	0.89	594.5	alcohol, ester	395.7 ± 21.6	Zobrist et al. 2008
Citric acid	C <sub>6</sub> H <sub>8</sub> O <sub>7</sub>	1.17	192.1	alcohol, carboxylic acid	280.1	Bodsworth et al. 2010
Malonic acid	C <sub>3</sub> H <sub>4</sub> O <sub>4</sub>	1.33	104.1	carboxylic acid	286 <sup>b</sup>	Koop et al. 2011

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710 <sup>a</sup> T<sub>g</sub> value is an estimate based on the molecular weight of the ploy (ethylene glycol 900) from Faucher et  
711 al. 1966.

712 <sup>b</sup> T<sub>g</sub> values are estimates based on the melting points of those organic compounds using the results from  
713 Koop et al. 2011.

714 - Literature data not available

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716 **Table 3.** Combined data set used to assess the effect of molecular weight on SRH in mixed  
717 organic-ammonium sulfate particles. This data set includes the ten types of particles studied here  
718 (see Table 1) and the SRH results of twenty-three types of particles containing single organic  
719 species and ammonium sulfate studied by You et al. (2013). OIR =  $2.0 \pm 0.1$  in all the  
720 experiments. Uncertainties are 95% confidence intervals considering  $\sigma$  of multiple SRH  
721 measurements and the uncertainty from the calibration.

Compounds	Formula	Molecular weight (Da)	O:C	SRH (%)	Reference
Glycerol	C <sub>3</sub> H <sub>8</sub> O <sub>3</sub>	92.1	1	Not observed	You et al. (2013)
Malonic acid	C <sub>3</sub> H <sub>4</sub> O <sub>4</sub>	104.1	1.33	Not observed	You et al. (2013)
Maleic acid	C <sub>4</sub> H <sub>4</sub> O <sub>4</sub>	116.1	1	Not observed	You et al. (2013)
2,5-hexanediol	C <sub>6</sub> H <sub>14</sub> O <sub>2</sub>	118.2	0.33	88.8 ± 7.1	You et al. (2013)
Glutaric acid	C <sub>5</sub> H <sub>8</sub> O <sub>4</sub>	132.1	0.8	Not observed	You et al. (2013)
Malic acid	C <sub>4</sub> H <sub>6</sub> O <sub>5</sub>	134.1	1.25	Not observed	You et al. (2013)
1,2,6-hexanetriol	C <sub>6</sub> H <sub>14</sub> O <sub>3</sub>	134.2	0.5	76.7 ± 6.2	You et al. (2013)
2-methylglutaric acid	C <sub>6</sub> H <sub>10</sub> O <sub>4</sub>	146.1	0.67	75.3 ± 6.4	You et al. (2013)
2,2-dimethylsuccinic acid	C <sub>6</sub> H <sub>10</sub> O <sub>4</sub>	146.2	0.67	Not observed	You et al. (2013)
2,5-hydroxybenzoic acid	C <sub>7</sub> H <sub>6</sub> O <sub>4</sub>	154.2	0.57	Not observed	You et al. (2013)
Diethylmalonic acid	C <sub>7</sub> H <sub>12</sub> O <sub>4</sub>	160.2	0.57	89.2 ± 4.2	You et al. (2013)
3,3-dimethylglutaric acid	C <sub>7</sub> H <sub>12</sub> O <sub>4</sub>	160.2	0.57	89.1 ± 6.9	You et al. (2013)
Levogluconan	C <sub>6</sub> H <sub>10</sub> O <sub>5</sub>	162.1	0.83	Not observed	You et al. (2013)
Glucose	C <sub>6</sub> H <sub>12</sub> O <sub>6</sub>	180.2	1	Not observed	Current study
Suberic acid monomethyl ester	C <sub>9</sub> H <sub>16</sub> O <sub>4</sub>	188.2	0.44	100 ± 6.2	You et al. (2013)
Citric acid	C <sub>6</sub> H <sub>8</sub> O <sub>7</sub>	192.1	1.17	Not observed	You et al. (2013)
α,4-dihydroxy-3-methoxybenzeneacetic acid	C <sub>9</sub> H <sub>10</sub> O <sub>5</sub>	198.2	0.56	72.6 ± 6.3	You et al. (2013)
Poly(ethylene glycol)	C <sub>2n</sub> H <sub>4n+2</sub> O <sub>n+1</sub>	200	0.63	79.8 ± 7.4	You et al. (2013)
Diethyl-L-tartrate	C <sub>8</sub> H <sub>14</sub> O <sub>6</sub>	206.2	0.75	90.2 ± 6.6	You et al. (2013)
Poly(ethylene glycol) bis(carboxymethyl) ether	C <sub>2n+4</sub> H <sub>4n+6</sub> O <sub>n+5</sub>	250	0.83	67.6 ± 6.2	Current study
Diethyl sabacate	C <sub>14</sub> H <sub>26</sub> O <sub>4</sub>	258.4	0.29	100 ± 6.2	You et al. (2013)
Poly(ethylene glycol)	C <sub>2n</sub> H <sub>4n+2</sub> O <sub>n+1</sub>	300	0.58	86.7 ± 6.4	You et al. (2013)

Sucrose	$C_{12}H_{22}O_{11}$	342.3	0.92	Not observed	Current study
Poly(ethylene glycol)	$C_{2n}H_{4n+2}O_{n+1}$	400	0.56	$88.3 \pm 6.6$	Current study
Poly(propylene glycol)	$C_{3n}H_{6n+2}O_{n+1}$	425	0.38	$94.1 \pm 6.7$	You et al. (2013)
Poly(ethylene glycol) diacrylate	$C_{2n+6}H_{4n+6}O_{n+3}$	575	0.5	$94.7 \pm 6.2$	You et al. (2013)
Ouabain	$C_{29}H_{44}O_{12}$	584	0.41	$90.1 \pm 6.8$	Current study
Raffinose	$C_{18}H_{32}O_{16}$	594.5	0.89	Not observed	Current study
Poly(ethylene glycol)	$C_{2n}H_{4n+2}O_{n+1}$	600	0.54	$89.5 \pm 6.3$	Current study
Poly(ethylene glycol) bis(carboxymethyl) ether	$C_{2n+4}H_{4n+6}O_{n+5}$	600	0.63	$92.0 \pm 6.3$	You et al. (2013)
Maltopentaose	$C_{30}H_{52}O_{26}$	829	0.87	Not observed	Current study
Poly(ethylene glycol)	$C_{2n}H_{4n+2}O_{n+1}$	900	0.53	$92.9 \pm 6.4$	Current study
Maltoheptaose	$C_{42}H_{72}O_{36}$	1153	0.86	Not observed	Current study

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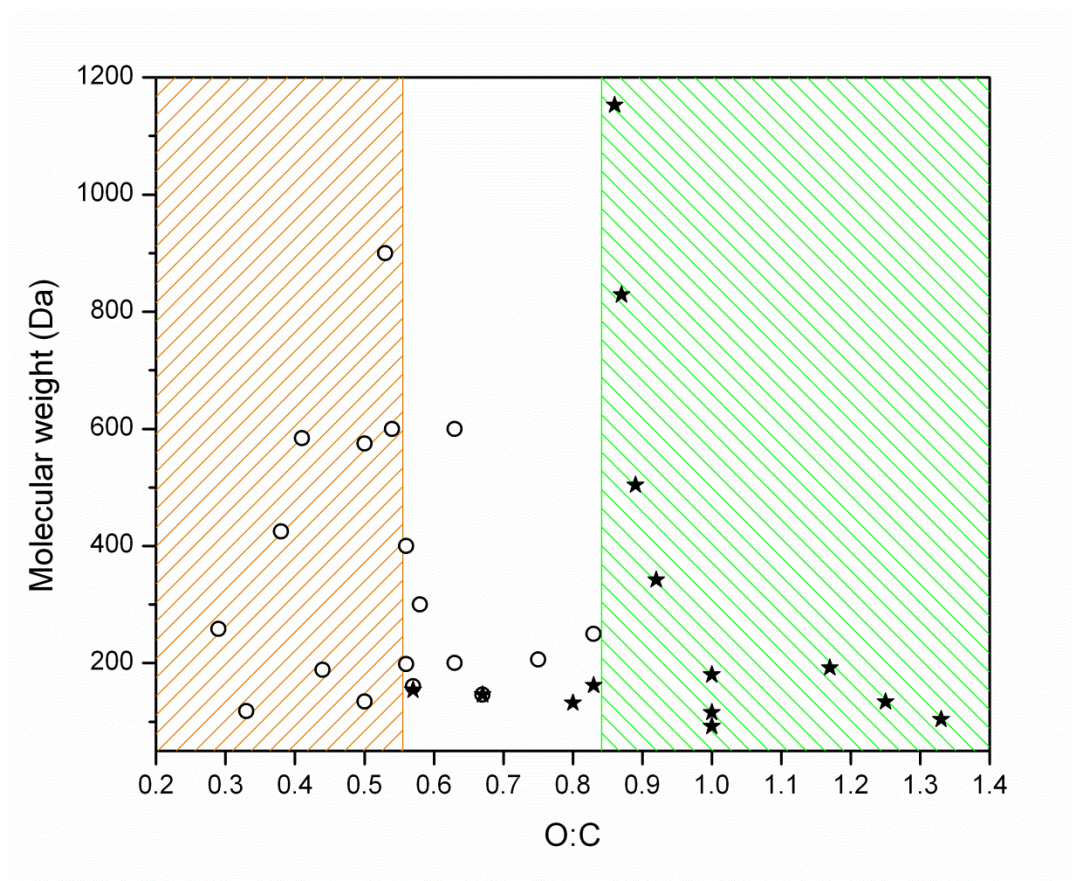
724 **Table 4.** Combined data set used to determine the effect of temperature on SRH. This includes  
 725 the measurements at  $244 \pm 1$  K,  $263 \pm 1$  K and  $278 \pm 1$  K in the current studies (Table 2) and  
 726 results from You et al. (2013) at  $290 \pm 1$  K. OIR =  $2.0 \pm 0.1$  in all the experiments. Uncertainties  
 727 are 95% confidence intervals considering  $\sigma$  of multiple SRH measurements and the uncertainty  
 728 from the calibration.

Compound	O:C	SRH (%) at different temperatures			
		$244 \pm 1$ K	$263 \pm 1$ K	$278 \pm 1$ K	$290 \pm 1$ K
2,5-hexanediol	0.33	$84.0 \pm 8.3$	$84.6 \pm 6.5$	$88.0 \pm 6.2$	$88.8 \pm 7.1^a$
Poly(propylene glycol)	0.38	$87.7 \pm 6.5$	$89.4 \pm 6.7$	$92.5 \pm 6.2$	$94.1 \pm 6.7^a$
Poly(ethylene glycol) diacrylate	0.5	$88.5 \pm 7.0$	$90.4 \pm 7.2$	$95.0 \pm 6.2$	$94.7 \pm 6.2$
Poly(ethylene glycol) 900	0.53	$89.2 \pm 9.2$	$88.7 \pm 6.2$	$91.8 \pm 6.3$	$92.9 \pm 6.4^a$
$\alpha$ ,4-dihydroxy-3-methoxybenzeneacetic acid	0.56	$76.0 \pm 6.3$	$67.3 \pm 8.7$	$72.3 \pm 6.4$	$72.6 \pm 6.3^a$
Diethylmalonic acid	0.57	$89.8 \pm 5.6$	$87.0 \pm 6.7$	$88.6 \pm 6.3$	$89.2 \pm 4.2^a$
3,3-dimethylglutaric acid	0.57	$98.2 \pm 4.3$	$88.5 \pm 6.3$	$88.5 \pm 6.3$	$89.1 \pm 6.9^a$
2,5-hydroxybenzoic acid	0.57	Not observed	Not observed	Not observed	Not observed <sup>a</sup>
Poly(ethylene glycol) 300	0.58	$85.6 \pm 9.7$	$83.6 \pm 6.5$	$85.6 \pm 6.4$	$87.6 \pm 6.4^a$
Poly(ethylene glycol) 200	0.63	$71.3 \pm 6.2$	$77.2 \pm 6.3$	$79.7 \pm 6.2$	$79.8 \pm 7.4^a$
Poly(ethylene glycol) bis(carboxymethyl) ether 600	0.63	$87.8 \pm 7.1$	$90.4 \pm 6.2$	$90.4 \pm 6.6$	$92.0 \pm 6.3^a$
2-methylglutaric acid	0.67	$76.7 \pm 6.6$	$76.2 \pm 6.3$	$76.6 \pm 6.2$	$75.3 \pm 6.4^a$
2,2-dimethylsuccinic acid	0.67	Not observed	Not observed	Not observed	Not observed <sup>a</sup>
Diethyl-L-tartrate	0.75	$86.9 \pm 7.3$	$85.0 \pm 6.5$	$87.4 \pm 4.1$	$90.2 \pm 6.6^a$
Glutaric acid	0.8	Not observed	Not observed	Not observed	Not observed <sup>a</sup>
Levogluconan	0.83	Not observed	Not observed	Not observed	Not observed <sup>a</sup>
Raffinose	0.89	Not observed	Not observed	Not observed	Not observed
Glycerol	1	Not observed	Not observed	Not observed	Not observed <sup>a</sup>
Citric acid	1.17	Not observed	Not observed	Not observed	Not observed <sup>a</sup>
Malonic acid	1.33	Not observed	Not observed	Not observed	Not observed <sup>a</sup>

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730 <sup>a</sup> Data taken from You et al. (2013). All other data are from this study

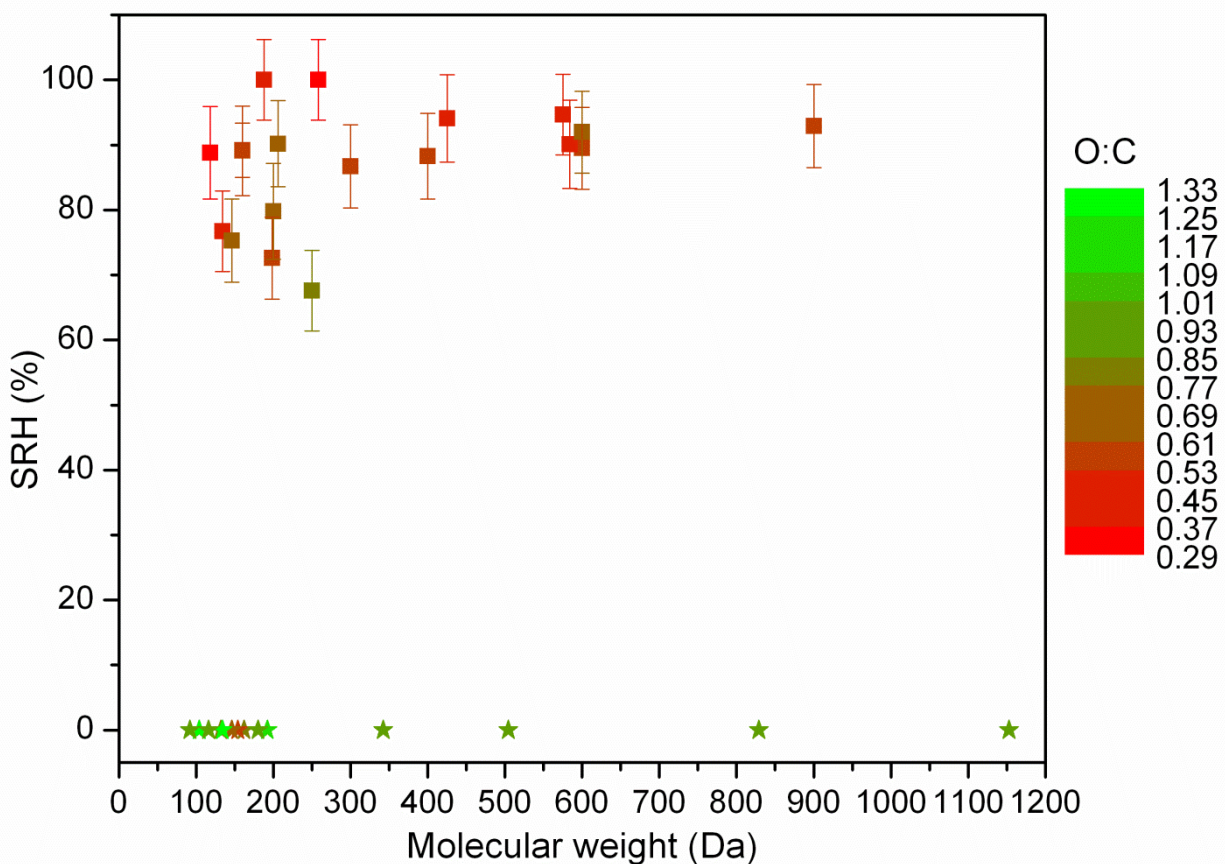
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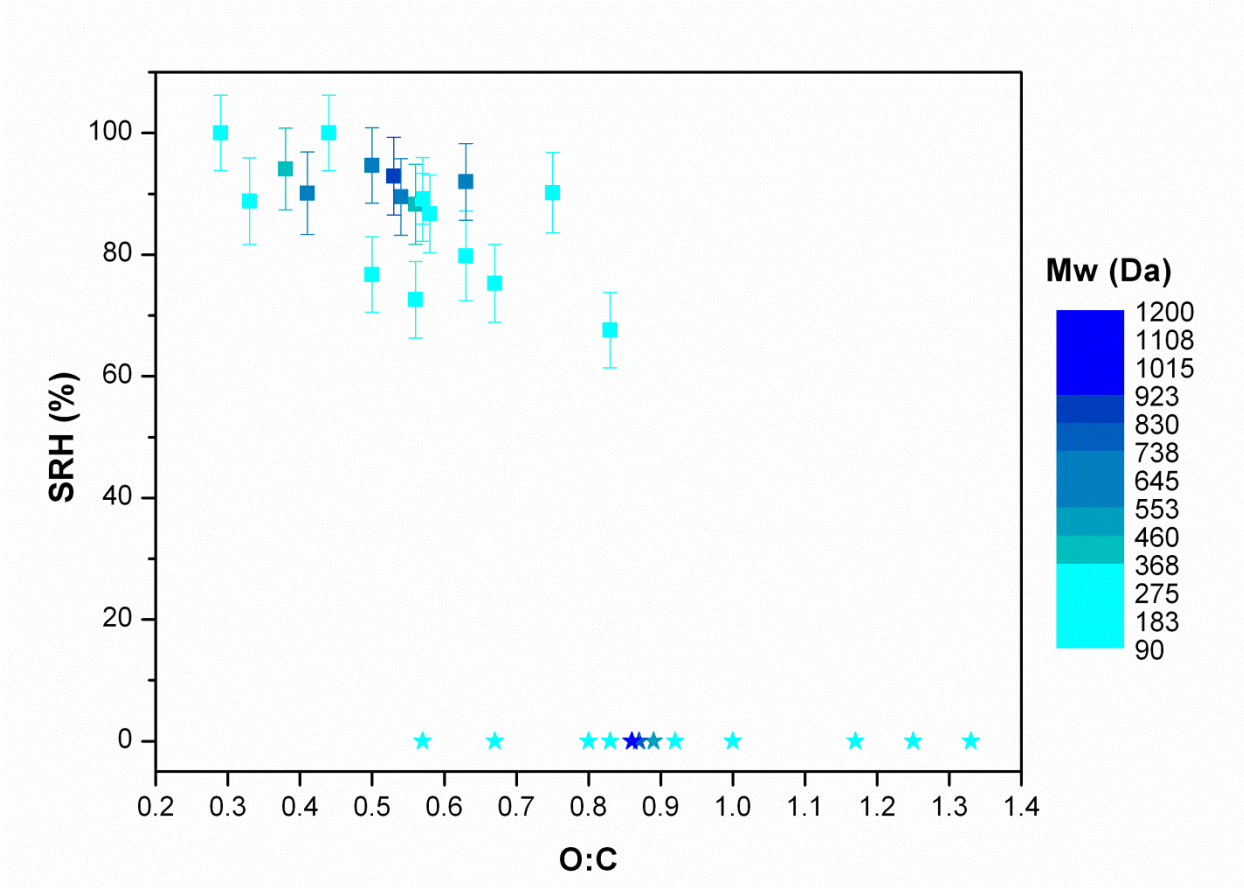
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735 **Figure 1** The effect of molecular weight and O:C of the organic species on the occurrence of  
736 liquid-liquid phase separation in mixed organic-ammonium sulfate particles ( $\text{OIR} = 2.0 \pm 0.1$ ).  
737 Data plotted are from the current study and You et al. (2013), and are summarized in Table 3.  
738 Open circles indicate liquid-liquid phase separation was observed, while stars indicate liquid-  
739 liquid phase separation was not observed. The orange hatched region corresponds to the  
740 molecular weight and O:C of the organic species when liquid-liquid phase separation was always  
741 observed, and the green hatched region corresponds to the molecular weight and O:C of the  
742 organic species when liquid-liquid phase separation was never observed.  
743



745 **Figure 2.** SRH as a function of molecular weight of organic species in the particles at  $290 \pm 1$  K.  
 746 The SRH results are from the current study and You et al. (2013) (see Table 3). The colors  
 747 represent the O:C of different organic species. Squares represent SRH of particles in which  
 748 liquid-liquid phase separation was observed. Bars for the squares are 95% confidence intervals  
 749 considering  $\sigma$  of multiple SRH measurements and the uncertainty from the calibration. Stars  
 750 indicate that liquid-liquid phase separation was not observed. OIR =  $2.0 \pm 0.1$  in all the  
 751 experiments.  
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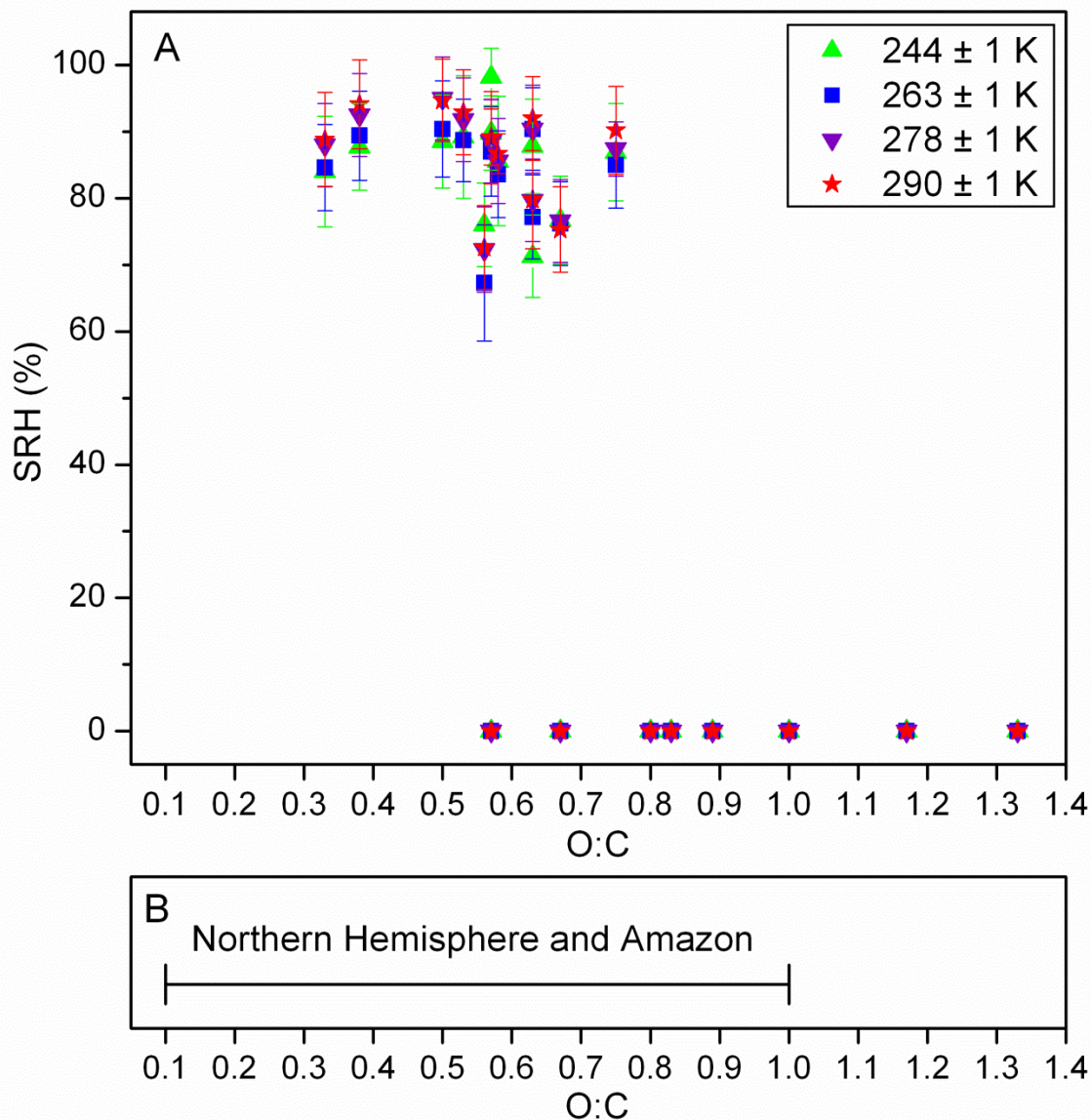
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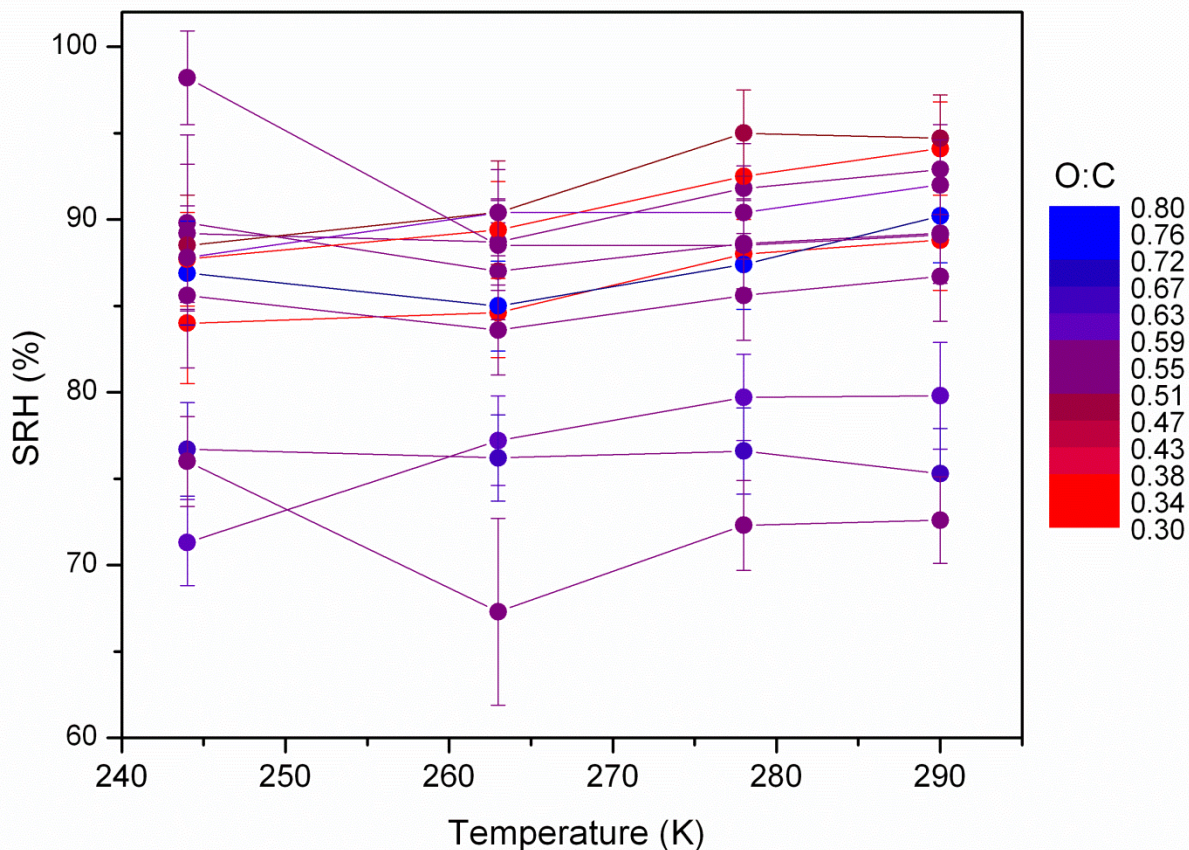
**Figure 3.** SRH as a function of O:C of the organic species at  $290 \pm 1$  K. The SRH results are from the current study and You et al. (2013) (see Table 3). The colors represent the molecular weight of the different organic species. Squares represent the SRH of particles in which liquid-liquid phase separation was observed. Bars for the squares are 95% confidence intervals considering  $\sigma$  of multiple SRH measurements and the uncertainty from the calibration. Stars indicate liquid-liquid phase separation was not observed. OIR =  $2.0 \pm 0.1$  in all the experiments.





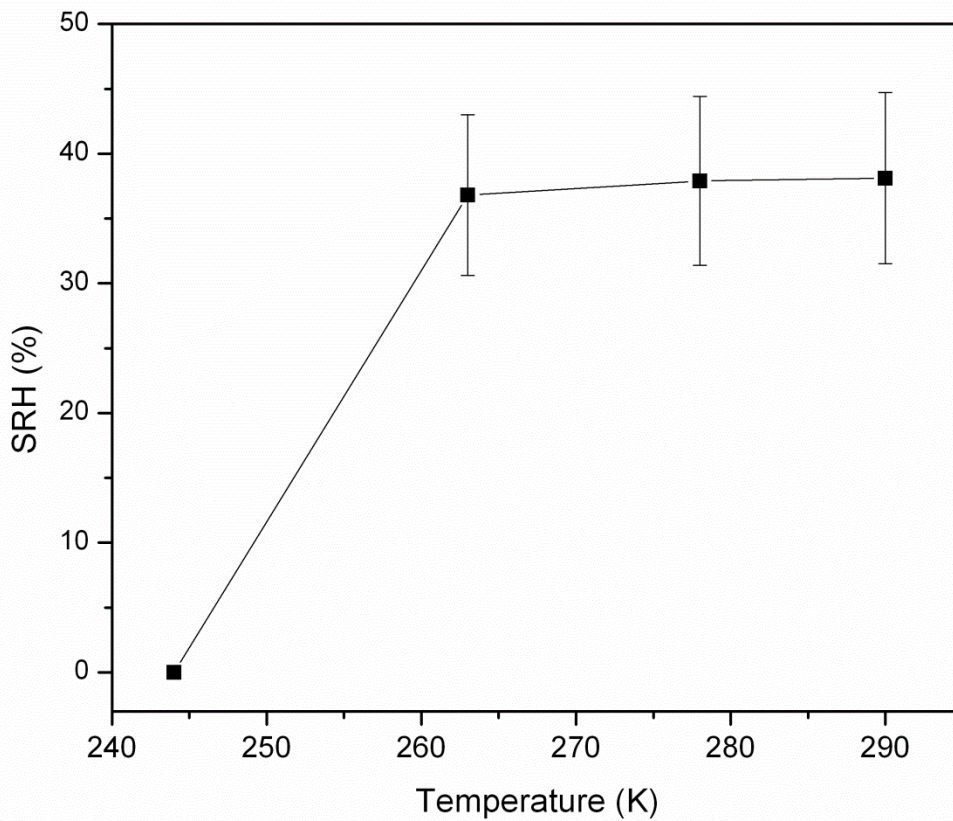
764  
 765 **Figure 4.** A SRH of mixed organic-ammonium sulfate particles as a function of O:C measured at  
 766 four different temperatures. Different symbols represent the different temperatures. Bars for the  
 767 data are 95% confidence intervals considering  $\sigma$  of multiple SRH measurements and the  
 768 uncertainty from the calibration. Data at SRH= 0% indicate liquid-liquid phase separation was  
 769 not observed. Data plotted are summarized in Table 4. The OIR =  $2.0 \pm 0.1$  in all the  
 770 experiments. B Range of the average O:C of organic material in particles from measurements at  
 771 many locations in the Northern Hemisphere and the Amazon.

772



773  
 774 **Figure 5.** Summary of SRH as a function of temperature for twelve types of mixed organic-  
 775 ammonium sulfate particles which underwent liquid-liquid phase separation. Data plotted were  
 776 taken from Table 4. Bars for the data are 95% confidence intervals considering  $\sigma$  of multiple  
 777 SRH measurements and the uncertainty from the calibration. Colors represent the O:C values of  
 778 different organic species in the particles. OIR =  $2.0 \pm 0.1$  in all the experiments.

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780

781 **Figure 6** SRH as a function of temperature for particles containing  $\alpha$ ,4-dihydroxy-3-  
782 methoxybenzeneacetic acid mixed with ammonium bisulfate. Bars for the data are 95%  
783 confidence intervals considering  $\sigma$  of multiple SRH measurements and the uncertainty from the  
784 calibration. Data at  $290 \pm 1$  K was taken from You et al. 2013.

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