

2 **Henry's Law Constant and Overall Mass Transfer Coefficient for**
3 **Formaldehyde Emission from Small Water Pools under**
4 **Simulated Indoor Environmental Conditions**

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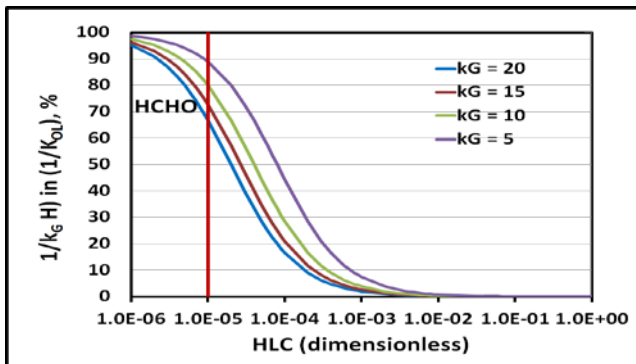
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13 **ABSTRACT:** The Henry's law constant (HLC) and the overall mass transfer coefficient
14 are both important parameters for modeling formaldehyde emissions from aqueous
15 solutions. In this work, the apparent HLCs for aqueous formaldehyde solutions were
16 determined in the concentration range from 0.01 % to 1 % (w/w) and at different
17 temperatures (23, 40 and 55 °C) by a static headspace extraction method. The aqueous
18 solutions tested included formaldehyde in water, formaldehyde-water with nonionic
19 surfactant, TergitolTM NP-9, and the anionic surfactant, sodium dodecyl sulfate. Overall,
20 the HLCs that were measured ranged from 8.93×10^{-6} to 1.12×10^{-4} (gas-
21 concentration/aqueous-concentration, dimensionless). Fourteen small chamber tests were

22 conducted with the formaldehyde solution in a small pool. By applying the measured
23 HLCs, the overall liquid-phase mass transfer coefficients (K_{OLS}) were determined to be in
24 the range of 8.12×10^{-5} to 1.10×10^{-4} m/h, and the overall gas-phase mass transfer
25 coefficients were between 2.84 and 17.9 m/h. The influence of the formaldehyde
26 concentration, temperature, agitation rate, and surfactant on the HLC and the K_{OL} was
27 investigated. The results from this study can provide data useful to support development
28 of source modeling for indoor formaldehyde originating from the use of household
29 products that contain formaldehyde-releasing biocides.

30 (Table of Contents Graphic:)



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33 KEYWORDS: formaldehyde, formaldehyde-releasing biocides, Henry's law constant,
34 surfactant, mass transfer coefficient, emission

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38 INTRODUCTION

39 Formaldehyde-releasing biocides are active ingredients used as antimicrobials for
40 professional and consumer products, such as adhesives, metalworking fluids, coatings,
41 construction compounds, surfactant/detergent solutions and emulsions.^{1,2} The biocides
42 slowly release formaldehyde (HCHO) by hydrolysis. The maximum concentrations of
43 formaldehyde generated from the biocides in products are on the order of 0.01 % to 0.1 %
44 (w/w).³ Human exposure to formaldehyde can occur via direct ingestion, dermal contact
45 and inhalation. The emission of formaldehyde during use of consumer products could be
46 a source for inhalational exposure to formaldehyde. The U.S. Environmental Protection
47 Agency (EPA) has been developing a Reregistration Eligibility Decision¹ for
48 antimicrobial biocides that release formaldehyde under the Federal Insecticide,
49 Fungicide, and Rodenticide Act (FIFRA). Indoor source emission models are useful tools
50 to support this development by predicting the formaldehyde emissions from household
51 systems that use products containing formaldehyde-releasing biocides. The key input
52 parameters for these models are the Henry's law constant (HLC) and the overall mass
53 transfer coefficient.

54

55 Formaldehyde in water is a complex system. The solubility of formaldehyde in
56 water is much greater than the solubility of common volatile organic compounds (VOCs).
57 Formaldehyde exists in an aqueous solution as a mixture of monomeric formaldehyde,
58 methylene glycol (CH₂(OH)₂) and a variety of formaldehyde oligomers. Under normal
59 conditions, the majority of the formaldehyde in an aqueous solution exists as methylene
60 glycol with monomeric formaldehyde present only in low concentrations of less than 0.1

61 %.⁴ The state of equilibrium in the solution is determined by the temperature, the
62 formaldehyde concentration and other conditions of the solution. In addition, equilibria
63 between the gaseous formaldehyde over and in the liquid solution exist. As one of the
64 most important components of various household cleaning products, surfactants can
65 comprise between 15 and 40 % of a total detergent formulation.⁵ The presence of
66 surfactants makes the composition of the formaldehyde aqueous solution even more
67 complicated.

68

69 The emission of formaldehyde from the aqueous surface to the air is driven by the
70 difference between the gaseous formaldehyde concentration at the surface of the liquid
71 and in the bulk air, which is dictated by the HLC and overall mass transfer coefficient.
72 The HLC predicts the partitioning of a chemical between the aqueous and gaseous phases
73 for dilute solutions. Experimentally determined HLC values for formaldehyde under
74 various conditions have been reported in the literature.⁶⁻¹¹ While a few references are
75 available for ascertaining the HLC of formaldehyde in water systems, little information is
76 available regarding the partitioning of formaldehyde from surfactant solutions.

77

78 The concept of an overall mass transfer coefficient is well established based on
79 the two-resistance theory, which expresses the overall resistance as the weighted sum of
80 the liquid and air resistances.^{12, 13} The overall mass transfer coefficient can be estimated
81 by using a regression analysis procedure to fit a mass transfer model to the experimental
82 data. The lumped overall mass transfer coefficient, the overall mass transfer coefficient
83 times the interfacial surface area (K_OA), was reported in a previous study on VOC

84 emissions from water to indoor air for the washing machine, the dishwasher, the shower
85 and the bathtub. ¹⁴ Guo and Roache ¹³ determined the overall liquid-phase mass transfer
86 coefficient (K_{OL}) experimentally for pollutant emissions from still aqueous solutions
87 under simulated indoor environmental conditions for six chemicals. Seyfioglu and
88 Odabasi ¹⁵ measured the average overall gas-phase mass transfer coefficients (K_{OG}) of
89 formaldehyde to be 21 ± 8 and 9 ± 4 m/h from laboratory and field experiments,
90 respectively, in a study of formaldehyde dry deposition into a water surface sampler. No
91 experimentally determined overall mass transfer coefficient data for formaldehyde
92 suitable for use in indoor emission models exists. ¹⁶

93
94 The aim of this study was to determine the HLC and the overall mass transfer
95 coefficient for formaldehyde needed to model the behavior of formaldehyde released
96 from biocides under various conditions of usage. A headspace method with 2, 4-
97 dinitrophenylhydrazine (DNPH) cartridge collection and extraction was developed and
98 applied to measure formaldehyde HLC in different aqueous solutions with and without
99 surfactants over a range of temperatures and formaldehyde concentrations. The
100 experimentally determined HLCs were used to estimate the overall mass transfer
101 coefficients by applying a mass transfer model to the small chamber test data. The HLC
102 and overall mass transfer coefficient obtained from this work can be used as key input
103 parameters to evaluate and develop improved emission models for formaldehyde from
104 biocides in occupational and residential settings.

105

106 MATERIALS AND METHODS

107 **Measurement of Henry's Law Constants.** The dimensionless HLC is defined by

108 Equation (1):

$$109 \quad H = \frac{C_G}{C_L} \quad (1)$$

110 where H is the dimensionless HLC, and C_G and C_L are equilibrium formaldehyde

111 concentrations ($\mu\text{g}/\text{m}^3$) in the gas and liquid phase, respectively.

112

113 The gas phase formaldehyde concentration was measured in triplicates using the
114 headspace method. The tests were conducted in 250 mL and 1L amber bottles with
115 aqueous formaldehyde solutions, with or without surfactant. The formaldehyde solutions
116 (0.01 to 1 %, w/w) were prepared by diluting a 37 % (w/w) formaldehyde/water solution.
117 Each sample bottle was sealed with a cap containing a polytetrafluoroethylene/silicone
118 septum. The bottles were inverted ten times to mix the solution and then placed on an
119 orbital shaker (Model 3500, VWR International, Radnor, PA, USA) located inside a
120 temperature-controlled incubator (Model 39900, Forma Scientific, Marietta, OH, USA),
121 for a minimum of 16 hours. For the preparation of the formaldehyde solution containing a
122 surfactant, the surfactant was first added to the sample bottle to make a solution of 15 %
123 surfactant in water by weight and agitated briefly to dissolve the surfactant fully prior to
124 the addition of formaldehyde. Gas phase formaldehyde, 30 mL from the 250 mL or 100
125 mL from a 1 L bottle, was withdrawn from the headspace using a gastight syringe and a
126 Sep-Pak DNPH silica plus short cartridge (Waters, Milford, MA, USA) at a rate of
127 approximately 1 mL/s. The DNPH cartridges were extracted with 5 mL of acetonitrile

128 and analyzed on an Agilent 1200 High Performance Liquid Chromatograph (HPLC) with
129 a Diode Array and Multiple Wavelength Detector (DAD) equipped with a Zorbax Eclipse
130 XDB-C18 column (4.6 x 150 mm x 3.5 μ m). The formaldehyde concentration in the
131 liquid was calculated from the known concentration of formaldehyde spiked into the
132 solution and verified by a liquid derivatization method followed by a modified version of
133 EPA Method 8315A described in the Supporting Information (SI).

134

135 The concentrated formaldehyde solution (37 % w/w in water), sodium dodecyl
136 sulfate (SDS, \geq 99.0%) and TergitolTM NP-9 surfactants were purchased from Sigma-
137 Aldrich (Sigma-Aldrich, St. Louis, MO, USA). Propanal (98.8 %) and pentanal (99.1 %)
138 were purchased from Chem Service, Inc. (West Chester, PA, USA). HPLC-grade water
139 and acetonitrile (Fisher Scientific, Fair Lawn, NJ, USA) were used for all extraction and
140 analysis procedures. The aldehyde/ketone-DNPH stock standard (Cerilliant Corporation,
141 Round Rock, TX, USA) was used for HPLC calibration. The formaldehyde-DNPH
142 standard purchased from Supelco (Bellefonte, PA, USA) was used as an internal audit
143 program (IAP) standard.

144

145 **Small Chamber Tests.** Fourteen small chamber tests were conducted to measure
146 formaldehyde emissions from small pools in 53-L stainless steel chambers that
147 conformed to ASTM Standard Guide D5116-10¹⁷. The chambers were placed in a
148 temperature-controlled incubator (Model SCN4-52, So-Low Environmental Equipment
149 Co., Inc., Cincinnati, Ohio, USA). The relative humidity was monitored for the clean dry
150 air to the chamber inlet and the air inside the chamber. A 3.8-cm computer cooling fan

151 (RadioShack, Fort Worth, TX, USA) was placed in the chamber to provide mixing inside
152 the chamber. A 140-mL round dish containing the test solution was situated in the center
153 of the chamber bottom. Both still and agitation tests were performed. For agitation tests, a
154 stir bar was placed in the dish on the stir plate with the speed setting of 3 to 6.5 (Model
155 PC-410, Corning Incorporated Life Sciences, Tewksbury, MA, USA). A setting range of
156 3.0-6.5 agitated the test solution at acceptable levels without producing erratic movement
157 or spillage of the solutions. The test conditions are summarized in Table 1. Air samples
158 from the chamber were collected on DNPH cartridges from the glass sampling manifold
159 connected to the chamber outlet at about 300 mL/min for 10 to 30 min at different time
160 intervals. Prior to the test, samples of the empty chamber background and the chamber
161 background after the pool with water was placed in the chamber overnight were
162 collected. After the tests, the formaldehyde in aqueous solutions in the pool was analyzed
163 by the liquid derivatization approach mentioned above.

164

165 The air speed during the small chamber test was determined 1 cm above the
166 solution surface using a Brüel & Krær Indoor Climate Analyzer (Model 1213, Nærum,
167 Denmark) in a chamber assembled similarly to the chamber used for tests. The speed of
168 the stir bar, revolutions per minute (RPM), was measured using a video camera, digital
169 timer and VLC Media Player software (<http://www.videolan.org/index.html>, VideoLAN
170 organization).

171

172 **Quality Assurance and Control.** The HPLC/DAD was calibrated for DNPH-
173 formaldehyde in the range of 0.03 to 15 µg/mL. An IAP standard was analyzed after the

174 calibration to evaluate the instrument performance in terms of accuracy and precision. A
175 daily calibration check (DCC) consisting of the midlevel calibration standard was
176 analyzed each day. The acceptable recovery range for both DCC and IAP was 85-115 %.

Table1. Summary of 0.04 % HCHO small chamber tests

Test ID	Surfactant ^a	Agitation rate		Chamber conditions \pm % RSD			Test duration (hr)	HCHO solution evaporation (g/hr)	
		Setting	RPM ^b	Air velocity (cm/s) \pm % RSD	% RH	Temperature ($^{\circ}$ C)			ACH (/h)
T1	None	0	0	13.8 \pm 5.8	55.8 \pm 2.7	22.7 \pm 0.1	0.93 \pm 1.09	73.4	0.54
T2	None	0	0	13.8 \pm 5.8	55.2 \pm 1.7	22.7 \pm 0.1	0.96 \pm 3.17	24.9	0.58
T5	None	3	90	13.7 \pm 5.9	61.5 \pm 2.9	23.0 \pm 0.1	0.94 \pm 0.41	24.8	0.61
T3	None	5.7	256	13.8 \pm 8.0	68.5 \pm 2.0	23.0 \pm 0.1	0.83 \pm 0.52	24.9	0.64
T4	None	6.5	372	13.9 \pm 7.3	62.1 \pm 2.8	23.0 \pm 0.2	0.94 \pm 0.13	23.6	0.66
T6	None	3	90	13.7 \pm 5.9	55.1 \pm 9.7	40.6 \pm 1.0	0.91 \pm 1.65	23.1	1.66
T7	None	3	90	13.7 \pm 5.9	46.7 \pm 7.0	54.7 \pm 2.0	0.90 \pm 4.76	23.4	2.96
T8	None	6.5	372	13.9 \pm 7.3	63.7 \pm 2.6	24.3 \pm 0.2	0.95 \pm 0.45	25.4	0.74
T9	NP-9	0	0	13.8 \pm 5.8	59.6 \pm 1.6	22.9 \pm 0.6	0.95 \pm 0.24	23.1	0.61
T10	SDS	0	0	13.8 \pm 5.8	61.3 \pm 0.88	22.9 \pm 0.4	0.95 \pm 0.16	24.4	0.63
T11	SDS	0	0	13.8 \pm 5.8	60.5 \pm 1.1	22.9 \pm 0.5	0.95 \pm 0.33	24.5	0.62
T12	SDS	3	90	13.7 \pm 5.9	64.3 \pm 2.1	23.0 \pm 0.4	0.94 \pm 0.39	24.4	0.66
T13	SDS	6.5	372	13.9 \pm 7.3	63.3 \pm 2.5	23.1 \pm 0.4	0.94 \pm 0.26	24.3	0.65
T14	SDS	6.5	372	13.9 \pm 7.3	66.1 \pm 2.1	23.1 \pm 0.4	0.95 \pm 1.1	24.3	0.68

^a. 15 % Surfactant. ^b. RPM is revolutions per minute.

177 RESULTS AND DISCUSSION

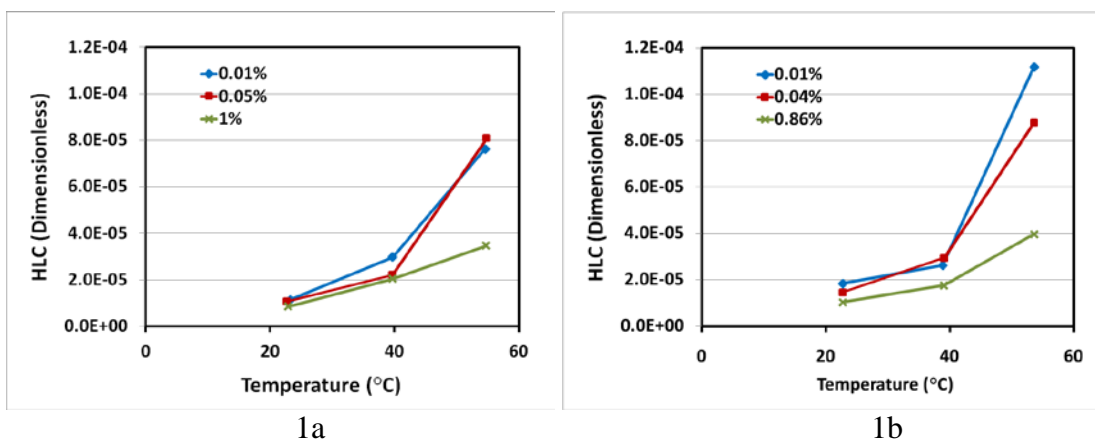
178 **Henry's Law Constants for Formaldehyde.** The Henry's law constant measured
179 in this study was the apparent HLC, since C_L in Equation (1) was the total concentration
180 of formaldehyde solubilized in a solution including monomers and various oligomers. At
181 least three replicate experiments were conducted under each set of experimental
182 conditions to provide a measure of the precision of the experimental method. The percent
183 relative standard deviations (% RSD) associated with the average HLC values were less
184 than 15 %. The liquid formaldehyde concentration measured using the DNPH
185 derivatization method showed a recovery of 95-99 % of formaldehyde that had been
186 spiked into the solution. Thus the known concentration of formaldehyde spiked into the
187 solution was used to calculate the liquid phase formaldehyde concentration. The DNPH
188 headspace method was validated by determining the HLCs for pentanal and propanal and
189 comparing the results with the literature. The measured HLC for 0.04 % pentanal was
190 5.94×10^{-3} and the measured HLC for 0.04 % propanal was 3.21×10^{-3} at 23 °C. The
191 data reported by Zhou and Mopper⁷ were 6.30×10^{-3} for pentanal and 3.35×10^{-3} for
192 propanal in the solutions ranging from 0.05 to 5 μ M at 25 °C. The HLC values of
193 propanal and pentanal obtained from our experiments agreed well with the literature data.

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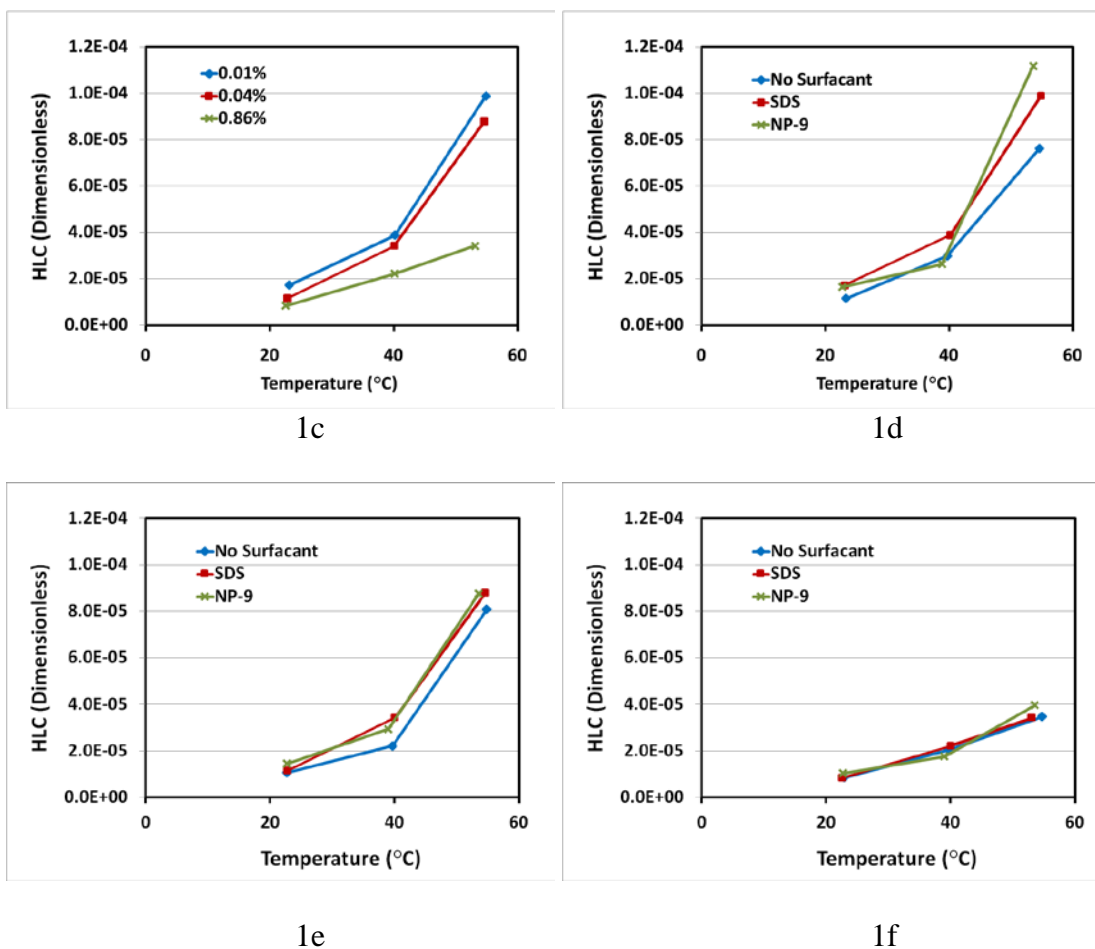
195 The HLCs of formaldehyde solutions are summarized in Tables S1 and S2. The
196 measured solutions included 0.01, 0.02, 0.03, 0.04, 0.05, 0.06, 0.07, 0.08, 0.5, 0.6, 0.8
197 and 1 % formaldehyde in water at 23 °C, 0.01, 0.05, and 1 % formaldehyde in water at 40
198 and 55 °C, and 0.01, 0.02, 0.04 and 0.86 % formaldehyde with SDS or NP-9 surfactant at
199 23, 40 and 55 °C. The critical micelle concentration (cmc) of SDS in pure water at 25 °C

200 is 0.0082 M^{18} and that of NP-9 is 60 ppm^{19} . Thus, 15 % (w/w) surfactant solution is
201 much higher than the cmc. Overall, the measured HLCs are in the range of 8.93×10^{-6} to
202 1.04×10^{-4} . At $23 \text{ }^\circ\text{C}$, for HCHO concentrations between 0.01 % and 1 %, the HLCs
203 ranged from 8.51×10^{-6} to 1.23×10^{-5} with the average of $1.06 \times 10^{-5} \pm 17 \%$ (% RSD) in
204 water solution. At the same temperature, the HLC value decreased slightly with
205 increasing formaldehyde concentrations in both water and surfactant solutions (Figures
206 1a-1c and data in Tables S1 and S2). The HLC values measured under similar conditions
207 agree reasonably well with the literature data, i. e. 1.38×10^{-5} from Betterton and
208 Hoffmann,⁶ 1.20×10^{-5} from Zhou and Mopper,⁷ 8.6×10^{-6} from Staudinger and
209 Roberts^{8,9}, 7.87×10^{-6} from Seyfioglu and Odabasi¹⁰ at $25 \text{ }^\circ\text{C}$ and 7.81×10^{-6} from
210 Allou et al.¹¹ at $20 \text{ }^\circ\text{C}$.

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Figure 1. Formaldehyde HLCs measured under different conditions. (1a. No surfactant, 1b. With NP-9, 1c. With SDS, 1d. 0.01 % HCHO, 1e. 0.04 % HCHO, 1f. 1 % HCHO)

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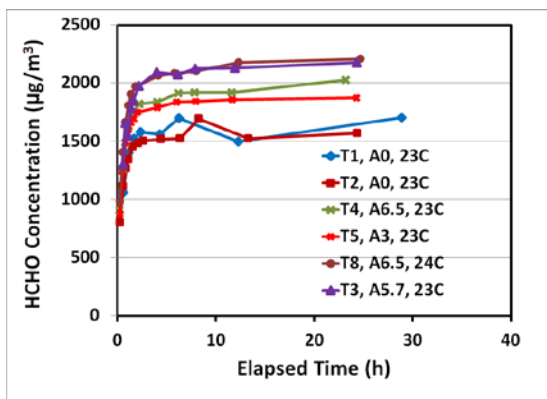
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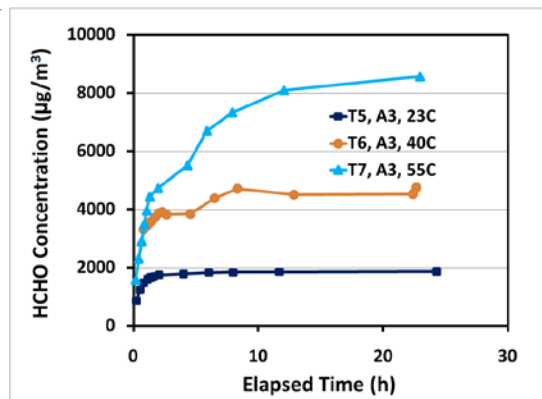
Temperature affects the HLC value markedly. As shown in Figure 1a, the HLC value increased as the temperature increased in the formaldehyde water solution. The same trend was observed for solutions with surfactants (Figures 1b and 1c). The effect of surfactants on the HLC of formaldehyde at different temperatures is illustrated in Figures 1d to 1f. At the same temperature, HLC value increased when surfactants were added to the solution, especially when the formaldehyde concentration was between 0.01 and 0.04 %. However, the effect was not significant between the nonionic surfactant, NP-9

233 and the anionic surfactant, SDS. When formaldehyde concentration increased to
234 approximately 1 %, the difference of HLC between no surfactant and surfactant solution
235 was minimal, contrary to the literature data for VOCs, such as toluene, trichloroethene
236 and hexane.^{18, 20, 21} Research has shown that the addition of a surfactant to the aqueous
237 VOC solution resulted in an HLC value smaller than the HLC value of solutions without
238 surfactant. In general, adding surfactants to solution creates hydrophobic zones to which
239 VOCs partition. As more hydrophobic zones are created, the partitioning of VOCs into
240 the headspace of the system becomes less and thus the apparent HLC decreases.
241 Formaldehyde surfactant solution did not follow this rule, as shown in our experiments.
242 The surfactants did not reduce the volatility of formaldehyde, possibly because
243 formaldehyde is hydrophilic while other VOCs, e.g. toluene and hexane, are more
244 hydrophobic. The higher solubility of formaldehyde in water was not impacted by the
245 addition of the surfactant. In the formaldehyde solution, the methylene glycol and
246 oligomers would be considerably more hydrophilic than monomeric formaldehyde and
247 thus much less likely to participate directly in the gas-liquid phase interaction. The added
248 surfactant may break the equilibrium between the different forms of formaldehyde and
249 result in more monomeric formaldehyde released to the gas phase when the formaldehyde
250 concentration in water is low. When formaldehyde concentration was up to 1 %, the
251 impact of surfactants on the equilibrium became less significant. Overall, the effect of
252 added surfactant on the HLC for formaldehyde is insignificant because of the hydrophilic
253 nature of the surfactants. More work is needed to confirm the observation and investigate
254 the possible reasons.
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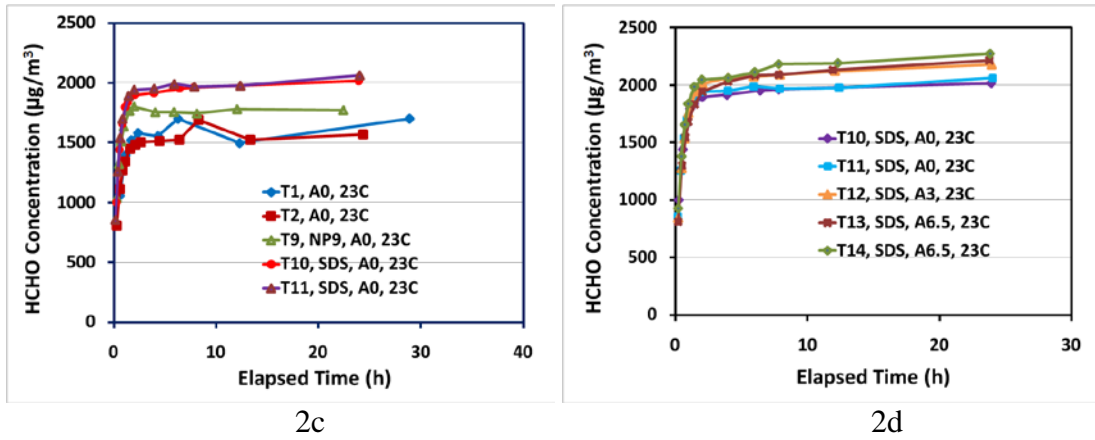
256 **Formaldehyde Emissions from Liquid Pools.** A total of 14 small chamber tests
257 were reported, including three replicate tests, T1 and T2, T10 and T11, and T13 and T14.
258 The time-concentration profiles of all tests are presented in Figure 2. The data from
259 replicate tests implies good precision for the experiments (% RSD < 15 %). At 23 °C, the
260 formaldehyde gas phase concentration quickly reached steady state after two hours, but it
261 took a much longer time when the water pool temperature increased to 40 and 55 °C. The
262 formaldehyde emission was strongly affected by the HLC. Formaldehyde from solutions
263 with surfactants had a higher emission concentration than solutions without surfactants.
264 The faster the agitation rate, the higher the formaldehyde emission concentration from the
265 solutions including water only and water with surfactants. However, in the presence of
266 the surfactant, SDS (Figure 1d), the impact of the agitation rate on the formaldehyde
267 emissions was less apparent than in the solution without the surfactant. After 41 (T6) and
268 55°C (T7) tests, especially the 55 °C test, the condensed aqueous solution was observed
269 on the unheated glass sampling manifold. The measured gas phase formaldehyde
270 concentration was therefore lower than the formaldehyde concentration actually emitted
271 inside the chamber.
272



273
274 2a



2b



275
276

277 **Figure 2.** Formaldehyde time - concentration profiles from small chamber tests (2a. No
278 surfactant, 2b. No surfactant, 2c. With and without surfactants, 2d. With SDS. A0, A3,
279 A5.7, and A6.5 is agitation setting at 0, 3, 5.7, and 6.5, respectively)
280

281 **Determination of the Mass Transfer Coefficients.** According to the two-
282 resistance theory,^{12, 13} the rate of formaldehyde emission from an aqueous solution is
283 determined by either equation (2) or (3):

284
$$R = SK_{OL}(C_L - C_G / H) \quad (2)$$

285
$$R = SK_{OG}(HC_L - C_G) \quad (3)$$

286 where R is the formaldehyde emission rate (mg/h), S is the source area (m²), H is the
287 dimensionless HLC, and the overall liquid-phase mass transfer coefficient (K_{OL}, m/h)
288 and overall gas-phase mass transfer coefficient, K_{OG} (m/h) are defined by equations (4)
289 and (5), respectively.

290
$$\frac{1}{K_{OL}} = \frac{1}{k_L} + \frac{1}{k_G H} \quad (4)$$

291
$$\frac{1}{K_{OG}} = \frac{H}{k_L} + \frac{1}{k_G} \quad (5)$$

292 where k_L (m/h) is the liquid phase-mass transfer coefficient and k_G (m/h) is the gas-phase
293 mass transfer coefficient. Thus, determination of the overall mass transfer coefficients
294 (K_{OL} or K_{OG}) is key to estimating the formaldehyde emission rate. In this study, the
295 overall liquid-phase mass transfer coefficient was determined by fitting the following
296 mass balance model (Equations 6–8) to the chamber air formaldehyde concentration data
297 with the overall liquid-phase mass transfer coefficient being the only unknown
298 parameter.¹³

$$299 \quad V \frac{dC_G}{dt} = SK_{OL}(C_L - C_G / H) - QC_G \quad (6)$$

$$300 \quad \frac{dW_L}{dt} = -SK_{OL}(C_L - \frac{C_G}{H}) \quad (7)$$

$$301 \quad C_L = \frac{W_L}{V_L - \frac{r_w t}{\rho_w}} \quad (8)$$

302 where V is the chamber volume (m^3), t is the time (h), S is the source area (m^2), Q is the
303 air exchange flow rate (m^3/h), W_L is the amount of formaldehyde in the liquid phase (μg),
304 V_L is the initial volume of liquid (m^3), r_w is the experimentally determined water
305 evaporation rate (g/h) and ρ_w is the density of water (g/m^3). Data fitting software
306 SCIENTIST (Version 2.0, MicroMath Scientific Software, Salt Lake City, UT, USA) was
307 used for the non-linear regression. The estimated overall liquid-phase mass transfer
308 coefficients are presented in Table 2 (column 3).

Table 2. Summary of mass transfer coefficients (m/h)

Test ID	From experimental data					From PARAMS program				
	H (Dimensionless)	K _{OL-HCHO}	K _{OG-HCHO}	k _{G-H₂O}	k _{G-HCHO}	k _{L-HCHO}	k _{G-HCHO}	k _{L-HCHO}	K _{OL-HCHO}	K _{OG-HCHO}
T1	9.86×10 ⁻⁶	8.39×10 ⁻⁵	8.51	14.8	10.9	3.84 ×10 ⁻⁴	14.6	7.92 ×10 ⁻³	1.42 ×10 ⁻⁴	14.4
T2	9.86×10 ⁻⁶	8.12 ×10 ⁻⁵	8.23	15.3	11.2	3.06 ×10 ⁻⁴	14.6	7.92 ×10 ⁻³	1.42 ×10 ⁻⁴	14.4
T5	9.86×10 ⁻⁶	1.01 ×10 ⁻⁴	10.3	19.0	14.5	3.48 ×10 ⁻⁴	14.5	NA ^a	NA	NA
T3	9.86×10 ⁻⁶	1.09 ×10 ⁻⁴	11.0	23.0	16.8	3.16 ×10 ⁻⁴	14.5	NA	NA	NA
T4	9.86×10 ⁻⁶	1.09 ×10 ⁻⁴	11.1	19.7	14.5	4.58 ×10 ⁻⁴	14.6	NA	NA	NA
T6	2.22×10 ⁻⁵	2.24 ×10 ⁻⁴	10.1	13.9	10.3	1.60 ×10 ⁻²	14.2	NA	NA	NA
T7	8.11×10 ⁻⁵	2.30 ×10 ⁻⁴	2.84	10.0	7.34	3.75 ×10 ⁻⁴	16.0	NA	NA	NA
T8	9.86×10 ⁻⁶	1.32 ×10 ⁻⁴	13.4	19.7	14.5	1.84 ×10 ⁻⁴	14.7	NA	NA	NA
T9	1.46×10 ⁻⁵	8.65 ×10 ⁻⁵	5.93	18.4	13.5	1.54 ×10 ⁻⁴	14.6	7.92 ×10 ⁻³	2.08 ×10 ⁻⁴	14.2
T10	1.15×10 ⁻⁵	1.10 ×10 ⁻⁴	9.57	19.7	14.4	3.26 ×10 ⁻⁴	14.6	7.92 ×10 ⁻³	1.65 ×10 ⁻⁴	14.3
T11	1.15×10 ⁻⁵	1.13 ×10 ⁻⁴	9.80	19.0	14.0	3.79 ×10 ⁻⁴	14.6	7.92 ×10 ⁻³	1.65 ×10 ⁻⁴	14.3
T12	1.15×10 ⁻⁵	1.17 ×10 ⁻⁴	10.2	22.3	16.3	3.13 ×10 ⁻⁴	14.6	NA	NA	NA
T13	1.15×10 ⁻⁵	1.14 ×10 ⁻⁴	9.95	21.2	15.5	3.18 ×10 ⁻⁴	14.7	NA	NA	NA
T14	1.15×10 ⁻⁵	1.26 ×10 ⁻⁴	11.0	24.4	17.9	3.24 ×10 ⁻⁴	14.7	NA	NA	NA

^a. NA is not applicable since PARAMS program applies only to still water solutions.

310 Once K_{OL} is determined, K_{OG} can then be calculated by

$$311 \quad K_{OG} = K_{OL} / H \quad (9)$$

312 The k_G for formaldehyde was inferred from the k_G for water vapor. The water
313 vapor concentrations in the chamber obtained from relative humidity data were used to
314 determine the water gas phase mass transfer coefficient, k_{G-H_2O} (m/h) with the following
315 mass balance model:

$$316 \quad V \frac{dC}{dt} = Sk_{G-H_2O}(C_v - C) + Q(C_{in} - C) \quad (10)$$

$$317 \quad \frac{dW}{dt} = -Sk_{G-H_2O}(C_v - C) \quad (11)$$

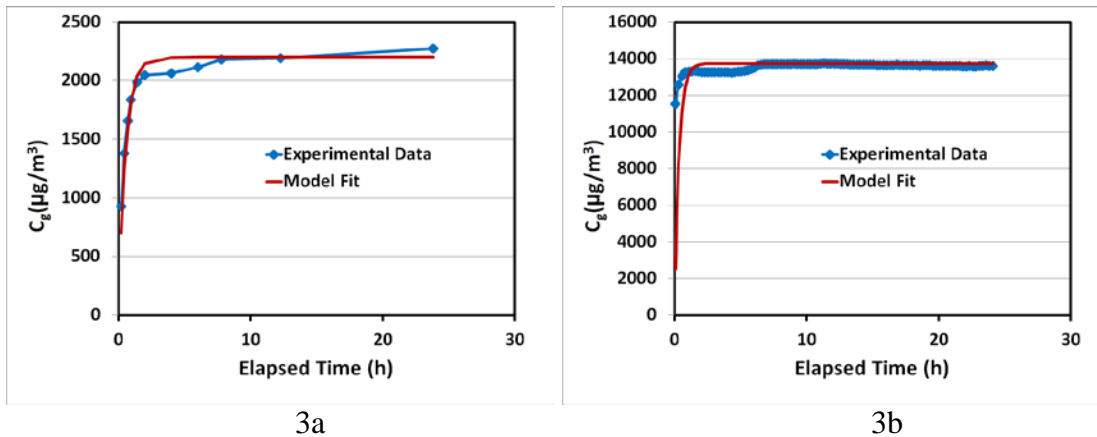
$$318 \quad RH = \frac{C}{C_v} \quad (12)$$

319 where C is the water concentration in the air (mg/m^3), C_v is the water vapor pressure in
320 concentration units (mg/m^3), C_{in} is the initial water concentration in the air (mg/m^3), W is
321 the amount of water in the water pool (mg), and RH is the relative humidity. Based on the
322 Sherwood number equation,²² under the same physical conditions, the formaldehyde gas
323 phase mass transfer coefficient, k_{g-HCHO} , can then be calculated by:

$$324 \quad \frac{k_{G-H_2O}}{k_{G-HCHO}} = \left(\frac{D_{a-H_2O}}{D_{a-HCHO}} \right)^{2/3} \quad (13)$$

325 where D_{a-H_2O} and D_{a-HCHO} are, respectively, the diffusivities of water and formaldehyde in
326 air (m^2/h), which can be calculated using the available computer program, PARAMS.²²

327 With known K_{OL} , K_{OG} , k_G and H , it is straightforward to calculate the k_L , through the
328 equation (4) or (5). The K_{OL} , K_{OG} , k_G and k_L results are presented in Table 2. The
329 coefficients of determination, R^2 , were greater than 0.99 for all data fits of formaldehyde
330 and water (Figure 3). In comparison with the experimentally determined k_G , PARAMS
331 was used to estimate the formaldehyde k_G based on the Sherwood number method. When
332 there was no agitation in the water pools, k_L was also calculated using PARAMS, and
333 thus K_{OG} and K_{OL} were calculated through equations (4) or (5). These results are listed in
334 Table 2 as well. The data show that they are in the same magnitude range. The
335 formaldehyde K_{OL} ranged from 8.12×10^{-5} to 2.30×10^{-4} m/h and K_{OG} was between 2.84
336 and 11.1 m/h from our experiments. The difference between the experimental and
337 PARAMS estimated data confirms the caution from the literature ¹³ that compounds with
338 smaller HLCs tend to have greater relative errors from predictions. The Sherwood
339 method implemented in PARAMS is for laminar flow while turbulent flow perhaps is
340 more realistic for the air over agitated water. Our experimental values of K_{OG} are closer
341 to the data reported by Seyfioglu and Odabasi ¹⁵ and are larger than the K_{OG} data used by
342 McCready et al. ¹⁶ in their evaluation of potential exposure to formaldehyde air emissions
343 from a washing machine using the indoor air quality and inhalation exposure (IAQX)
344 model ²³.

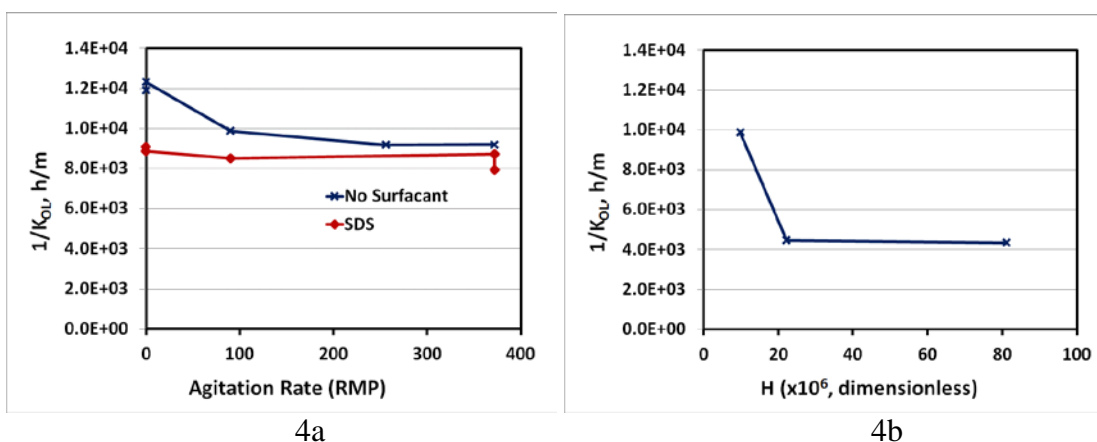


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Figure 3. An example of goodness of fit of the model to data – T14 small chamber test, formaldehyde emission (3a) and water vapor (3b).

351 The overall mass transfer coefficients (K_{OL} and K_{OG}) reflect the combined effects
352 of k_L , k_G and H as shown in equations (4) and (5). The HLC for formaldehyde is less than
353 10^{-4} . The gas-phase resistance, $1/(k_g H)$, is a significant factor for formaldehyde
354 emissions. The K_{OL} values presented in Table 2 fall in a narrow range despite different
355 experimental conditions, such as temperature, surfactants, and agitation rate. However,
356 the data in Figure 4 showed that the overall mass transfer resistance ($1/K_{OL}$) decreased
357 when (1) the agitation rate was increased, (2) the surfactant was added, and (3) the HLC
358 value was increased due to the temperature change from 23 to 40 to 55 °C. The results in
359 Figure 4a also demonstrate that the effect of the agitation rate is less significant for the
360 SDS solution than for the solution without surfactants. When the agitation rate was
361 increased to above 90 RPM (A3), the decrease of $1/K_{OL}$ was much smaller, possibly
362 implying that the complex mixture reached a new equilibrium once the agitation rate
363 reached a certain point.

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Figure 4. Overall liquid-phase mass transfer resistance ($1/K_{OL}$) under different agitation rates (4a) and Henry's law constants (4b).

371 The experimentally determined formaldehyde Henry's law constants and overall
372 mass transfer coefficients in this work **can be used to improve indoor formaldehyde**
373 **source emission models**. More work is needed to investigate how the surfactants impact
374 equilibrium partitioning of formaldehyde between gas and liquid phase. Because the data
375 collected in this study were under well-controlled environmental conditions, a cautionary
376 note is appropriate when applying the data from this study to realistic environmental
377 conditions. It is also beyond the scope of this work to link the data to human exposure
378 and potential health risks.

379 **ASSOCIATED CONTENT**

380 **Supporting information.** The liquid formaldehyde analysis by the DNPH
381 derivatization method and HLC data are presented.

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389 **DISCLAIMER**

390 The views expressed in this article are those of the authors and do not necessarily
391 represent the views or policies of the U.S. EPA. Mention of trade names or commercial
392 products does not constitute endorsement or recommendation for use by the U.S. EPA.

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464 **Supporting Information**

465

466 Modified EPA Method 8315A for liquid formaldehyde analysis

467 Solution from the bottle (1 mL) was transferred to a 125 mL Erlenmeyer flask to which 4
468 mL of citrate buffer (pH 5.0) and 6 mL of DNPH solution (3.00 mg/mL) were added. The
469 samples were mixed on the orbital shaker inside the incubator at a temperature of
470 approximately 23 °C for exactly one hour. The sample was removed from the mixer,
471 extracted with three 20 mL portions of dichloromethane, dried over sodium sulfate, and
472 concentrated to approximately 1.5 mL using a RapidVap[®] vacuum evaporation system
473 (Model 79100-00, Labconco Corporation, Kansas City, MO, USA) with a nitrogen gas
474 flow. The concentrate was transferred and brought to volume in a 10 mL volumetric flask
475 using acetonitrile for HPLC analysis.

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Table S1. Henry's Law Constants of formaldehyde in water

Weight %	Temperature (°C)	H (dimensionless) ± % RSD	N^a
0.01	23.14	1.55E-05 ± 1.99	3
0.02	22.64	1.08E-05 ± 2.82	6
0.03	22.65	9.70E-06 ± 3.20	3
0.04	22.65	9.86E-06 ± 4.30	3
0.05	22.66	1.06E-05 ± 5.72	3
0.06	22.62	1.23E-05 ± 5.24	3
0.07	22.62	1.06E-05 ± 0.20	3
0.08	22.59	1.10E-05 ± 9.92	3
0.51	22.94	8.93E-06 ± 2.00	3
0.59	22.54	9.33E-06 ± 3.68	4
0.78	22.51	1.04E-05 ± 4.53	4
1.01	22.94	8.51E-06 ± 1.88	3
0.01	39.70	2.98E-05 ± 9.85	3
0.01	54.56	7.63E-05 ± 5.50	3
0.05	39.70	2.22E-05 ± 2.55	3
0.05	54.91	8.11E-05 ± 7.50	6
1.01	39.70	2.05E-05 ± 8.32	2
1.01	54.71	3.47E-05 ± 4.54	3

^a. Number of samples.

Table S2. Henry's Law Constants (dimensionless) of formaldehyde in water solution containing Surfactants (N=3)

Weight %	Temperature (°C)	15 % SDS, H ± % RSD	15 % NP-9, H ± % RSD
0.01	23.11	1.71E-05 ± 4.27	1.64E-05 ± 8.66
0.01	40.13	3.88E-05 ± 2.76	2.63E-05 ± 11.71
0.01	54.83	9.88E-05 ± 9.62	1.12E-04 ± 12.13
0.02	22.65	1.34E-05 ± 7.99	1.35E-05 ± 9.75
0.04	22.83	1.15E-05 ± 3.79	1.46E-05 ± 15.31
0.04	40.07	3.42E-05 ± 3.77	2.94E-05 ± 11.75
0.04	54.56	8.79E-05 ± 6.43	8.77E-05 ± 12.58
0.86	22.56	8.33E-06 ± 5.48	1.03E-05 ± 1.38
0.86	40.05	2.22E-05 ± 9.31	1.76E-05 ± 9.16
0.86	53.07	3.41E-05 ± 1.30 ^a	3.96E-05 ± 5.00

^a. Only duplicate samples were analyzed.