Electronic Supplementary Information

# Ion-strength and pH dependent reactivities of ascorbic acid toward ozone in aqueous micro-droplets studied by aerosol optical tweezers

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## I. Experimental conditions

**Table S1.** Experimental conditions of every reaction kinetic measurements at pH ≈ 2. *P*: pressure of gaseous ozone pressure; *r*: radius; *H*: Henry's law coefficient; *I*: ionic strength.

| Expt. # | *P* / ppm | $[AH_2]_0$ / M | *r* / μm | *H* / mol $m^{-3}$ $atm^{-1}$ | *I* / M | pH | gradient / $10^{-4}$ $s^{-1}$ | $k_2$ / $10^5$ $M^{-1}s^{-1}$ |
|---|---|---|---|---|---|---|---|---|
| 01 | 42 | 3.55 | 3.44 | 4.12 | 1.07 | 1.8 | 13.9±0.1 | 6.69±0.82 |
| 02 | 97 | 3.29 | 2.95 | 4.44 | 0.99 | 1.8 | 29.3±0.2 | 3.30±0.39 |
| 03 | 110 | 3.82 | 2.71 | 3.81 | 1.15 | 1.8 | 27.2±0.3 | 2.89±0.50 |
| 04 | 18.4 | 1.63 | 3.00 | 6.96 | 0.50 | 1.9 | 9.06±0.29 | 2.13±0.21 |
| 05 | 18.1 | 2.36 | 2.36 | 5.56 | 0.72 | 1.9 | 9.72±0.26 | 2.94±0.31 |
| 06 | 17.6 | 2.77 | 2.45 | 4.90 | 0.85 | 1.8 | 10.3±0.3 | 5.88±0.60 |
| 07 | 3.96 | 2.58 | 2.12 | 5.20 | 0.79 | 1.8 | 3.33±0.12 | 7.45±0.85 |
| 08 | 2.98 | 3.79 | 2.48 | 3.58 | 1.16 | 1.8 | 2.26±0.04 | 26.0±0.3 |
| 09 | 3.12 | 1.79 | 2.12 | 6.61 | 0.55 | 1.9 | 5.17±0.25 | 12.4±0.2 |
| 10 | 3.47 | 3.43 | 2.78 | 3.98 | 1.06 | 1.8 | 2.46±0.02 | 20.8±0.2 |
| 11 | 3.51 | 2.51 | 1.92 | 5.30 | 0.77 | 1.9 | 4.15±0.13 | 11.3±0.1 |
| 12 | 1.88 | 1.96 | 2.10 | 6.31 | 0.59 | 1.9 | 3.52±0.20 | 18.9±0.3 |
| 13 | 1.85 | 5.57 | 2.31 | 2.08 | 1.68 | 1.7 | 2.80±0.06 | 393±36 |
| 14 | 1.72 | 5.23 | 2.19 | 2.31 | 1.58 | 1.7 | 2.10±0.04 | 174±17 |
| 15 | 1.70 | 3.23 | 2.68 | 4.24 | 0.99 | 1.8 | 1.35±0.02 | 15.7±1.4 |
| 16 | 1.60 | 3.64 | 2.36 | 3.73 | 1.12 | 1.8 | 1.45±0.04 | 31.8±3.1 |
| 17 | 1.13 | 3.13 | 2.79 | 4.39 | 0.95 | 1.8 | 1.28±0.02 | 39.4±3.6 |
| 18 | 1.18 | 3.42 | 2.21 | 4.01 | 1.04 | 1.8 | 1.64±0.04 | 50.2±5.2 |
| 19 | 1.44 | 3.38 | 2.08 | 4.06 | 1.03 | 1.8 | 1.08±0.01 | 12.5±1.3 |

**Table S2.** Experimental conditions of every reaction kinetic measurements at pH ≈ 6. *P*: pressure of gaseous ozone; *I*: ionic strength; $pH_i$: pH measured before reaction; $pH_f$: pH measured after reaction.

| Expt. # | *P* / ppm | $[AH_2]_0$ / M | *r* / μm | *H* / mol $m^{-3}$ $atm^{-1}$ | *I* / M | $pH_i$ | $pH_f$ | gradient / $10^{-4}$ $s^{-1}$ | $k_2$ / $10^7$ $M^{-1}s^{-1}$ |
|---|---|---|---|---|---|---|---|---|---|
| 20 | 1.17 | 0.98 | 1.90 | 2.17 | 4.25 | 6.3 | 6.5 | 9.07 ± 2.29 | 11.1 ± 4.2 |
| 21 | 0.92 | 0.52 | 2.40 | 4.75 | 2.26 | 6.2 | 6.9 | 8.03 ± 1.71 | 2.48 ± 0.79 |
| 22 | 1.13 | 1.05 | 3.18 | 1.93 | 4.56 | 6.1 | 6.2 | 5.29 ± 0.84 | 15.5 ± 3.8 |
| 23 | 0.90 | 0.89 | 2.34 | 2.53 | 3.86 | 6.3 | 6.4 | 5.15 ± 0.97 | 6.08 ± 1.74 |
| 24 | 0.63 | 0.75 | 2.80 | 2.98 | 3.48 | 6.2 | 6.7 | 4.84 ± 0.42 | 9.54 ± 1.50 |
| 25 | 1.10 | 0.38 | 2.30 | 5.95 | 1.70 | 6.1 | 7.0 | 11.7 ± 0.51 | 1.58 ± 1.00 |
| 26 | 1.07 | 0.85 | 2.20 | 2.63 | 3.81 | 6.4 | 6.5 | 7.18 ± 1.83 | 6.63 ± 2.50 |
| 27 | 1.24 | 0.53 | 2.10 | 4.62 | 2.36 | 6.4 | 6.5 | 10.6 ± 0.35 | 1.97 ± 0.93 |
| 28 | 1.21 | 1.09 | 3.10 | 1.62 | 5.06 | 5.9 | 6.3 | 5.93 ± 1.15 | 23.6 ± 6.9 |
| 29 | 1.19 | 1.14 | 2.70 | 1.48 | 5.30 | 6.4 | 6.8 | 5.01 ± 0.98 | 16.6 ± 4.9 |

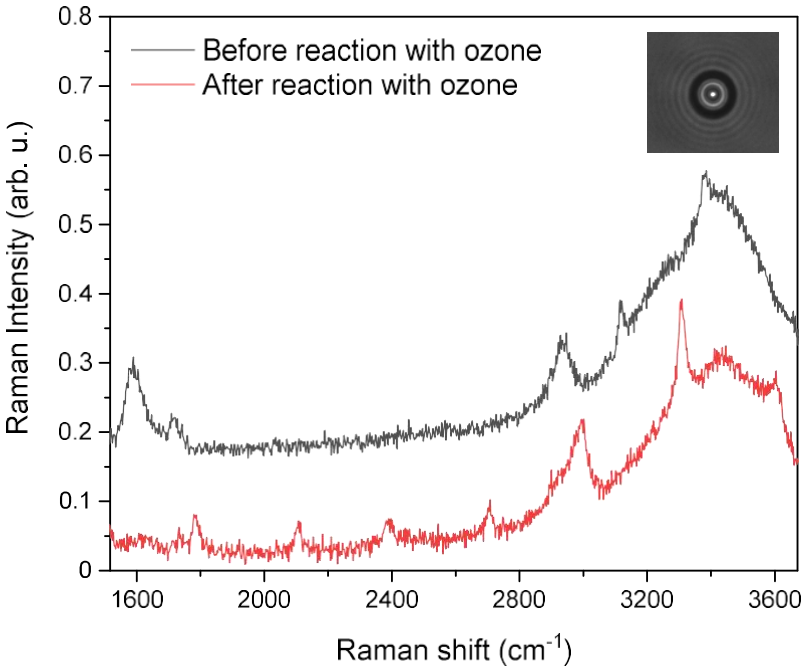


Figure S1. Representative Raman spectra of an optically trapped aqueous $AH_2$ droplet in pH ≈ 6 before (top data in black line) and after (bottom data in red line) the reaction with ozone at 90% RH. Two spectra are offset for clarity. Inset:

brightfield image of the droplet before the reaction with ozone.

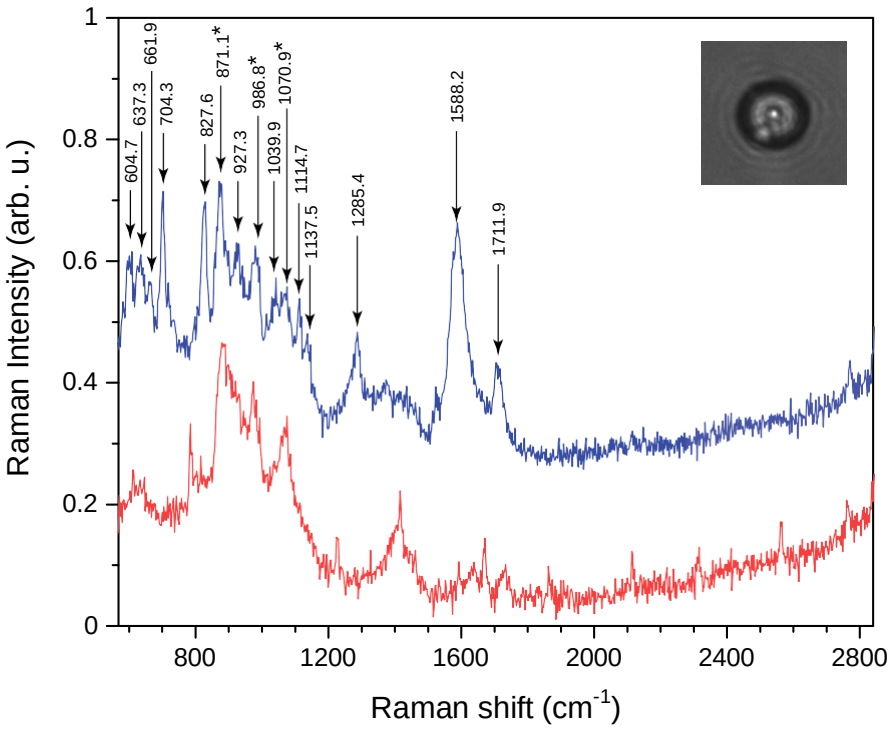


Figure S2. Representative Raman spectra of an optically trapped aqueous $AH_2$ droplet in pH ≈ 6 before (top data in black line) and after (bottom data in red line) the reaction with ozone at 90% RH. Two spectra are offset for clarity. The inset shows the brightfield image of the droplet before the reaction with ozone. The peak assignments (arrows with wavenumbers) without asterisk belong to aqueous $AH^-$ based on literature,[1] and three peak assignments with asterisks belong to phosphate, according to Figure S4. Note that the relatively sharp peaks in the spectra, particularly in the spectrum after the reaction, are CERS peaks.

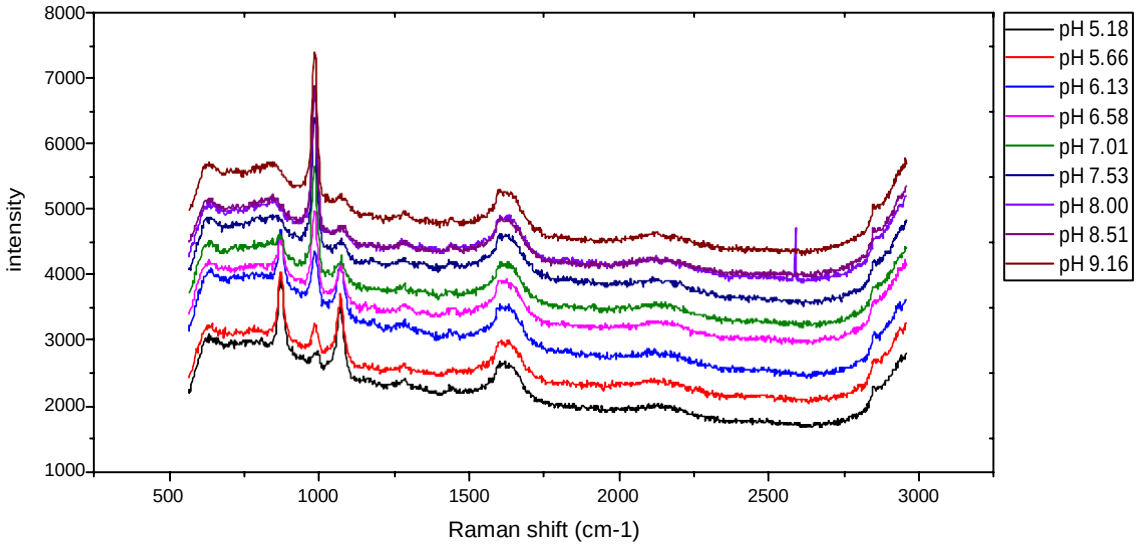


Figure S3. The Raman spectra of 0.5M bulk solutions of sodium phosphate adjusted to specific pH, excited by 532 nm.

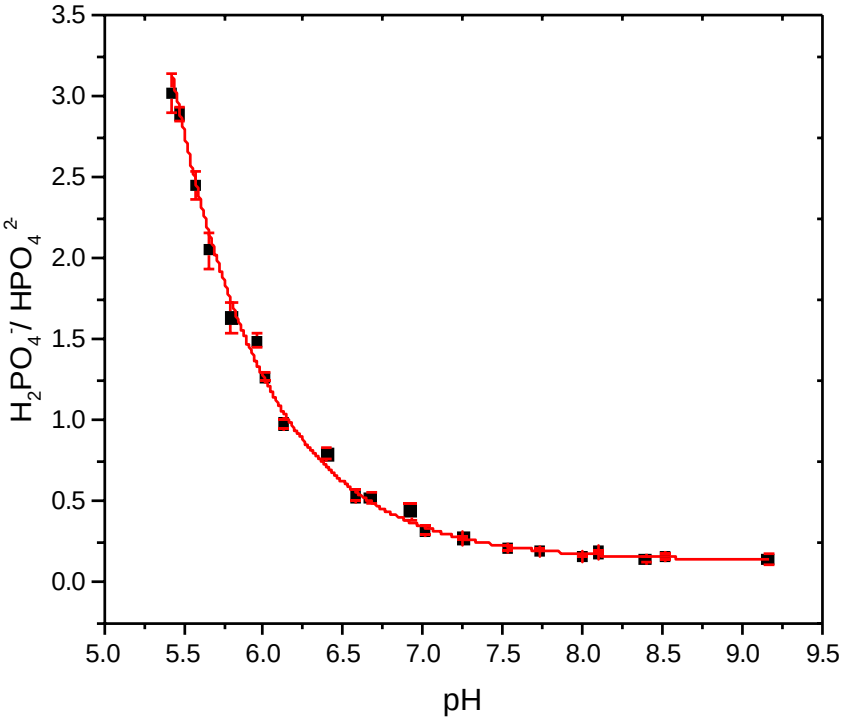


Figure S4. Calibration curve for the pH versus Raman peak area ratios of $H_2PO_4^-$ (874 $cm^{-1}$) and $HPO_4^{2-}$ (987 $cm^{-1}$), based on the results in Figure S3. The red curved line is the fit to the data (symbol) which yields the empirical relationship: $y = 0.1338 + 31869 \exp(-x/0.5856)$.

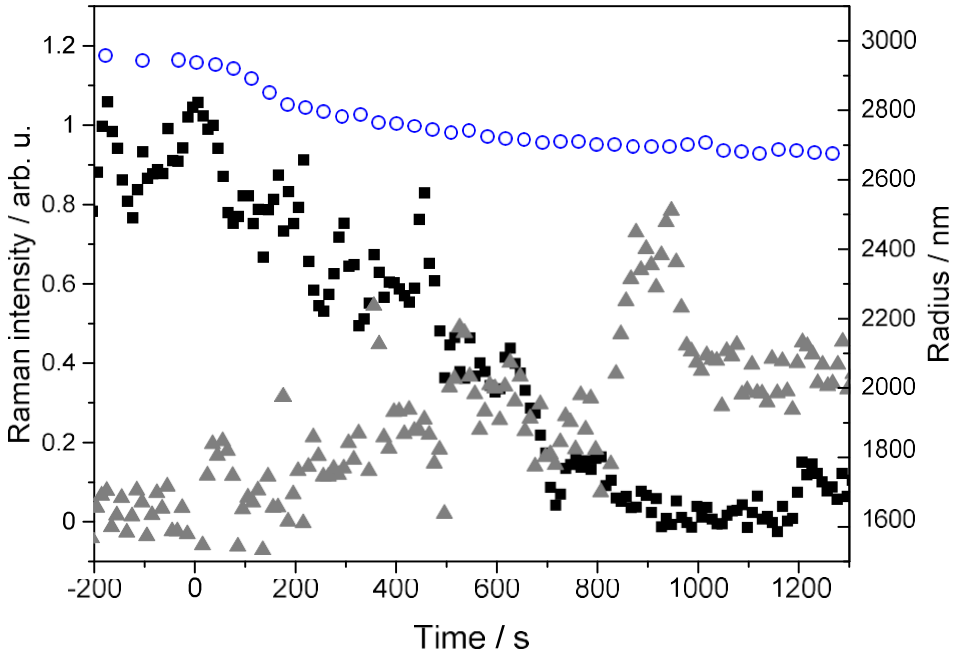


Figure S5. Representative time profiles of radius (circles) and integrated Raman intensities of a trapped $AH_2(aq)$ droplet of pH ≈ 6 (expt. 22) which was exposed to gaseous ozone after 0 second. The Raman intensities of $AH_2$ (squares) and products (triangles) were obtained from integrating the areas of the Raman peaks centered at 1590 $cm^{-1}$ and 3000 $cm^{-1}$, respectively. Most jumps in Raman intensities are ascribed to drifting CERS peaks.

**II. Effect of ionic strength on Henry's law constant**

Here we followed the methodology utilized by Weisenberger and Schumpe[2] to estimate the Henry's law coefficient of ozone in salt solutions, $H_S$, with Sechenov constants of ion $i$, $K_i$:

$$\log(\frac{H}{H_s}) = \sum_i K_i [i] = \sum_i (h_i + h_{O3})[i] \qquad \text{(S1)}$$

where $H$ is the Henry's law coefficient of ozone in pure water, $h_i$, is an ion-specific parameter, $h_{O3}$ is an ozone-specific parameter, and $[i]$ is the concentration of ion $i$. The values of $h_i$ for $i$ = $Na^+$, $Cl^-$, $H_2PO_4^-$ and $HPO_4^{2-}$ have been measured by Weisenberger and Schumpe.[2] We cannot find any value of $h_i$ for ascorbate in literature, and thus we assumed its value to be 0.1464 $m^3$/kmol, which is the value for $IO_4^-$, which has the same charge and similar molecular weight of ascorbate. The

expression for the Sechenov constant of ozone, $h_{O3}$, is assumed to be a linear function of the temperature $T$:

$$h_{O3} = h_{O3,0} + h_T(T - 298.15\text{K}) \quad \text{(S2)}$$

with $h_{O3,0}$ = 0.00396 m$^3$/kmol and $h_T$ = 0.00179 m$^3$/(kmol••K).[3] The temperature in this study is 298 K. For the case of the aqueous solution containing nonelectrolytes, such as free acid form of $AH_2$, the corresponding Sechenov constant $K_n$ can be expressed as:[4]

$$K_n = b_n + b_{O3,o} + b_{O3,T}(T - 298.15\text{K}) \quad \text{(S3)}$$

As we cannot find any literature value of $b_n$ for $AH_2$, we assume its value to be 4.81 × $10^{-4}$ m$^3$ kg$^{-1}$, which is the value for citric acid, which has the similar molecular weight of $AH_2$.

**III. Error analysis**

The percentage error of $[AH_2]_0$ is about 4%, which is attributed to fitting error of calibration curves. The error bar of the radius is assumed to be 0.15 μm, which is an averaged change of the radius during the reaction progress. The percentage error of the ozone pressure is 2.6%, which is the assumed maximum error of the measured UV absorption cross section of ozone at 250 nm estimated by literature.[5] The fitting of each normalized $[AH_2]^{1/2}$ time profile yield an fitting error bar for each fitted gradients listed in Tables S1 and S2. We propagate these error bars through the following equations:

$$\varepsilon^2 = \sum_i \varepsilon_i^2 \quad \text{(S4)}$$

where $\varepsilon$ is the percentage error of the bimolecular reaction rate coefficient or normalized Raman intensity, and $\varepsilon_i$ is the percentage error of each term required to derive the rate coefficient or the normalized Raman intensity. For the function of square root, such as $f = I^{1/2}$, we utilize the following equation to propagate the error of $I$:

$$\varepsilon_f = \frac{1}{2}\varepsilon_I \quad \text{(S5)}$$

where $\varepsilon_f$ and $\varepsilon_I$ are percentage errors of $f$ and $I$, respectively.

## IV. Droplet size dependence

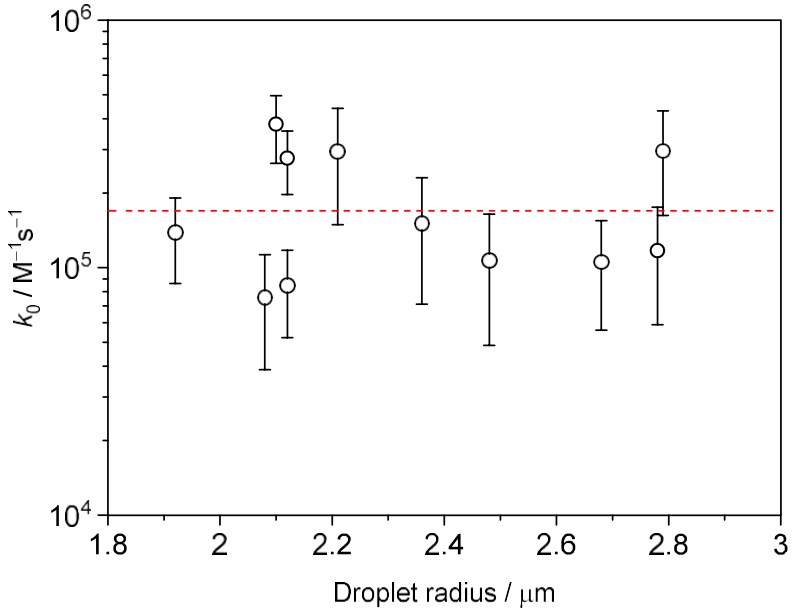


**Figure S6.** Bimolecular reaction rate coefficient corrected to zero ionic strength $k_0$ (symbols) of pH ≈ 2 plotted as a function of droplet radius. Dashed line: the fitted value of $k_0$ obtained from the fit in Figure 4.

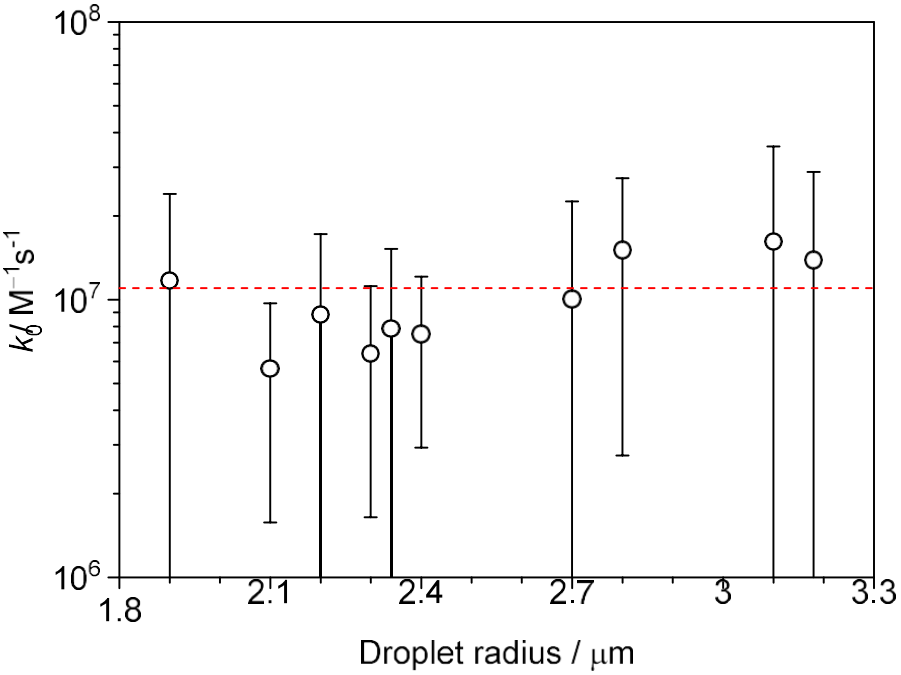


**Figure S7.** Bimolecular reaction rate coefficient corrected to zero ionic strength $k_0$ (symbols) of pH ≈ 6 plotted as a function of droplet radius. Dashed line: the

fitted value of $k_0$ obtained from the fit in Figure 5.

## References

[1] R.W. Berg, Appl. Spectrosc. Rev. **50**, 193 (2015).

[2] S. Weisenberger and A. Schumpe, AIChE J. **42**, 298 (1996).

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