Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.

Supplementary Information
for
Isotherm Model for Moisture-Controlled CO_2 Sorption

Yuta Kaneko and Klaus S. Lackner
School of Sustainable Engineering & the Built Environment
Arizona State University

1 Derivation of the approximate isotherm equation for negligible $[CO_2]$ and $[H^+]$ (S_{III})

When $[H^+]$ is negligible, $[OH^-]$ can be explicitly expressed as a function of $[CO_2]$ by solving the following quadratic equation:

$$2K_1K_2[CO_2][OH^-]^2 + (1 + K_1[CO_2])[OH^-] - [A] = 0 \tag{S.1}$$

Namely,

$$[OH^-] = \frac{-(1 + K_1[CO_2]) + \sqrt{(1 + K_1[CO_2])^2 + 8K_1K_2[CO_2][A]}}{4K_1K_2[CO_2]} \tag{S.2}$$

We can express θ using this explicit form of $[OH^-]$. Since K_1 always appears with $[CO_2]$, we define ζ for convenience as:

$$\zeta \equiv K_1[CO_2] \tag{S.3}$$

Then,

$$\begin{aligned}[OH^-] + K_2[OH^-]^2 &= \frac{-(1+\zeta) + \sqrt{(1+\zeta)^2 + 8\zeta K_2[A]}}{4\zeta K_2} \\ &\quad + K_2 \left\{ \frac{-(1+\zeta) + \sqrt{(1+\zeta)^2 + 8\zeta K_2[A]}}{4\zeta K_2} \right\}^2 \qquad \text{(S.4)} \\ &= (\zeta - 1)\frac{\sqrt{(1+\zeta)^2 + 8\zeta K_2[A]} - (1+\zeta)}{8\zeta^2 K_2} \\ &\quad + \frac{[A]}{2\zeta} \qquad \text{(S.5)}\end{aligned}$$

So,

$$\begin{aligned}[DIC] &\sim \zeta\left([OH^-] + K_2[OH^-]^2\right) \qquad \text{(S.6)} \\ &= (\zeta - 1)\frac{\sqrt{(1+\zeta)^2 + 8\zeta K_2[A]} - (1+\zeta)}{8\zeta K_2} \\ &\quad + \frac{[A]}{2} \qquad \text{(S.7)}\end{aligned}$$

Therefore,

$$
\begin{aligned}
\theta &= [\mathrm{DIC}]/[\mathrm{A}] && \text{(S.8)} \\
&\sim (\zeta - 1)\frac{\sqrt{(1+\zeta)^2 + 8\zeta K_2[\mathrm{A}]} - (1+\zeta)}{8\zeta K_2[\mathrm{A}]} + \frac{1}{2} && \text{(S.9)} \\
&= (K_1[\mathrm{CO_2}] - 1)\frac{\sqrt{(1+K_1[\mathrm{CO_2}])^2 + 8K_1[\mathrm{CO_2}]K_2[\mathrm{A}]} - (1+K_1[\mathrm{CO_2}])}{8K_1[\mathrm{CO_2}]K_2[\mathrm{A}]} \\
&\quad + \frac{1}{2} && \text{(S.10)}
\end{aligned}
$$

Substituting $[\mathrm{CO_2}] = K_H P_{\mathrm{CO_2}}$ into this equation yields

$$
\begin{aligned}
\theta &\sim (K_H K_1 P_{\mathrm{CO_2}} - 1)\frac{\sqrt{(1+K_H K_1 P_{\mathrm{CO_2}})^2 + 8K_H K_1 K_2 P_{\mathrm{CO_2}}[\mathrm{A}]} - (1+K_H K_1 P_{\mathrm{CO_2}})}{8K_H K_1 K_2 P_{\mathrm{CO_2}}[\mathrm{A}]} \\
&\quad + \frac{1}{2} && \text{(S.11)} \\
&\equiv S_{\mathrm{III}}(P_{\mathrm{CO_2}}) && \text{(S.12)}
\end{aligned}
$$

2 Derivation of the approximate isotherm equation for negligible $[CO_2]$, $[H^+]$ and $[OH^-]$ (S_{IV})

If $\zeta = K_H K_1 P_{CO_2} (= [HCO_3^-]/[OH^-]) \gg 1$ is satisfied (negligible $[OH^-]$ approximation), Eq.(S.9) can be rewritten as:

$$\theta \sim (\zeta - 1)\frac{\sqrt{(1+\zeta)^2 + 8\zeta K_2[\mathrm{A}]} - (1+\zeta)}{8\zeta K_2[\mathrm{A}]} + \frac{1}{2} \tag{S.13}$$

$$= (\zeta^2 - 1)\frac{\sqrt{1 + \frac{8\zeta K_2[\mathrm{A}]}{(\zeta+1)^2}} - 1}{8\zeta K_2[\mathrm{A}]} + \frac{1}{2} \tag{S.14}$$

$$= \zeta(1 - \frac{1}{\zeta^2})\frac{\sqrt{1 + \frac{8K_2[\mathrm{A}]}{\zeta+\{2+(1/\zeta)\}}} - 1}{8K_2[\mathrm{A}]} + \frac{1}{2} \tag{S.15}$$

$$\sim \zeta\frac{\sqrt{1 + \frac{8K_2[\mathrm{A}]}{\zeta}} - 1}{8K_2[\mathrm{A}]} + \frac{1}{2} \quad (\because \zeta \gg 1) \tag{S.16}$$

$$= \frac{\zeta}{8K_2[\mathrm{A}]}\left(\sqrt{1 + \frac{8K_2[\mathrm{A}]}{\zeta}} - 1\right) + \frac{1}{2} \tag{S.17}$$

$$= \frac{K_{\mathrm{eq}} P_{CO_2}}{4}\left(\sqrt{1 + \frac{4}{K_{\mathrm{eq}} P_{CO_2}}} - 1\right) + \frac{1}{2} \tag{S.18}$$

$$\equiv S_{\mathrm{IV}}(P_{CO_2}) \tag{S.19}$$

where,

$$K_{\mathrm{eq}} \equiv \frac{K_1 K_H}{2K_2[\mathrm{A}]} \tag{S.20}$$

3 Derivation of the Langmuir approximation of the isotherm (S_{V})

If we assume $\frac{4}{K_{\mathrm{eq}}P_{\mathrm{CO_2}}} \ll 1$, then a Taylor expansion of Eq.(S.18) up to the 2nd-order term yields:

$$
\begin{aligned}
\theta - \frac{1}{2} &\sim \frac{K_{\mathrm{eq}}P_{\mathrm{CO_2}}}{4}\left(\sqrt{1+\frac{4}{K_{\mathrm{eq}}P_{\mathrm{CO_2}}}}-1\right) && \text{(S.21)}\\
&= \cancel{\frac{K_{\mathrm{eq}}P_{\mathrm{CO_2}}}{4}}\left\{\left(\cancel{1}+\frac{1}{2}\cancel{\left(\frac{4}{K_{\mathrm{eq}}P_{\mathrm{CO_2}}}\right)}-\frac{1}{8}\left(\frac{4}{K_{\mathrm{eq}}P_{\mathrm{CO_2}}}\right)^{\cancel{2}}+\ldots\right)-\cancel{1}\right\} && \text{(S.22)}\\
&\sim \frac{1}{2}\cdot\left(1-\frac{1}{K_{\mathrm{eq}}P_{\mathrm{CO_2}}}\right) && \text{(S.23)}\\
&\sim \frac{1}{2}\cdot\frac{1}{1+\frac{1}{K_{\mathrm{eq}}P_{\mathrm{CO_2}}}}\ \left(\because \frac{1}{K_{\mathrm{eq}}P_{\mathrm{CO_2}}} \ll 1\right) && \text{(S.24)}\\
&= \frac{1}{2}\cdot\frac{K_{\mathrm{eq}}P_{\mathrm{CO_2}}}{1+K_{\mathrm{eq}}P_{\mathrm{CO_2}}} && \text{(S.25)}
\end{aligned}
$$

Namely,

$$
\begin{aligned}
\theta &\sim \frac{1}{2}\cdot\left(\frac{K_{\mathrm{eq}}P_{\mathrm{CO_2}}}{1+K_{\mathrm{eq}}P_{\mathrm{CO_2}}}\right)+\frac{1}{2} && \text{(S.26)}\\
&\equiv S_{\mathrm{V}}(P_{\mathrm{CO_2}}) && \text{(S.27)}
\end{aligned}
$$