Electronic Supplementary Information for

Stoichiometric analysis of competing intermolecular hydrogen bonds using infrared spectroscopy

Ian Seungwan Ryu,[†a] Xiaohui Liu,[†b] Ying Jin,[a] Jirun Sun,[*b] Young Jong Lee [*a]

[a] Biosystems and Biomaterials Division, National Institute of Standards and Technology, Gaithersburg, Maryland, 20899, USA
[b] Volpe Research Center, American Dental Association Foundation, Gaithersburg, Maryland, 20899, USA
† These authors contributed equally to this work.
* Corresponding authors: J.S. (jsun@nist.gov) and Y.J.L. (yjlee@nist.gov)

Contents:

1. Derivation of stoichiometric equation (Eq. 8) for (1+1) model

$$K_{\mathrm{U}} = \frac{[\mathrm{H}\cdots\mathrm{O_U}]}{[\mathrm{H}][\mathrm{O_U}]} \tag{S1}$$

$$K_{\mathrm{T}} = \frac{[\mathrm{H}\cdots\mathrm{O_T}]}{[\mathrm{H}][\mathrm{O_T}]} \tag{S2}$$

$$P \equiv K_{\mathrm{U}}/K_{\mathrm{T}} \tag{S3}$$

$$[\mathrm{H}\cdots\mathrm{O_U}] + [\mathrm{O_U}] = 4[\mathrm{U}] \tag{S4}$$

$$[\mathrm{H}\cdots\mathrm{O_T}] + [\mathrm{O_T}] = 4[\mathrm{T}] \tag{S5}$$

$$[\mathrm{H}\cdots\mathrm{O_U}] + [\mathrm{H}\cdots\mathrm{O_T}] = 2[\mathrm{U}] \tag{S6}$$

To simplify the equations above, we introduce the fractions of C=O groups satisfying $\Phi + \varphi = 1$.

$$\Phi \equiv \frac{[\mathrm{O_U}]}{[\mathrm{O_U}] + [\mathrm{H}\cdots\mathrm{O_U}]} = \frac{[\mathrm{O_U}]}{4[\mathrm{U}]} \tag{S7}$$

$$\varphi \equiv \frac{[\mathrm{H}\cdots\mathrm{O_U}]}{[\mathrm{O_U}] + [\mathrm{H}\cdots\mathrm{O_U}]} = \frac{[\mathrm{H}\cdots\mathrm{O_U}]}{4[\mathrm{U}]} \tag{S8}$$

Also, the mole fraction of UDMA is defined as described in the main text.

$$\phi_{\mathrm{U}} = \frac{[\mathrm{U}]}{[\mathrm{U}] + [\mathrm{T}]} \tag{S9}$$

Substracting Eq. S6 from S5,

$$[\mathrm{O_T}] = 4[\mathrm{T}] - 2[\mathrm{U}] + [\mathrm{H}\cdots\mathrm{O_U}] \tag{S10}$$

Utilizing Eqs. S7–S10, Eq. S3 can be expressed as following

$$\begin{aligned} P &= \frac{K_{\mathrm{U}}}{K_{\mathrm{T}}} = \frac{[\mathrm{H}\cdots\mathrm{O_U}]}{[\mathrm{O_U}]}\frac{[\mathrm{O_T}]}{[\mathrm{H}\cdots\mathrm{O_T}]} \\ &= \frac{[\mathrm{H}\cdots\mathrm{O_U}]}{[\mathrm{O_U}]}\frac{4[\mathrm{T}] - 2[\mathrm{U}] + [\mathrm{H}\cdots\mathrm{O_U}]}{2[\mathrm{U}] - [\mathrm{H}\cdots\mathrm{O_U}]} \\ &= \frac{1-\Phi}{\Phi}\frac{\frac{4(1-\phi_{\mathrm{U}})}{\phi_{\mathrm{U}}} + 2 - 4\Phi}{-2 + 4\Phi} \end{aligned} \tag{S11}$$

Eq. S11 can be rearranged to the following quadratic equation with respect to Φ, and its solution is Eq. 8 in the main text.

$$2(P-1)\Phi^2 + \left(-P + 1 + \frac{2}{\phi_{\mathrm{U}}}\right)\Phi + \left(1 - \frac{2}{\phi_{\mathrm{U}}}\right) = 0$$

2. Derivation of stoichiometric equation (Eq. 16) for (2+1) model

$$K_{\mathrm{U1}} = \frac{[\mathrm{H\cdots O_{U1}}]}{[\mathrm{H}][\mathrm{O_{U1}}]} \qquad (S12)$$

$$K_{\mathrm{U2}} = \frac{[\mathrm{H\cdots O_{U2}}]}{[\mathrm{H}][\mathrm{O_{U2}}]} \qquad (S13)$$

$$K_{\mathrm{T}} = \frac{[\mathrm{H\cdots O_{T}}]}{[\mathrm{H}][\mathrm{O_{T}}]} \qquad (S14)$$

$$Q \equiv K_{\mathrm{U2}}/K_{\mathrm{U1}} \qquad R \equiv K_{\mathrm{U1}}/K_{\mathrm{T}} \qquad (S15)$$

$$[\mathrm{H\cdots O_{U1}}] + [\mathrm{O_{U1}}] = 4[\mathrm{U}] \qquad (S16)$$

$$[\mathrm{H\cdots O_{U2}}] + [\mathrm{O_{U2}}] = 4[\mathrm{U}] \qquad (S17)$$

$$[\mathrm{H\cdots O_{T}}] + [\mathrm{O_{T}}] = 4[\mathrm{T}] \qquad (S18)$$

$$[\mathrm{H\cdots O_{U1}}] + [\mathrm{H\cdots O_{U2}}] + [\mathrm{H\cdots O_{T}}] = 2[\mathrm{U}] \qquad (S19)$$

Similar to Eqs. S7 and S8, we introduce the fractions of C=O groups satisfying $\Phi + \varphi = 1$.

$$\Phi \equiv \frac{[\mathrm{O_{U1}}]}{[\mathrm{O_{U1}}] + [\mathrm{H\cdots O_{U1}}]} = \frac{[\mathrm{O_{U1}}]}{4[\mathrm{U}]} \qquad \varphi \equiv \frac{[\mathrm{H\cdots O_{U1}}]}{[\mathrm{O_{U1}}] + [\mathrm{H\cdots O_{U1}}]} = \frac{[\mathrm{H\cdots O_{U}}]}{4[\mathrm{U}]} \qquad (S20)$$

From the definition of $Q \equiv K_{\mathrm{U2}}/K_{\mathrm{U1}}$ and Eq. S17 and S20

$$Q\,\frac{[\mathrm{H\cdots O_{U1}}][\mathrm{O_{U2}}]}{[\mathrm{O_{U1}}]} + [\mathrm{O_{U2}}] = 4[\mathrm{U}]$$

$$[\mathrm{O_{U2}}] = 4[\mathrm{U}]\left(\frac{[\mathrm{O_{U1}}]}{Q[\mathrm{H\cdots O_{U1}}] + [\mathrm{O_{U1}}]}\right)$$

$$= 4[\mathrm{U}]\left(\frac{\Phi}{Q - Q\Phi + \Phi}\right) \qquad (S21)$$

From Eqs. S17–S21,

$$[\mathrm{O_T}] = [\mathrm{H\cdots O_{U1}}] - [\mathrm{O_{U2}}] + 2[\mathrm{U}] + 4[\mathrm{T}]$$

$$= 4[\mathrm{U}](1-\Phi) - 4[\mathrm{U}]\left(\frac{\Phi}{Q - Q\Phi + \Phi}\right) + 2[\mathrm{U}] + 4[\mathrm{T}] \qquad (S22)$$

The definition of $R \equiv K_{\mathrm{U1}}/K_{\mathrm{T}}$ can be rearranged into the following Eq. S23

$$R[\mathrm{O_{U1}}][\mathrm{H\cdots O_{T}}] = [\mathrm{H\cdots O_{U1}}][\mathrm{O_{T}}] \qquad (S23)$$

Utilizing Eqs. S18, S20–S22 into Eq. S23 and rearranging the resultant Eq. S23 with respect to the mole fraction of UDMA (Eq. S9) lead to Eq. 16 in the main text.

$$\phi_{\mathrm{U}} = \frac{2Q\Phi^2 - 2\Phi^2 - 4Q\Phi + 2\Phi + 2Q}{2(-RQ + R + Q - 1)\Phi^3 + (5RQ - R - 5Q + 1)\Phi^2 + (-3RQ + 4Q + 1)\Phi - Q}$$