Electronic Supplementary Information for

Stoichiometric analysis of competing intermolecular hydrogen bonds using infrared spectroscopy

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

\[ K_U = \frac{[H \cdots O_U]}{[H][O_U]} \quad (S1) \]

\[ K_T = \frac{[H \cdots O_T]}{[H][O_T]} \quad (S2) \]

\[ P \equiv \frac{K_U}{K_T} \quad (S3) \]

\[ [H \cdots O_U] + [O_U] = 4[U] \quad (S4) \]

\[ [H \cdots O_T] + [O_T] = 4[T] \quad (S5) \]

\[ [H \cdots O_U] + [H \cdots O_T] = 2[U] \quad (S6) \]

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

\[ \Phi \equiv \frac{[O_U]}{[O_U] + [H \cdots O_U]} = \frac{[O_U]}{4[U]} \quad (S7) \]

\[ \varphi \equiv \frac{[H \cdots O_U]}{[O_U] + [H \cdots O_U]} = \frac{[H \cdots O_U]}{4[U]} \quad (S8) \]

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

\[ \phi_U = \frac{[U]}{[U] + [T]} \quad (S9) \]

Subtracting Eq. S6 from S5,

\[ [O_T] = 4[T] - 2[U] + [H \cdots O_U] \quad (S10) \]

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

\[ P = \frac{K_U}{K_T} = \frac{[H \cdots O_U]}{[O_U]} \frac{[O_T]}{[H \cdots O_T]} \]

\[ = \frac{[H \cdots O_U]}{[O_U]} \frac{4[T] - 2[U] + [H \cdots O_U]}{2[U] - [H \cdots O_U]} \]

\[ = \frac{1 - \Phi}{\varphi_U} + \frac{2 - 4\Phi}{2 + 4\Phi} \quad (S11) \]

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

\[ 2(P - 1)\Phi^2 + \left(-P + 1 + \frac{2}{\phi_U}\right)\Phi + \left(1 - \frac{2}{\phi_U}\right) = 0 \]
2. Derivation of stoichiometric equation (Eq. 16) for (2+1) model

\[ K_{U1} = \frac{[\text{H} \cdots \text{O}_{U1}]}{[\text{H}][\text{O}_{U1}]} \]  

(S12)

\[ K_{U2} = \frac{[\text{H} \cdots \text{O}_{U2}]}{[\text{H}][\text{O}_{U2}]} \]  

(S13)

\[ K_T = \frac{[\text{H} \cdots \text{O}_T]}{[\text{H}][\text{O}_T]} \]  

(S14)

\[ Q \equiv K_{U2}/K_{U1} \quad R \equiv K_{U1}/K_T \]  

(S15)

\[ [\text{H} \cdots \text{O}_{U1}] + [\text{O}_{U1}] = 4[U] \]  

(S16)

\[ [\text{H} \cdots \text{O}_{U2}] + [\text{O}_{U2}] = 4[U] \]  

(S17)

\[ [\text{H} \cdots \text{O}_T] + [\text{O}_T] = 4[T] \]  

(S18)

\[ [\text{H} \cdots \text{O}_{U1}] + [\text{H} \cdots \text{O}_{U2}] + [\text{H} \cdots \text{O}_T] = 2[U] \]  

(S19)

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

\[ \Phi \equiv \frac{[\text{O}_{U1}]}{[\text{O}_{U1}] + [\text{H} \cdots \text{O}_{U1}]} = \frac{[\text{O}_{U1}]}{4[U]} \]

\[ \Psi \equiv \frac{[\text{H} \cdots \text{O}_{U1}]}{[\text{O}_{U1}] + [\text{H} \cdots \text{O}_{U1}]} = \frac{[\text{H} \cdots \text{O}_{U1}]}{4[U]} \]  

(S20)

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

\[ Q \frac{[\text{H} \cdots \text{O}_{U1}][\text{O}_{U2}]}{[\text{O}_{U1}]} + [\text{O}_{U2}] = 4[U] \]

\[ [\text{O}_{U2}] = 4[U] \left( \frac{[\text{O}_{U1}]}{Q[\text{H} \cdots \text{O}_{U1}] + [\text{O}_{U1}]} \right) \]

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

(S21)

From Eqs. S17–S21,

\[ [\text{O}_T] = [\text{H} \cdots \text{O}_{U1}] - [\text{O}_{U2}] + 2[U] + 4[T] \]

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

(S22)

The definition of \( R \equiv K_{U1}/K_T \) can be rearranged into the following Eq. S23

\[ R[\text{O}_{U1}][\text{H} \cdots \text{O}_T] = [\text{H} \cdots \text{O}_{U1}][\text{O}_T] \]  

(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.

\[ \phi_U = \frac{2Q\Phi^2 - 2\Phi^2 - 4Q\Phi + 2\Phi + 2Q}{2(-RQ + R + Q - 1)\Phi^3 + (5RQ - R - 5Q + 1)\Phi^2 + (-3RQ + 4Q + 1)\Phi - Q} \]