Tetra-molecular Self-Complementary $nA \leftrightarrow A_n$

$$G = -RT\ln K \tag{1}$$
$$G = \Delta H - T\Delta S \tag{2}$$
$$\therefore \Delta H - T\Delta S = -RT\ln K \tag{3}$$

At T_m,

$$\Delta H - T_m\Delta S = -RT_m \ln K_{T_m} \tag{4}$$
$$T_m\Delta S = \Delta H + RT_m \ln K_{T_m} \tag{5}$$
$$\Delta S = \frac{\Delta H}{T_m} + R\ln K_{T_m} \tag{6}$$

Substitute ΔS to equation 3,

$$\Delta H - T(\frac{\Delta H}{T_m} + R\ln K_{T_m}) = -RT\ln K \tag{7}$$

Divide both sides by $-RT$,

$$\ln K = -\frac{\Delta H}{RT} + \frac{\Delta H}{RT_m} - \ln K_{T_m} \tag{8}$$
$$K = K_{T_m} e^{\frac{\Delta H}{R}\left(\frac{1}{T_m} - \frac{1}{T}\right)} \tag{9}$$
$$\frac{K}{K_{T_m}} = e^{\frac{\Delta H}{R}\left(\frac{1}{T_m} - \frac{1}{T}\right)} \tag{10}$$

From [Marky and Breslauer 1987], assuming at T_m $\alpha = 1/2$, association equilibrium constant K for Self-complementary sequence are,

$$K = \frac{\alpha}{nC_T^{n-1}(1-\alpha)^n} \tag{11}$$
$$K_{T_m} = \frac{1}{n(C_T/2)^{n-1}} \tag{12}$$

Thus when $n = 4$ for tetra-molecular associations,

$$K = \frac{\alpha}{4C_T^3(1-\alpha)^4} \tag{13}$$
$$K_{T_m} = \frac{1}{4(C_T/2)^3} = \frac{2}{C_T^3} \tag{14}$$
$$\frac{K}{K_{T_m}} = \frac{\alpha}{8\,(1-\alpha)^4} \qquad \text{(Association)} \tag{15}$$
$$= \frac{8\,(1-\alpha)^4}{\alpha} \qquad \text{(Dissociation)} \tag{16}$$

Substitute equation 15 or 16 to equation 10,

$$e^{\frac{\Delta H}{R}\left(\frac{1}{T_m}-\frac{1}{T}\right)} = \frac{8\,(1-\alpha)^4}{\alpha} \tag{17}$$

Solve for α,
where $x = e^{\frac{\Delta H}{R}\left(\frac{1}{T_m}-\frac{1}{T}\right)}$
let $u_1 = \sqrt[3]{9x^2+\sqrt{3}\sqrt{27x^4+2048x^3}}$
let $u_2 = \sqrt[3]{18}$
let $u_3 = \sqrt[3]{\frac{2}{3}}x$

$$\alpha = \pm\frac{1}{4}\sqrt{\left(\frac{u_1}{u_2}-\frac{8u_3}{u_1}\right)} \pm \frac{1}{2}\sqrt{\left(\frac{2u_3}{u_1}+\frac{x}{2\sqrt{\frac{u_1}{u_2}-\frac{8u_3}{u_1}}}-\frac{u_1}{4u_2}\right)}+1 \tag{18}$$

Signs are probably +,- or -,+ for each $\pm$ respectively to get physical values.

To normalise the α use the relation,

$$\frac{A_b-(N+aT)}{(D+bT)-(N+aT)} \tag{19}$$

where A_b is the absorbance or y-value, N and D are y-intercepts, and a and b are slopes of the flat region. Thus,

$$A_b = N+aT+((b-a)T+D-N)\alpha \tag{20}$$

※ Temperature are in Kelvins