Chemistry 2740 Spring 2022 Test 4 Solutions

1. For the two binding reactions given, we have

$$k_1[\text{AChBP}][\text{ACh}] = k_{-1}[\text{AchBP}\cdot\text{ACh}]$$
$$\therefore K_1 = \frac{[\text{AchBP}\cdot\text{ACh}]}{[\text{AChBP}][\text{ACh}]} = \frac{k_1}{k_{-1}}$$
$$k_2[\text{AChBP}][\alpha\text{CT}] = k_{-2}[\text{AchBP}\cdot\alpha\text{CT}]$$
$$\therefore K_2 = \frac{[\text{AchBP}\cdot\alpha\text{CT}]}{[\text{AChBP}][\alpha\text{CT}]} = \frac{k_2}{k_{-2}}$$

The equilibrium constant for the displacement of ACh by αCT on the other hand is

$$K = \frac{[\text{AchBP}\cdot\alpha\text{CT}][\text{ACh}]}{[\text{AchBP}\cdot\text{ACh}][\alpha\text{CT}]} = \frac{K_2}{K_1}$$
$$\therefore K = \frac{k_2k_{-1}}{k_{-2}k_1} = \frac{(3.3\times10^6\,\text{L}\,\text{mol}^{-1}\text{s}^{-1})(120\,\text{s}^{-1})}{(0.011\,\text{s}^{-1})(1.1\times10^8\,\text{L}\,\text{mol}^{-1}\text{s}^{-1})}$$
$$= 327$$

This large equilibrium constant implies that a relatively small amount of α-cobratoxin can outcompete ACh for binding to ACh binding protein (or to related ACh receptors), which is what makes cobra venom so toxic.

2. (a) The overall reaction per chlorohydrin functional group is

$$\text{chlorohydrin} + \text{OH}^- \rightarrow \text{epoxide} + \text{H}_2\text{O} + \text{Cl}^-.$$

The rate of reaction is therefore

$$v = \frac{d[\text{epoxide}]}{dt} = k_2[\text{I}].$$

We will use the steady-state approximation for the intermediate I.

$$\frac{d[\text{I}]}{dt} = k_1[\text{chl}][\text{OH}^-] - k_{-1}[\text{I}][\text{H}_2\text{O}] - k_2[\text{I}] \approx 0$$
$$\therefore (k_{-1}[\text{H}_2\text{O}] + k_2)[\text{I}] \approx k_1[\text{chl}][\text{OH}^-]$$
$$\therefore [\text{I}] \approx \frac{k_1[\text{chl}][\text{OH}^-]}{k_{-1}[\text{H}_2\text{O}] + k_2}$$
$$\therefore v \approx \frac{k_1k_2[\text{chl}][\text{OH}^-]}{k_{-1}[\text{H}_2\text{O}] + k_2}$$

(b) If the concentration of water is constant, we get the rate law

$$v = k_{\text{app}}[\text{chl}][\text{OH}^-]$$

with

$$k_{\text{app}} = \frac{k_1k_2}{k_{-1}[\text{H}_2\text{O}] + k_2}$$

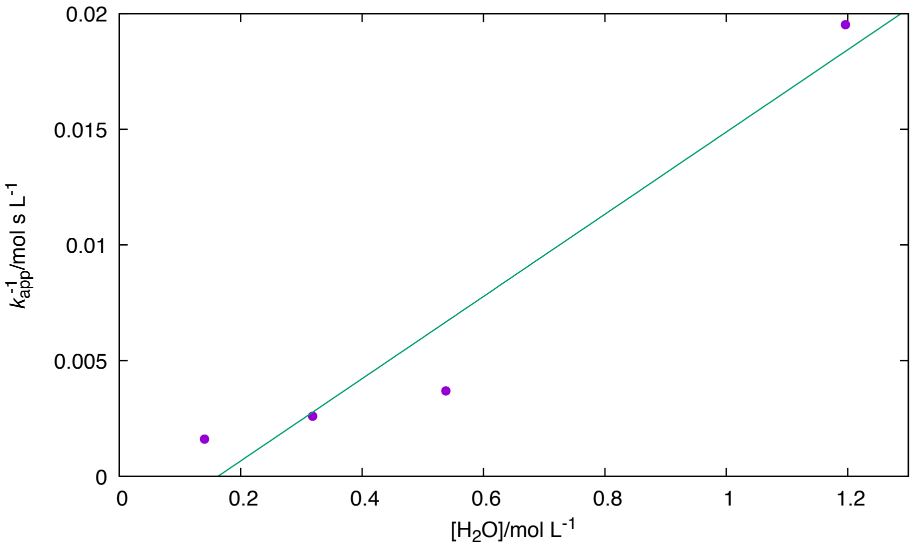

Figure 1: k_{app}^{-1} vs [H_2O].

Bonus: Note that

$$\frac{1}{k_{\text{app}}} = \frac{k_{-1}[\text{H}_2\text{O}] + k_2}{k_1 k_2} = \frac{k_{-1}}{k_1 k_2}[\text{H}_2\text{O}] + \frac{1}{k_1}.$$

A graph of k_{app}^{-1} vs [H_2O] should therefore be linear. The graph is shown in figure 1. The graph is clearly not linear. This suggests that the proposed mechanism is incorrect.