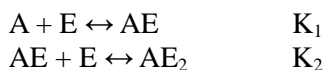


**Problem 7 Esterification of a dicarboxylic acid**

Let: A: diacid                      E: monoalcohol                      AE: monoester                      AE<sub>2</sub>: diester

Then the esterification reactions are:



Now:

Equilibrium constants:

$$K_1 = \frac{[AE]}{[A][E]} \dots (a) \qquad K_2 = \frac{[AE_2]}{[AE][E]} \dots (b)$$

Mass Balance:

$$[A]_{\text{total}} = 1 = [A] + [AE] + [AE_2] \dots (c)$$

$$[E]_{\text{total}} = X = [E] + [AE] + 2[AE_2] \dots (d)$$

Using (a) and (b) in (c)

$$1 = [A] \cdot (1 + K_1[E] + K_1 \cdot K_2[E]^2) \text{ and}$$

$$[AE] = K_1[A][E] = K_1 \cdot \frac{1}{(1 + K_1[E] + K_1 K_2[E]^2)} \cdot [E]$$

7.1

If yield of a monoester is maximal then  $\frac{d[AE]}{d[E]} = 0$

$$\frac{d[AE]}{d[E]} = \frac{K_1 \left\{ (1 + K_1[E] + K_1 K_2[E]^2) - [E] \cdot (K_1 + 2 K_1 K_2[E]) \right\}}{(1 + K_1[A][E] + K_1 K_2[A][E]^2)^2} = 0$$

$$1 + K_1[E] + K_1 \cdot K_2[E]^2 = K_1[E] + 2K_1 \cdot K_2[E]^2$$

$$[E] = \sqrt{\frac{1}{K_1 K_2}}$$

$$\text{If } K_1 = K_2 = 20 \rightarrow [E] = \frac{1}{20}$$

$$[A] = \frac{1}{1 + 20 \cdot \left(\frac{1}{20}\right) + 400 \cdot \left(\frac{1}{400}\right)} = \frac{1}{3} \quad [AE] = 20 \cdot (1/3) \cdot (1/20) = 1/3 \quad [AE_2] = 20 \cdot (1/3) \cdot (1/20) = (1/3)$$

$$X = [E] + [AE] + 2[AE_2] = (1/20) + 1/3 + 2 \cdot (1/3) = 1.05$$

7.2

The maximum yield is  $[AE]/[A]_{\text{total}} = (1/3)/1 = 1/3$  or 33.33 %

7.3

In general

$$[E] = \sqrt{\frac{1}{K_1 K_2}} \qquad [A] = \frac{1}{(1 + K_1[E] + K_1 K_2[E]^2)} = \frac{1}{(1 + \sqrt{\frac{K_1}{K_2}} + 1)}$$

$$[AE] = K_1 \cdot [A][E] = \frac{\sqrt{\frac{K_1}{K_2}}}{(2 + \sqrt{\frac{K_1}{K_2}})}$$

$$[AE_2] = K_2[AE][E] = \sqrt{\frac{K_2}{K_1}} \frac{\sqrt{\frac{K_1}{K_2}}}{\left(2 + \sqrt{\frac{K_1}{K_2}}\right)} = \frac{1}{\left(2 + \sqrt{\frac{K_1}{K_2}}\right)}$$

$$X = [E] + [AE] + 2[AE_2] = \sqrt{\frac{1}{K_1 K_2}} + \frac{\sqrt{\frac{K_1}{K_2}}}{\left(2 + \sqrt{\frac{K_1}{K_2}}\right)} + 2 \cdot \frac{1}{\left(2 + \sqrt{\frac{K_1}{K_2}}\right)} = 1 + \sqrt{\frac{1}{K_1 K_2}}$$

$$\text{Maximum yield} = [AE]/[A]_{\text{total}} = \frac{\sqrt{\frac{K_1}{K_2}}}{\left(2 + \sqrt{\frac{K_1}{K_2}}\right)}$$

Solution proposed by

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