Problem 7 Esterification of a dicarboxylic acid

Let: A: diacid E: monoalcohol AE: monoester AE_2: diester
Then the esterification reactions are:
$A + E \leftrightarrow AE$ K_1
$AE + E \leftrightarrow AE_2$ K_2

Now:

Equilibrium constants:

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

Mass Balance:
$[A]total = 1 = [A]+[AE]+[AE_2]$ … (c)
$[E]total = X = [E] + [AE] + 2[AE_2]$ … (d)

Using (a) and (b) in (c)
$1 = [A].(1 + K_1[E] + K_1.K_2[E]^2)$ and

$$[AE] = K_1[A][E] = K_1 . \frac{1}{(1+K_1[E]+K_1K_2[E]^2)} . [E]$$

7.1

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

$$\frac{d[AE]}{d[E]} = \frac{K_1\{(1+K_1[E]+K_1K_2[E]^2)-[E].(K_1+2K_1K_2[E])\}}{(1+K_1[A][E]+K_1K_2[A][E]^2)^2} = 0$$

$1 + K_1[E] + K_1.K_2[E]^2 = K_1[E] + 2K_1.K_2[E]^2$

$$[E] = \sqrt{\frac{1}{K_1K_2}}$$

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

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

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

7.2
The maximum yield is $[AE]/[A]total = (1/3)/1 = 1/3$ or 33.33 %

7.3
In general

$$[E] = \sqrt{\frac{1}{K_1K_2}} \qquad [A] = \frac{1}{(1+K_1[E]+K_1K_2[E]^2)} = \frac{1}{(1+\sqrt{\frac{K_1}{K_2}}+1)}$$

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

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

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

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

Solution proposed by
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