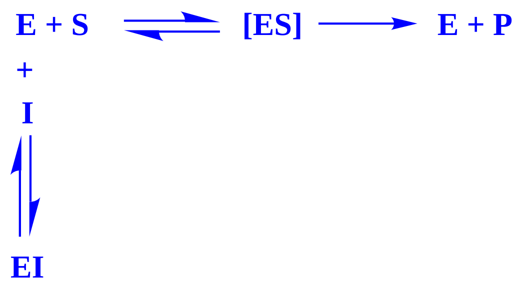
MBMB451b
Bonus Problem #1

Initial studies of an esterase using a racemic mixture as substrate revealed that the L enantiomer was the true substrate, as it was completely converted into product whereas the D enantiomer could be recovered unchanged at the end of the reaction. On the basis of this result the kinetics of the reaction were analyzed assuming that the D enantiomer had no effect on the enzyme, and a Michaelis constant for the L enantiomer was estimated to be 2 mM. Subsequent work made it clear that it would have been more reasonable to assume that the D enantiomer was a competitive inhibitor with K_{ic} equal to the K_m value of the L enantiomer. How should the original K_m estimate be revised to take account of this information?



From these reactions develop a velocity expression dependent on expected values of the kinetic parameters:

$$v = \frac{V_{max}^{exp} \cdot [S]}{K_m^{exp} \cdot \left(1 + \frac{[I]}{K_{ic}}\right) + [S]}$$

Now from the problem we know that S is a racemic mixture, so $[S] = [I]$ and the expression becomes (with a little math),

$$v = \frac{V_{max}^{exp} \cdot [S]}{K_m^{exp} \cdot \left(1 + \frac{[S]}{K_{ic}}\right) + [S]} = \frac{V_{max}^{exp} \cdot [S]}{K_m^{exp} + \left(1 + \frac{K_m^{exp}}{K_{ic}}\right) \cdot [S]}$$

Now divide the numerator and denominator by $(1 + K^{exp}_m/K_{ic})$

and define $V_{max} = V^{exp}_{max}/(1 + K^{exp}_m/K_{ic})$

$K_m = K^{exp}_m/(1 + K^{exp}_m/K_{ic})$

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$$v = \frac{V_{\max}^{\exp} \Big/ \left(1+\frac{K_{\mathrm{m}}^{\exp}}{K_{\mathrm{ic}}}\right) \cdot [S]}{K_{\mathrm{m}}^{\exp} \Big/ \left(1+\frac{K_{\mathrm{m}}^{\exp}}{K_{\mathrm{ic}}}\right) + [S]} = \frac{V_{\max} \cdot [S]}{K_m + [S]}$$ (4 pts to develop logic)

We are told that K_{m} = 2 mM and that $K^{\exp}_{\mathrm{m}} = K_{\mathrm{ic}}$,

and therefore $K^{\exp}_{\mathrm{m}}$ = 2 mM · (1 + 1) = 4 mM (1 pt for answer)