Deacon's Challenge No. 17 Answer

25mg of bilirubin ($C_{33}H_{36}O_6N_4$) were dissolved in 4 mL of dimethyl sulphoxide; 200 mL of this solution was diluted to 250 mL with chloroform. This solution gave an absorbance of 0.502 when measured in a 1 cm cell against a chloroform blank. Given that the molar absorbtivity of bilirubin under these conditions is 6.07 x 10^4, calculate the percentage purity of the bilirubin.

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First calculate the concentration of bilirubin in the final solution:

$$A = \varepsilon \times c \times l$$

Where A = absorbance = 0.502
e = molar absorbivity = 6.07×10^4 cm^{-1}
c = concentration in mol/L = ?
l = path length = 1 cm

$$0.502 = 6.07 \times 10^4 \times c \times 1$$

Rearranging: $c = \frac{0.502}{6.07 \times 10^4} = 8.27 \times 10^{-6}$ mol/L $= 8.27 \times 10^{-3}$ mmol/L

Use this concentration of the final solution to calculate the bilirubin content of the weighed bilirubin:

The final solution was prepared by diluting 200 mL (i.e. 0.2 mL) of stock to 250 mL

Therefore concentration of stock $= \frac{8.27 \times 10^{-3} \times 250}{0.2} = 10.34$ mmol/L

4 mL (the volume of DMSO the bilirubin was dissolved in) contains:

$$\frac{10.34 \times 4}{1000} = 0.0414 \text{ mmol bilirubin}$$

Convert to wt of bilirubin:

Wt bilirubin (mg) = mmol bilirubin x MW

MW bilirubin = (33 x 12) + (36 x 1) + (6 x 16) + (4 x 14) = 584

Therefore wt bilirubin = 0.0414 x 584 = 24.2 mg

$$\% \text{ purity} = \frac{\text{Amount of bilirubin by assay} \times 100}{\text{Weighed amount of bilirubin}} = \frac{24.2 \times 100}{25} = 97\% \text{ (2 sig figs)}$$

Question No. 18

A tumour marker X is used to guide a decision on chemotherapy after the resection of the main tumour mass. The concentration decays exponentially. If the half-life of the tumour marker is less than 75 hours, then this is indicative of tumour clearance and chemotherapy is withheld. If the half-life is greater than this, it indicates that residual disease is present and chemotherapy is indicated. The precision of the assay is such that measurements can be safely made at a precisely timed interval of more than 36 hours from two or more days after surgery.

The level of X at 50 hours post surgery is 1756 ng/L and at 94 hours it is 1050 ng/L. Calculate the half-life and indicate whether you can say with confidence whether chemotherapy needs to be given.

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