

QUESTIONS AND PROBLEMS

- 3-1. What is the minimum value of K_D which would allow the extraction of 99.9% of a solute from 50 ml of water with five successive 50-ml portions of ether? *Ans. $K = 3$*
- 3-2. If five extractions with 100-ml portions of ether extract 90% of a solute from an aqueous solution, what fraction of the solute will ten similar extractions remove? *Ans. 99%*
- 3-3. Derive an expression similar to Equation 3-10 for the distribution of pyridine between water and benzene:



- 3-4. In the Craig process, some of the solute remains in the first vessel no matter how many transfers are made. Assuming that $V_s = V_m$, and that $K_D = 1$, what fraction of the solute will remain in the first two vessels after ten transfers?

Ans. $1/1024 + 1/102 \approx 1\%$

- 3-5. A sample containing approximately 1 g of an organic substance A is dissolved in 100 ml of water. The aqueous solution is then shaken with 100 ml of ether. Analysis of the ether layer shows that 0.7 g of A is extracted.

(a) What is the value of $K_D = C_{et}/C_{aq}$ for this system? *Ans. 2.33*

(b) How many additional extractions with 100-ml portions of ether would be required to extract 95% of the substance? *Ans. 2 (additional)*

(c) What fraction of A would have been extracted by four 25-ml portions of ether? *Ans. 84%*

- 3-6. The distribution coefficient of an organic compound is $K_D = C_{aq}/C_{pent} = 5.0$. A 0.55-g sample is placed in vessel 0 of a Craig apparatus. Each vessel holds 4 ml of water and 4 ml of pentane (the lighter solvent which is transferred). Calculate the fraction of the compound which is in each vessel after four transfers.

Ans. 48.2%, 38.6%, 11.6%, 1.5%, 0.1%

- 3-7. Three extractions with 50-ml portions of chloroform removed 97% of a solute from 200 ml of an aqueous solution. Calculate the distribution coefficient of the solute: $K_D = C_{chlor}/C_{aq}$. *Ans. 8.9*

- 3-8. Two weak bases (organic amines) have basic dissociation constants of $K_{bA} = 1 \times 10^{-4}$ and $K_{bB} = 1 \times 10^{-8}$. Both bases have distribution coefficients of approximately 10 between chloroform and water. Describe a procedure, making use of the difference in K_b , for separating the two by extraction.

- 3-9. Two weak acids, HX and HY, have distribution coefficients, $K_D = C_{et}/C_{aq}$, of 5 and 50, respectively, and dissociation constants of 1×10^{-4} and 1×10^{-8} , respectively. Calculate the distribution ratios of the two acids at integral values of pH of the aqueous solution from pH 4 to pH 11, assuming equal volumes of the two solvents. What is the minimum pH for which the ratio of D values is at least 10^5 ?

Ans. At pH 4 $D_{HX} = 2.5$, $D_{HY} = 50$

At pH 7 $D_{HX} = 0.005$, $D_{HY} = 45$

Minimum pH = 10

- 3-10. Formaldehyde has a distribution coefficient, $C_{et}/C_{aq} = 0.111$ at 25°. How many liters of water will be required to remove in one extraction 95% of the formaldehyde from 1 liter of ether containing 0.5 mole of formaldehyde? *Ans. 2.1 liters*

- 3-11. How much formaldehyde would remain in 50 ml of ether initially containing 5 g of formaldehyde after five successive extractions with 25-ml portions of water? *Ans. 1 mg*

- 3-12. Suppose you were given 100 ml of an aqueous solution containing 1 mg of LSD. You wish to extract the LSD into ether. The distribution coefficient is given by

$$K_D = \frac{C_{et}}{C_{aq}} = 10$$

- (a) How much LSD would be extracted with one 150-ml portion of ether?

(b) How much LSD would be extracted with three successive 50-ml portions of ether?
Ans. (a) 0.935 mg (b) 0.995 mg

- 3-13. The dissociation constant for propionic acid, HOPr, in water is $K_a = 1.00 \times 10^{-5}$, and its distribution coefficient between ether and water is $K_D = 2.85$. You are given a solution of 8.00 g of HOPr in 500 ml of water which has been adjusted to pH 4.00 by the addition of base. The HOPr is extracted from the aqueous solution with two 250-ml portions of ether. What is the pH of the water layer after the second extraction?
Ans. 4.72

REFERENCES

- L. C. Craig and D. Craig, in *Technique of Organic Chemistry*, 2nd ed., A. Weissberger, Editor, Vol. III, Part I, Wiley-Interscience, New York, 1956; pp. 150-392. A comprehensive and definitive discussion of extraction and distribution.
- E. W. Berg, *Physical and Chemical Methods of Separation*, McGraw-Hill, New York, 1963; Chapter 3. Intermediate level discussion of extraction, probably more useful to the student than Weissberger.
- H. Irving and R. J. P. Williams in *Treatise on Analytical Chemistry*, Part I, Volume 3, edited by I. M. Kolthoff and P. J. Elving, Wiley-Interscience, New York, 1959; pp. 1309-65.
- G. H. Morrison and H. Freiser, *Solvent Extraction in Analytical Chemistry*, Wiley, New York, 1957.
- B. L. Karger, L. R. Snyder and C. Horvath, *An Introduction to Separation Science*, Wiley-Interscience, New York, 1973.