

Practice 6 - Calculation of the extraction process

1 академический час

A solvent extraction

A solvent extraction is an important separation technique for environmental, clinical, and industrial laboratories.

In a simple liquid–liquid extraction the solute partitions between two immiscible phases. One phase usually is aqueous and the other phase is an organic solvent, such as the pentane used in extracting trihalomethanes from water. Because the phases are immiscible they form two layers, with the denser phase on the bottom. The solute is initially present in one of the two phases; after the extraction it is present in both phases.

Extraction efficiency—that is, the percentage of solute moving from one phase to the other—is determined by the equilibrium constant for the solute's partitioning between the phases and any other reactions involving the solute. Examples of other reactions affecting extraction efficiency include acid–base reactions and complexation reactions.

7.7.1 Partition Coefficients and Distribution Ratios

As we learned earlier in this chapter, a solute's partitioning between two phases is described by a partition coefficient, K_D . If we extract a solute from an aqueous phase into an organic phase



then the partition coefficient is

$$K_D = \frac{[S_{\text{org}}]}{[S_{\text{aq}}]} \quad (7.7.2)$$

A large value for K_D indicates that the solute's extraction into the organic phase is favorable. To evaluate an extraction's efficiency we must consider the solute's total concentration in each phase. We define the **distribution ratio**, D , as the ratio of the solute's total concentration in each phase.

$$D = \frac{[S_{\text{org}}]_{\text{total}}}{[S_{\text{aq}}]_{\text{total}}} \quad (7.7.3)$$

The partition coefficient and the distribution ratio are identical if the solute has only one chemical form in each phase. If the solute exists in more than one chemical form in either phase, then K_D and D usually have different values. For example, if the solute exists in two forms in the aqueous phase, A and B, only one of which, A, partitions between the two phases, then

$$D = \frac{[S_{\text{org}}]_A}{[S_{\text{aq}}]_A + [S_{\text{aq}}]_B} \leq K_D = \frac{[S_{\text{org}}]_A}{[S_{\text{aq}}]_A} \quad (7.7.4)$$

This distinction between K_D and D is important. The partition coefficient is an equilibrium constant and has a fixed value for the solute's partitioning between the two phases. The distribution ratio's value, however, changes with solution conditions if the relative amounts of A and B change. If we know the equilibrium reactions taking place within each phase and between the phases, we can derive an algebraic relationship between K_D and D .

where the subscripts indicate the extraction number. (The subscript 0 represents the system before the extraction and the subscript 1 represents the system after the first extraction.) After the extraction, the solute's concentration in the aqueous phase is

$$[S_{\text{aq}}]_1 = \frac{(\text{moles } S_{\text{aq}})_1}{V_{\text{aq}}} \quad (7.7.7)$$

and its concentration in the organic phase is

$$[S_{\text{org}}]_1 = \frac{(\text{moles } S_{\text{org}})_1}{V_{\text{org}}} \quad (7.7.8)$$

where V_{aq} and V_{org} are the volumes of the aqueous phase and the organic phase. Solving Equation 7.7.6 for $(\text{moles } S_{\text{org}})_1$ and substituting into Equation 7.7.8 leave us with

$$[S_{\text{org}}]_1 = \frac{(\text{moles } S_{\text{aq}})_0 - (\text{moles } S_{\text{aq}})_1}{V_{\text{org}}} \quad (7.7.9)$$

Substituting Equations 7.7.7 and 7.7.9 into Equation 7.7.5 gives

$$D = \frac{\frac{(\text{moles } S_{\text{aq}})_0 - (\text{moles } S_{\text{aq}})_1}{V_{\text{org}}}}{\frac{(\text{moles } S_{\text{aq}})_1}{V_{\text{aq}}}} = \frac{(\text{moles } S_{\text{aq}})_0 \times V_{\text{aq}} - (\text{moles } S_{\text{aq}})_1 \times V_{\text{aq}}}{(\text{moles } S_{\text{aq}})_1 \times V_{\text{org}}} \quad (7.7.10)$$

Rearranging, and solving for the fraction of solute remaining in the aqueous phase after one extraction, $(q_{\text{aq}})_1$, gives

$$(q_{\text{aq}})_1 = \frac{(\text{moles } S_{\text{aq}})_1}{(\text{moles } S_{\text{aq}})_0} = \frac{V_{\text{aq}}}{DV_{\text{org}} + V_{\text{aq}}} \quad (7.7.11)$$

The fraction present in the organic phase after one extraction, $(q_{\text{org}})_1$, is

$$(q_{\text{org}})_1 = \frac{(\text{moles } S_{\text{org}})_1}{(\text{moles } S_{\text{org}})_0} = 1 - (q_{\text{aq}})_1 = \frac{DV_{\text{org}}}{DV_{\text{org}} + V_{\text{aq}}} \quad (7.7.12)$$

Example 7.14 shows how we can use Equation 7.7.11 to calculate the efficiency of a simple liquid-liquid extraction.

The last two examples provide us with an important observation—for any extraction efficiency, we need less solvent if we complete several extractions using smaller portions of solvent instead of one extraction using a larger volume of solvent. For the conditions in Example 7.14 and Example 7.15, an extraction efficiency of 99.9% requires one extraction with 9990 mL of chloroform, or 120 mL when using eight 15-mL portions of chloroform. Although extraction efficiency increases dramatically with the first few multiple extractions, the effect quickly diminishes as we increase the number of extractions (Figure 7.27). In most cases there is little improvement in extraction efficiency after five or six extractions. For the conditions in Example 7.15, we reach an extraction efficiency of 99% after five extractions and need three additional extractions to obtain the extra 0.9% increase in extraction efficiency.

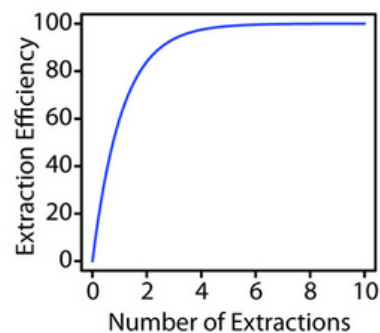


Figure 7.27: Plot of extraction efficiency versus the number of extractions for the liquid-liquid extraction in Example 7.15.

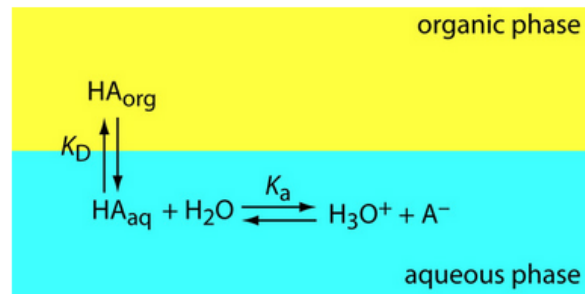


Figure 7.28: Scheme for a liquid–liquid extraction of the weak acid, HA. Although the weak acid is soluble in both phases, its conjugate weak base, A^- , is soluble only in the aqueous phase. The K_a reaction, which is called a **secondary equilibrium reaction**, affects the extraction efficiency because it controls the relative abundance of HA in solution.

If the solute participates in an additional equilibrium reaction within a phase, then the distribution ratio and the partition coefficient may not be the same. For example, Figure 7.28 shows the equilibrium reactions affecting the extraction of the weak acid, HA, by an organic phase in which ionic species are not soluble. In this case the partition coefficient and the distribution ratio are

$$K_D = \frac{[HA_{org}]}{[HA_{aq}]} \quad (8.7.23)$$

EXERCISE

To plan a liquid–liquid extraction we need to know the solute’s distribution ratio between the two phases. One approach is to carry out the extraction on a solution containing a known amount of solute. After extracting the solution, we isolate the organic phase and allow it to evaporate, leaving behind the solute. In one such experiment, 1.235 g of a solute with a molar mass of 117.3 g/mol is dissolved in 10.00 mL of water. After extracting with 5.00 mL of toluene, 0.889 g of the solute is recovered in the organic phase.

- a. What is the solute’s distribution ratio between water and toluene?
- b. If we extract 20.00 mL of an aqueous solution containing the solute with 10.00 mL of toluene, what is the extraction efficiency? (c) How many extractions will we need to recover 99.9% of the solute?

7.7.3 Liquid–Liquid Extractions Involving Acid–Base Equilibria

As shown by Equation 8.7.5, in a simple liquid–liquid extraction the distribution ratio and the partition coefficient are identical. As a result, the distribution ratio does not depend on the composition of the aqueous phase or the organic phase. Changing the pH of the aqueous phase, for example, will not affect the solute’s extraction efficiency.

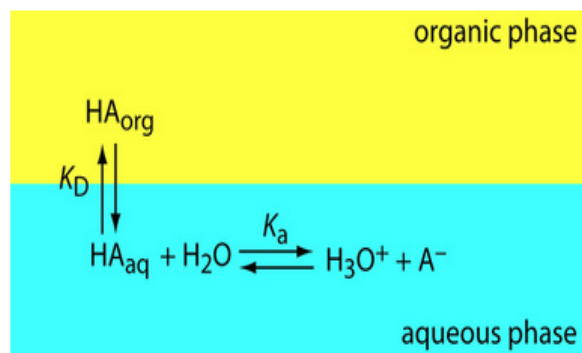


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$$K_D = \frac{[HA_{org}]}{[HA_{aq}]} \quad (8.7.23)$$

$$D = \frac{[\text{HA}_{\text{org}}]_{\text{total}}}{[\text{HA}_{\text{aq}}]_{\text{total}}} = \frac{[\text{HA}_{\text{org}}]}{[\text{HA}_{\text{aq}}] + [\text{A}_{\text{aq}}^-]} \quad (8.7.24)$$

Because the position of an acid–base equilibrium depends on the pH, the distribution ratio is pH-dependent. To derive an equation for D that shows this dependency, we begin with the acid dissociation constant for HA.

$$K_a = \frac{[\text{H}_3\text{O}_{\text{aq}}^+][\text{A}_{\text{aq}}^-]}{[\text{HA}_{\text{aq}}]} \quad (8.7.25)$$

Solving Equation 8.7.25 for the concentration of A^-

$$[\text{A}_{\text{aq}}^-] = \frac{K_a \times [\text{HA}_{\text{aq}}]}{[\text{H}_3\text{O}_{\text{aq}}^+]} \quad (8.7.26)$$

and substituting into Equation 8.7.24 gives

$$D = \frac{[\text{HA}_{\text{org}}]}{[\text{HA}_{\text{aq}}] + \frac{K_a \times [\text{HA}_{\text{aq}}]}{[\text{H}_3\text{O}^+]}} \quad (8.7.27)$$

Factoring $[\text{HA}_{\text{aq}}]$ from the denominator, replacing $[\text{HA}_{\text{org}}] / [\text{HA}_{\text{aq}}]$ with K_D (Equation 8.7.23), and simplifying leaves us with a relationship between the distribution ratio, D , and the pH of the aqueous solution.

$$D = \frac{K_D [\text{H}_3\text{O}_{\text{aq}}^+]}{[\text{H}_3\text{O}_{\text{aq}}^+] + K_a} \quad (8.7.28)$$

EXAMPLE 7.16

An acidic solute, HA, has a K_a of 1.00×10^{-5} and a K_D between water and hexane of 3.00. Calculate the extraction efficiency if we extract a 50.00 mL sample of a 0.025 M aqueous solution of HA, buffered to a pH of 3.00, with 50.00 mL of hexane. Repeat for pH levels of 5.00 and 7.00.

Solution

When the pH is 3.00, $[H_3O^+_{aq}]$ is 1.0×10^{-3} and the distribution ratio is

$$D = \frac{(3.00)(1.0 \times 10^{-3})}{1.0 \times 10^{-3} + 1.0 \times 10^{-5}} = 2.97 \quad (8.7.29)$$

The fraction of solute remaining in the aqueous phase is

$$(Q_{aq})_1 = \frac{50.00 \text{ mL}}{(2.97)(50.00 \text{ mL}) + 50.00 \text{ mL}} = 0.252 \quad (8.7.30)$$

The extraction efficiency, therefore, is almost 75%. The same calculation at a pH of 5.00 gives the extraction efficiency as 60%. At a pH of 7.00 the extraction efficiency is only 3%.

EXAMPLE 7.14

A solute has a K_D between water and chloroform of 5.00. Suppose we extract a 50.00-mL sample of a 0.050 M aqueous solution of the solute with 15.00 mL of chloroform. (a) What is the separation's extraction efficiency? (b) What volume of chloroform must we use to extract 99.9% of the solute?

Solution

For a simple liquid–liquid extraction the distribution ratio, D , and the partition coefficient, K_D , are identical.

(a) The fraction of solute remaining in the aqueous phase after the extraction is given by Equation 8.7.11.

$$(q_{\text{aq}})_1 = \frac{V_{\text{aq}}}{DV_{\text{org}} + V_{\text{aq}}} = \frac{50.00 \text{ mL}}{(5.00)(15.00 \text{ mL}) + 50.00 \text{ mL}} = 0.400 \quad (8.7.13)$$

The fraction of solute in the organic phase is $1 - 0.400$, or 0.600. Extraction efficiency is the percentage of solute moving into the extracting phase. The extraction efficiency, therefore, is 60.0%.

(b) To extract 99.9% of the solute $(q_{\text{aq}})_1$ must be 0.001. Solving Equation 8.7.11 for V_{org} , and making appropriate substitutions for $(q_{\text{aq}})_1$ and V_{aq} gives

$$V_{\text{org}} = \frac{V_{\text{aq}} - (q_{\text{aq}})_1 V_{\text{aq}}}{(q_{\text{aq}})_1 D} = \frac{50.0(q_{\text{aq}})_2}{(q_{\text{aq}})_1} = \frac{V_{\text{aq}}}{DV_{\text{org}} + V_{\text{aq}}} 50 \text{ mL} - (0.001)(50.00 \text{ mL}) \quad (8.7.14)$$

This is large volume of chloroform. Clearly, a single extraction is not reasonable under these conditions.

In Example 7.14, a single extraction provides an extraction efficiency of only 60%. If we carry out a second extraction, the fraction of solute remaining in the aqueous phase, $(q_{\text{aq}})_2$, is

$$(q_{\text{aq}})_2 = \frac{(\text{moles } S_{\text{aq}})_2}{(\text{moles } S_{\text{aq}})_1} = \frac{V_{\text{aq}}}{DV_{\text{org}} + V_{\text{aq}}} \quad (7.7.15)$$

If V_{aq} and V_{org} are the same for both extractions, then the cumulative fraction of solute remaining in the aqueous layer after two extractions, $(Q_{\text{aq}})_2$, is

$$(Q_{\text{aq}})_2 = \frac{(\text{moles } S_{\text{aq}})_2}{(\text{moles } S_{\text{aq}})_0} = (q_{\text{aq}})_1 \times (q_{\text{aq}})_2 = \left(\frac{V_{\text{aq}}}{DV_{\text{org}} + V_{\text{aq}}} \right)^2 \quad (7.7.16)$$

In general, for a series of n identical extractions, the fraction of analyte remaining in the aqueous phase after the last extraction is

$$(Q_{\text{aq}})_n = \left(\frac{V_{\text{aq}}}{DV_{\text{org}} + V_{\text{aq}}} \right)^n \quad (7.7.17)$$

EXAMPLE 7.15

For the extraction described in [Example 7.14](#), determine (a) the extraction efficiency for two extractions and for three extractions; and (b) the number of extractions required to ensure that we extract 99.9% of the solute.

Solution

(a) The fraction of solute remaining in the aqueous phase after two extractions and three extractions is

$$(Q_{\text{aq}})_2 = \left(\frac{50.00 \text{ mL}}{(5.00)(15.00 \text{ mL}) + 50.00 \text{ mL}} \right)^2 = 0.160 \quad (8.7.18)$$

$$(Q_{\text{aq}})_3 = \left(\frac{50.00 \text{ mL}}{(5.00)(15.00 \text{ mL}) + 50.00 \text{ mL}} \right)^3 = 0.0640 \quad (8.7.19)$$

The extraction efficiencies are 84.0% with two extractions and 93.6% with three extractions.

(b) To determine the minimum number of extractions for an efficiency of 99.9%, we set $(Q_{\text{aq}})_n$ to 0.001 and solve for n in Equation [8.7.17](#).

$$0.001 = \left(\frac{50.00 \text{ mL}}{(5.00)(15.00 \text{ mL}) + 50.00 \text{ mL}} \right)^n = (0.400)^n \quad (8.7.20)$$

Taking the log of both sides and solving for n

$$\log(0.001) = n \log(0.400) \quad (8.7.21)$$

$$n = 7.54 \quad (8.7.22)$$

we find that a minimum of 8 extractions is necessary.

The last two examples provide us with an important observation—for any extraction efficiency, we need less solvent if we complete several extractions using smaller portions of solvent instead of one extraction using a larger volume of solvent. For the conditions in [Example 7.14](#) and [Example 7.15](#), an extraction efficiency of 99.9% requires one extraction with 9990 mL of chloroform, or 120 mL when using eight 15-mL portions of chloroform. Although extraction efficiency increases dramatically with the first few multiple extractions, the effect quickly diminishes as we increase the number of extractions (Figure 7.27). In most cases there is little improvement in extraction efficiency after five or six extractions. For the conditions in [Example 7.15](#), we reach an extraction efficiency of 99% after five extractions and need three additional extractions to obtain the extra 0.9% increase in extraction efficiency.

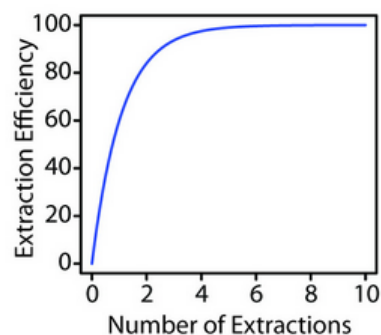


Figure 7.27: Plot of extraction efficiency versus the number of extractions for the liquid–liquid extraction in [Example 7.15](#).

EXERCISE 7.8

To plan a liquid–liquid extraction we need to know the solute’s distribution ratio between the two phases. One approach is to carry out the extraction on a solution containing a known amount of solute. After extracting the solution, we isolate the organic phase and allow it to evaporate, leaving behind the solute. In one such experiment, 1.235 g of a solute with a molar mass of 117.3 g/mol is dissolved in 10.00 mL of water. After extracting with 5.00 mL of toluene, 0.889 g of the solute is recovered in the organic phase.

- What is the solute’s distribution ratio between water and toluene?
- If we extract 20.00 mL of an aqueous solution containing the solute with 10.00 mL of toluene, what is the extraction efficiency? (c) How many extractions will we need to recover 99.9% of the solute?

7.9.1 Key Terms

centrifugation
composite sample
coning and quartering
convenience sampling
density gradient centrifugation
dialysis
distillation
distribution ratio
extraction
extraction efficiency
filtrate
filtration
grab sample
gross sample

heterogeneous
homogeneous
in situ sampling
judgmental sampling
laboratory sample
masking
masking agents
Nyquist theorem
partition coefficient
preconcentration
purge-and-trap
random sampling
recovery
recrystallization

retentate
sampling plan
secondary equilibrium reaction
selectivity coefficient
separation factor
size exclusion chromatography
Soxhlet extractor
stratified sampling
sublimation
subsamples
supercritical fluid
systematic-judgmental sampling
systematic sampling
target population

Liquid–Liquid Extraction of a Metal–Ligand Complex

One important application of liquid–liquid extractions is the selective extraction of metal ions using a ligand. Unfortunately, many ligands are not very soluble in water or undergo hydrolysis or oxidation in aqueous solutions. For these reasons the ligand is added to the organic solvent instead of the aqueous phase. Figure 7.30 shows the relevant equilibria (and equilibrium constants) for the extraction of M^{n+} by the ligand HL, including the ligand's extraction into the aqueous phase ($K_{D,HL}$), the ligand's acid dissociation reaction (K_a), the formation of the metal–ligand complex (β_n), and the complex's extraction into the organic phase ($K_{D,c}$).

In coordination chemistry, a ligand[help 1] is an ion or molecule (functional group) that binds to a central metal atom to form a coordination complex.

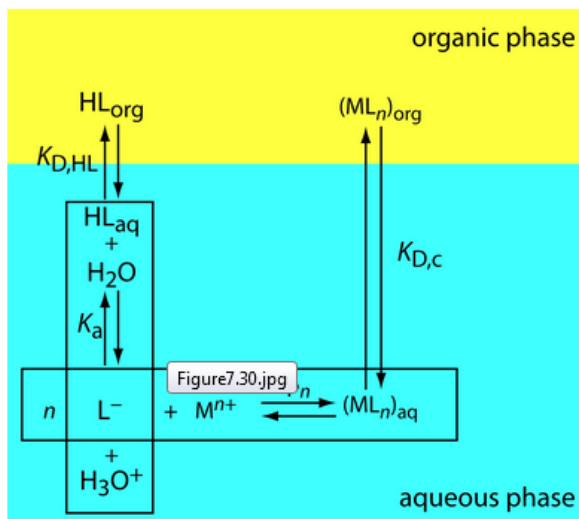
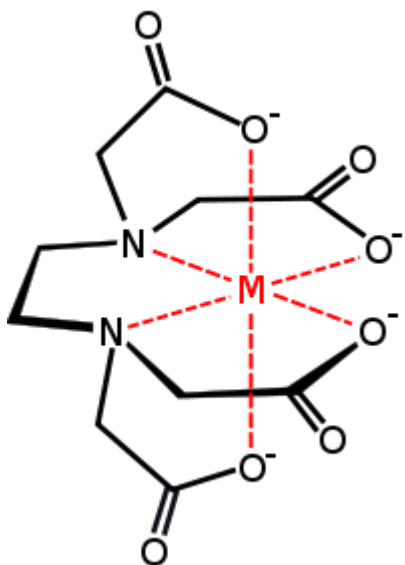


Figure 7.30 Scheme for the liquid–liquid extraction of a metal ion, M^{n+} , by the ligand L^- . The ligand initially is present in the organic phase as HL. Four equilibrium reactions are needed to explain the extraction efficiency.



If the ligand's concentration is much greater than the metal ion's concentration, then the distribution ratio is

$$D = \frac{\beta_n K_{D,c} (K_a)^n (C_{HL})^n}{(K_{D,HL})^n [\text{H}_3\text{O}^+]^n + \beta_n (K_a)^n (C_{HL})^n} \quad (8.7.33)$$

where C_{HL} is the ligand's initial concentration in the organic phase. As shown in Example 7.17, the extraction efficiency for metal ions shows a marked pH dependency.

EXAMPLE 7.17

A liquid–liquid extraction of the divalent metal ion, M^{2+} , uses the scheme outlined in Figure 7.30. The partition coefficients for the ligand, $K_{D,HL}$, and for the metal–ligand complex, $K_{D,CL}$, are 1.0×10^4 and 7.0×10^4 , respectively. The ligand’s acid dissociation constant, K_a , is 5.0×10^{-5} , and the formation constant for the metal–ligand complex, β_2 , is 2.5×10^{16} .

Calculate the extraction efficiency if we extract 100.0 mL of a 1.0×10^{-6} M aqueous solution of M^{2+} , buffered to a pH of 1.00, with 10.00 mL of an organic solvent that is 0.1 mM in the chelating agent. Repeat the calculation at a pH of 3.00.

Solution

When the pH is 1.00 the distribution ratio is

$$D = \frac{(2.5 \times 10^{16})(7.0 \times 10^4)(5.0 \times 10^{-5})^2(1.0 \times 10^{-4})^2}{(1.0 \times 10^4)^2(0.10)^2 + (2.5 \times 10^{16})(5.0 \times 10^{-5})^2(1.0 \times 10^{-4})^2} \quad (8.7.34)$$

$$D = 0.0438 \quad (8.7.35)$$

and the fraction of metal ion remaining in the aqueous phase is

$$(Q_{aq})_1 = \frac{100.0 \text{ mL}}{(0.0438)(10.00 \text{ mL}) + 100.0 \text{ mL}} = 0.996 \quad (8.7.36)$$

At a pH of 1.00, we extract only 0.40% of the metal into the organic phase. Changing the pH to 3.00, however, increases the extraction efficiency to 97.8%. Figure 7.31 shows how the pH of the aqueous phase affects the extraction efficiency for M^{2+} .

One advantage of using a ligand to extract a metal ion is the high degree of selectivity that it brings to a liquid–liquid extraction. As seen in Figure 7.31, a divalent metal ion’s extraction efficiency increases from approximately 0% to 100% over a range of 2 pH units. Because a ligand’s ability to form a metal–ligand complex varies substantially from metal ion to metal ion, significant selectivity is possible by carefully controlling pH. Table 7.9 shows the minimum pH for extracting 99% of a metal ion from an aqueous solution using an equal volume of 4 mM dithizone in CCl₄.

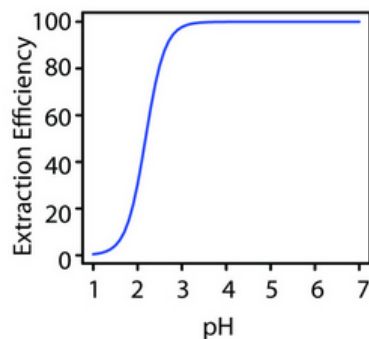


Figure 7.31 Plot of extraction efficiency versus pH for the extraction of the metal ion, M^{2+} , in Example 7.17.

Example 7.18 Using Table 7.9, explain how you can separate the metal ions in an aqueous mixture of Cu^{2+} , Cd^{2+} and Ni^{2+} by extracting with an equal volume of dithizone in CCl_4 .



Solution From Table 7.9, a quantitative separation of Cu^{2+} from Cd^{2+} and Ni^{2+} is possible if we acidify the aqueous phase to a pH of less than 1. This pH is greater than the minimum pH for extracting Cu^{2+} and significantly smaller than the minimum pH for extracting either Cd^{2+} or Ni^{2+} . After the extraction is complete, buffering the aqueous phase to 4.0 allows us to extract the Cd^{2+} leaving the Ni^{2+} in the aqueous phase.

Metal Ion	Minimum pH
Hg^{2+}	-8.7
Ag^+	-1.7
Cu^{2+}	-0.8

Bi³⁺	0.9
Zn²⁺	2.3
Cd²⁺	3.6
Co²⁺	3.6
Pb²⁺	4.1
Ni²⁺	6.0
Tl⁺	8.7