Liquid-Liquid Extractions

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In organic chemistry, extractions are used to separate compounds by exploiting the differences in their solubility in various solvents. There are varying types of extractions, but only two are commonly used in lab-scale procedures. Liquid-solid extractions can be used to isolate a compound present in a solid mixture by choosing a solvent such that the desired compound is selectively dissolved. This type of extraction has the distinct disadvantage that dissolution is a kinetic property, thus extended times and/or harsh conditions are required to ensure a good efficiency. Liquid-liquid extractions circumvent this by extracting a compound which is already dissolved. The solute merely has to migrate from one solvent to another, this is a much faster process. In fact, these extractions are quick enough that they can be performed in under a minute per extraction using a separatory funnel.

Liquid-liquid extractions require two separate solvents, one for the impure solute to be dissolved in initially, and the extraction solvent which extracts the desired compound from the impure mixture. There is a wide variety of extraction solvents, but there are some characteristics which they must posses. Firstly, they must be immiscible with the initial solvent, so that the two can be physically separated after the extraction. Secondly, they must show a good solubility for the compound to be extracted, for example, dichloromethane and diethyl ether are good extraction solvents for polar compounds, whereas hexane is good extraction solvent for nonpolar compounds. Thirdly, the extraction solvent ideally shows minimal solvation towards the impurities in the compound to be extracted, to achieve a better separation. Finally, the extraction solvent must have a boiling point which varies greatly from the compound being extracted, so that the two are easily separated after the extraction. For solids, solvents with low boiling points are ideally used so that they can be removed quickly and, in the case that the substrate is heat sensitive, the compound doesn't decompose when the solvent is removed. For obvious reasons, the extraction should not form an azeotrope with the target compound.

The amount of solute which is extracted in one extraction is given by the following equation :

$$\text{Partition coefficient} = \frac{\dfrac{x}{\text{volume of extraction solvent}}}{\dfrac{\text{amount of solute} - x}{\text{volume of solution to be extracted}}}$$

where x is the amount of solute which is extracted in that extraction. The partition coefficient, k, is defined as follows :

$$k = \frac{\text{solubility of compound in extraction solvent}}{\text{solubility of compound in starting solvent}}$$

The coefficient k is unique to a solute in a certain set of solvents, and can either be determined based on reported solubilities or experimentally.

I'm going to define some variables to clean this up a bit :

$$x : \text{Amount of solute extracted}$$

$$s_0 : \text{Initial amount of solute}$$

$$s : \text{Amount of solute present at the beginning of the current extraction}$$

$$k : \text{Partition coefficient}$$

$$r : \text{Ratio of volume of extraction solvent to volume of starting solvent}$$

$$n : \# \text{ of extractions}$$

So, with these new variables we can rewrite the equation above as :

$$k = \frac{\frac{x}{r}}{s_0 - x} = \frac{x}{r(s_0 - x)} \tag{1}$$

This can be rearranged to yield the following equation, solved for x :

$$x = \frac{s_0 k r}{1 + kr} \tag{2}$$

Now let's do an example to demonstrate the use of this equation : Assume that the partition coefficient of caffeine in a dichloromethane/water solvent system is 6.4. 200ml of coffee contains 140mg of caffeine. If the coffee is extracted with 2×100ml dichloromethane, how much caffeine remains in the coffee. So, to start off, we plug all of the variables into Equation 2 :

$$x = \frac{.140 \cdot 6.4 \cdot 0.5}{1 + 6.4 \cdot 0.5} = .107 \text{ g}$$

Thus, 107mg of caffeine are extracted in the first extraction. Now we find our new s and solve for x in the second extraction :

$$s = s_0 - .107 = .033 \text{ g}$$

$$x = \frac{.033 \cdot 6.4 \cdot 0.5}{1 + 6.4 \cdot 0.5} = .025 \text{ g}$$

Finally we add up the amount of caffeine extracted in the first and second extraction, and subtract from the original amount in the coffee to find the amount of caffeine remaining in the coffee.

$$.140 - (.025 + .107) = .008 \text{ g}$$

So, in those two extractions, 94% of the caffeine was removed from the coffee using 200ml total of dichloromethane. Now let's repeat the problem except this time, we're going to use one 200ml portion of dichloromethane :

$$x = \frac{.140 \cdot 6.4 \cdot 1}{1 + 6.4 \cdot 1} = .121 \text{ g}$$

So now, using the same amount of dichloromethane, 19mg of caffeine remain in the coffee, thus the extraction was only 86% efficient. This demonstrates an important concept in extractions, **more extractions using lesser amounts of solvent are more efficient than fewer extractions using greater amounts of solvent**. Of course, this is only the theoretical aspect, in reality mechanical losses provide a limit to how small the amount of extraction solvent can truly become.

Ignoring that for a moment though, let's look at a way of speeding up determining the amount of solvent extracted in the nth extraction in a series of extractions. Firstly, I am going to define one more constant, b, which will make the following equations more aesthetically pleasing :

$$b = \frac{kr}{1 + kr}$$

Now consider an arbitrary number of successive extractions, the total amount of solute extracted can be described by :

$$\sum_{i=1}^{n} b\, s_i = bs_0 + bs_1 ... + bs_n$$

where s_i is the amount of solute remaining in the beginning of that extraction. We are given s_0 in the original problem, but we need to define the rest. We can define s_1 however, in terms of bs_0 by realizing that $s_0 - bs_0$ is equal to the solute remaining after the first extraction which is equal to s_1. If we make the same argument for the subsequent terms, we get the following :

$$bs_0 + bs_1 + \cdots + bs_n = bs_0 + b\left(s_0 - bs_0\right) + b\left((s_0 - bs_0) - b\left(s_0 - bs_0\right)\right) = bs_0 + bs_0\left(1-b\right) + bs_0\left(1-b\right)^2 \cdots$$

Thus, the amount of solute extracted in the nth extraction can be defined by :

$$bs_0(1-b)^{n-1} \tag{3}$$

and the total amount extracted by n extractions is :

$$\sum_{i=1}^{n} bs_0(1-b)^{n-1} \tag{4}$$

This can be used to directly compute something quite interesting. As mentioned previously, a greater number of extractions with smaller amounts of solvent is more efficient than fewer extractions with greater amounts of solvent, even if the total solvent used is the same. Using the previous definitions, we can adapt the derived equation to represent the efficiency of a varying number of extractions. If we let :

$$r = \frac{r}{n}$$

then we get the following equation :

$$b = \frac{kr}{1 + kr} = \frac{\frac{kr}{n}}{1 + \frac{kr}{n}} = \frac{kr}{n + kr}$$

Finally, this can be plugged into Eq. 4. This allows us to calculate and compare the efficiency of two series of extractions which utilize different numbers of extractions, but the same total amount of solvent.

Just as a note, we can see that :

$$\lim_{n \to \infty} \left(\sum_{i=1}^{n} bs_0(1-b)^{n-1} \right) = s_0$$

thus, theoretically, as the number of extractions performed goes to infinity, the extraction efficiency approaches 100% (again ignoring mechanical losses).