The Separatory Funnel

As the name implies, the separatory funnel is used for separating substances by *extraction*. This technique is usually carried out using two immiscible solvents—that is, that do not mix with each other—one of which is almost always water. Typical organic solvents include ethyl acetate, hexane, chloroform, dichloromethane, and diethyl ether. All of these form a crisp delineation between the two liquids.

The two layers are commonly referred to as the *aqueous phase* and the *organic phase*. It is important to keep track of these phases, as their positions are solvent dependent. For solvents lighter than water (i.e., density < 1), the organic phase will rest on top in the separatory funnel, whereas solvents denser than water (density > 1) will sink to the bottom (Figure 1). Many are the students who have realized only too late that they have discarded the wrong layer from an extraction.

The basis of extractive techniques is the "like dissolves like" rule. Water typically dissolves inorganic salts (such as lithium chloride) and other charged species, while organic solvents (ethyl acetate, dichloromethane, diethyl ether, etc.) dissolve neutral organic molecules. It is important to remember that this method of separation relies on *partitioning*—that is, the preferential dissolution of a compound into one solvent over another. For example, 2-pentanol is somewhat soluble in water (ca. 17 g / 100 mL H_2O), but infinitely soluble in diethyl ether. Thus, even though it is somewhat soluble in water, 2-pentanol can be preferentially *partitioned* into ether.

By way of vocabulary, actually two operations are encountered in the separatory funnel. When components are removed from an organic layer by shaking with an aqueous solution, the organic phase is said to be washed (e.g., “The combined ether extracts were washed with aqueous sodium bicarbonate solution.”). On the other hand, when components are removed from water by treatment with an organic solvent, the aqueous phase is said to be extracted (e.g., “The aqueous layer was extracted with three portions of ethyl acetate.”). Thus, aqueous layers are extracted, and organic layers are washed—although these two terms are sometimes (erroneously) used interchangeably.

To use a separatory funnel, a sample or reaction mixture is quantitatively transferred into the funnel and roughly equal amounts of water and organic solvent are introduced. The funnel is shaken, taking care to vent frequently—this is accomplished by tilting the funnel so that the stem is up and briefly opening the stopcock to relieve pressure. The funnel is then allowed to stand upright in an iron ring (never a clamp!) until the phases separate. The lower phase is then drained out through the stopcock and the remaining upper phase is poured out the neck by decantation.

Usually low-boiling organic solvents are used for extractions because they are easily removed by evaporation, leaving behind the organic compound of interest. Many of these, however, carry over a considerable amount of residual water from the aqueous washes. Ethyl acetate and diethyl ether both dissolve large quantities of water (3.3% and 1.2% water, respectively). Therefore, it is wise to wash these organic layers with brine (saturated NaCl solution) at the end of the extraction sequence—the brine draws out the dissolved water through an osmotic-like effect. For methylene chloride and chloroform a brine wash is unnecessary, since the solubility of water in these solvents is quite low. Once freed from the bulk of residual water, the organic layer is dried over a desiccant, such as sodium sulfate, calcium chloride, or magnesium sulfate, and then decanted or filtered before evaporation.

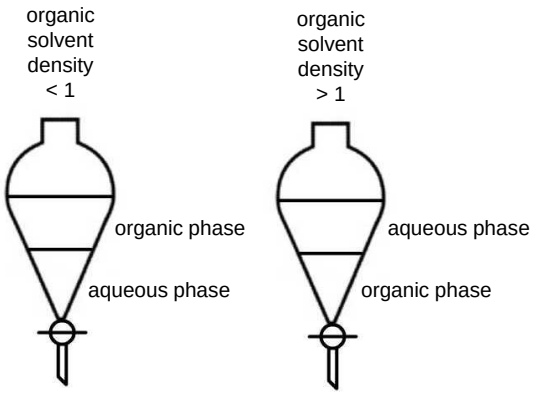

Figure 1. Two possibilities for aqueous extraction.