

2. Distillation

J.R. Mohrig,
C.N. Hammond,
and P.F. Schatz: Technique 12 Boiling points and distillation
173-174 (general introduction)
176-180 (distillation and separation of mixtures)
194-196 (steam distillation)
203-205 (sources of confusion)

Vocabulary:

Vaporization	The process of turning a liquid into vapor.
Condensation	The process of turning a vapor into a liquid.
Azeotrope	It is a mixture of two or more liquids, which boils at a constant boiling point.

This procedure has been adapted from the macroscale procedure described in *Macroscale and Microscale Organic Chemistry Experiments* by Kenneth L. Williamson.

In a nutshell:

Normally, we distill solvents (the liquid in which we run the reaction) from a drying agent to dry the solvent if water is undesirable using a simple distillation. A fractional distillation is used to distill two or more components with similar boiling points. The *Laboratory Techniques in Organic Chemistry's* authors (J.R. Mohrig, D.G. Alberg, G.E. Hofmeister, P.F. Schatz, and C.N. Hammond, pg 164) describes steam distillation as the “codistillation with water” and “allows the distillation of relatively nonvolatile organic compounds without complex vacuum systems; it is especially useful for separating volatile organic compounds from nonvolatile inorganic salts or from the leaves and seeds of plants”.

Background

What is distillation? It is the separation of liquids by vaporization and subsequent condensation of the vapors into a separate container. You are probably familiar with this process because it is used in the fragrance as well as the alcohol industry. In a normal chemistry lab, we use distillation for purification of starting materials, solvents, and products. In various experiments in organic chemistry lab, you will be performing both simple and fractional distillations. You may ask what is the difference between the two different techniques. Well, simple distillation is used to separate two or more liquids with boiling points less than

150 °C at 1 atmosphere but more than 25 °C difference between each of them. Fractional distillation is used when the different components of the mixture have boiling point ranges less than 25 °C from one another.

Not all liquids, even ones with more than 25 °C difference in the boiling points, can be separated using a normal distillation process. For example, do not try to distill alcohol at home to see if you can produce 100% ethanol. It does not work. Why? Well, water and alcohol (ethanol) form an azeotrope, a mixture with a constant boiling point that cannot be purified by distillation. Azeotropes behave a lot like pure compounds. Even though the boiling point of ethanol is 78.3 °C and that of water is 100 °C, you will not be able to obtain purity better than 96% alcohol / 4% water which is the composition of the azeotrope.

Now, let's consider steam distillation. As Mohrig points out, it “depends on the mutual insolubility or immiscibility of many organic compounds with water”. In this experiment, you will separate two miscible organic compounds (toluene and benzil) using steam distillation, which will be generated by the addition of water into your starting flask. The benefits of this technique are reduced temperatures (which is important because many organic compounds decompose at high sustained temperatures), increased selectivity, and good separation. Steam distillation is used in the manufacture of essential oils for use in perfumes.

Table 1. Vapor pressure of water (in mmHg) for temperatures between 65 – 101 °C. (R.C. Weast (Ed). *CRC Handbook of Chemistry and Physics*, CRC Press, Baton Rouge, FL p D-232 (1978).

Temp (°C)	<i>p</i> (mmHg)
65	187.54
66	196.09
67	204.96
68	214.17
69	223.73
70	233.7
71	243.9
72	254.6
73	265.7
74	277.2
75	289.1
76	301.4
77	314.1
78	327.3
79	341.0
80	355.1
81	369.7
82	384.9
83	400.6

Temp (°C)	<i>p</i> (mmHg)
84	416.8
85	433.6
86	450.9
87	468.7
88	487.1
89	506.1
90	525.76
91	546.05
92	566.99
93	588.60
94	610.90
95	633.90
96	657.62
97	682.07
98	707.27
99	733.24
100	760.00
101	787.57

It is possible to calculate the “amount of water required for distillation of a given amount of organic” material (Williamson). The two different partial pressures must be equal to 760 mmHg (one atmosphere). Using Dalton’s law and assuming that the more volatile material occupies more vapor, then the following equation is valid.

$$\frac{\text{Moles of water}}{\text{Moles of organic material}} = \frac{p_{\text{water}}}{p_{\text{organic material}}}$$

where the vapor pressure of water and the organic material are p_{water} and $p_{\text{organic material}}$, respectively. Given that the partial pressure of the organic material then must be equal to $760 - p_{\text{water}}$. Therefore the weight of water required per gram for the distillation of an organic material is

$$\frac{\text{Wt. of water per g of organic material}}{1} = \frac{18 \times p_{\text{water}}}{\text{MW of organic material} \times (760 - p_{\text{water}})}$$

For example, using Table 1 on the previous page, we can calculate the amount of water required to steam distill nitrobenzene (MW 123.11), which forms an azeotropic mixture with water at 99 °C. Considering that nitrobenzene has a boiling point of 210 °C at 760 mmHg, is steam distillation an improvement for purification of nitrobenzene?

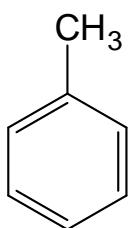
There is one more thing to consider, the density difference. You know that “like dissolves like” so alcohols (R-OH) are miscible in water but hydrocarbons are not. Normally, the hydrocarbons have a density less than water so they float on the top of the water layer. On the other hand, the general rule is that halogenated hydrocarbons (like chloroform, CHCl_3 , or dichloromethane, CH_2Cl_2) have densities greater than that of water. This information is something to keep in mind when you are measuring the volumes of water and toluene in this experiment, as well as later for other experiments.

Experiment

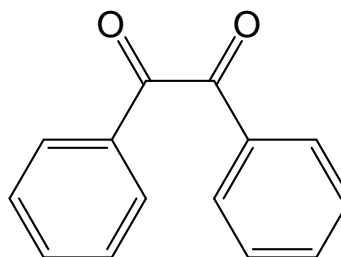
Caution. Boiling stones or sticks should never be added to hot solutions. When performing a distillation, do not heat any flask until dryness because it is difficult to clean and may cause other dangerous situations. You may have experienced this situation if you have heated water on your stove until all the water has evaporated.

Before starting your experiment, please ask your TA to give you the atmospheric pressure for the room you are in.

Steam distillation of a toluene-benzil mixture



toluene
MW 92.14



benzil
MW 210.23

Add 10 mL of the toluene-benzil solution and a boiling chip to 20 mL of water in a 50-mL round-bottomed flask (your starting or distilling flask). Set up your distillation for a simple distillation similar to the one depicted in Figure 13.7 on pg 149 of your lab textbook (J.R. Mohrig, D.G. Alberg, G.E. Hofmeister, P.F. Schatz, and C.N. Hammond, pg 149). When the temperature of the distillation remains constant (the azeotrope), collect about (but not more than) 10 mL of the distillate, which is the solution being distilled into the receiver flask. Record this temperature in your lab notebook. Replace the receiver flask with a new one. Transfer the collected distillate from the first receiver flask to a graduated cylinder, and record the volumes of water and toluene from their separation (two layers) in the graduated cylinder. Determine the weight of water per gram of toluene. Does this result compare to the theoretical value determined from the vapor pressure of water at its azeotropic temperature?

Continue the distillation until the distillate becomes clear. At that point, all of the toluene will be distilled from the starting to the receiver flask. Cool the starting flask in ice water and collect the resulting solid (the benzil) using vacuum filtration. Record the amount of recovered benzil.