Experiment 9

Distillation: Separating a Mixture of Two Liquids

Study Questions

1) In Boulder, CO, the atmospheric pressure is always less than standard atmospheric pressure, and therefore the observed boiling points will be lower than those reported in the literature. The barometric pressure in Boulder is usually around 625 mm Hg (625 Torr). What will be the observed boiling points of acetone and ethyl acetate? (Refer to the first three pages of the Distillation chapter in the *Handbook for Organic Chemistry*.)
Answer: The literature boiling point of acetone is 56.2°C and that of ethyl acetate is 77.1°C. The value at 625 mm Hg is calculated as follows:

$$T_{corr} = T_{obs} + 0.00010(760\text{-}p)(T_{obs} + 273)$$

For acetone:
$56.2° = T_{obs} + 0.00010(760\text{-}625)(T_{obs} + 273)$
$56.2° = T_{obs} + 0.0135(T_{obs} + 273)$
$56.2° = T_{obs} + 0.0135\ T_{obs} + 3.685$
$52.5° = 1.0135\ T_{obs}$
$51.8° = T_{obs}$

For ethyl acetate:
$77.1° = T_{obs} + 0.00010(760\text{-}625)(T_{obs} + 273)$
$77.1° = T_{obs} + 0.0135(T_{obs} + 273)$
$77.1° = T_{obs} + 0.0135\ T_{obs} + 3.685$
$73.4° = 1.0135\ T_{obs}$
$72.4° = T_{obs}$

2) Why does a rapid distillation that floods the fractionating column lead to poor separation of components? **Answer:** The vapor-liquid equilibrium is not established, leading to decreased efficiency (fewer theoretical plates).

3) Two alcohols have a low retention time and are not separable on a silicone GC column. Explain why they have a longer retention time and are separable on a Carbowax column. (Hint: the structures and relative polarities of the two types of columns are given in the gas chromatography chapter in the *Handbook for Organic Chemistry*.) **Answer:** Alcohols can form hydrogen bonds with the oxygen atoms in a Carbowax (a polyethylene glycol; see the Handbook).

4) When a careful distillation is performed on a mixture of liquids with widely different boiling points, the head temperature rises and plateaus, then drops before rising again during the distillation. Explain what is happening during each of these phases. **Answer:** The head temperature rises as the vapors of lower-boiling compound fill the distillation head. The temperature drops because the lower-boiling compound finishes distilling before vapors of the higher-boiling compound can fill the distillation head, which then cause the head temperature to rise.
Phase one: initial rise - vapors of low boiling material reaching thermometer.
Phase two: plateau - vapors of low boiling material in thermal equilibrium with condensate on thermometer bulb.

Phase three: drop - too little vapor of lower boiling component is reaching thermometer to remain in equilibrium with condensate; higher boiling vapors not yet reaching thermometer.
Phase four: higher boiling vapors reaching thermometer.

5) Why is it necessary to carry out a slow, even distillation in order to achieve good separation between components in a mixture? **Answer:** If the distillation flask is superheated, larger quantities of the higher-boiling components distill in the early fractions. Also, the added heat and excess quantities of vapors prevent equilibrium between liquid and gas in the distillation head. A slow, even distillation is necessary to achieve a good separation because only under these conditions will vapor and liquid be in equilibrium with one another in the distillation apparatus. If a mixture is heated too rapidly the rising vapor will have a chance of being carried over to the receiver without condensing. Thus, more higher-boiling material will be found mixed in with the lower boiling material.