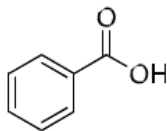


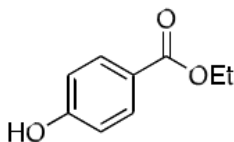
## Separation of a Three-Component Mixture by Extraction

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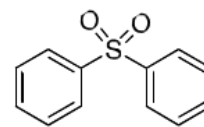
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benzoic acid  
formula C<sub>7</sub>H<sub>6</sub>O<sub>2</sub>  
form. wt. 122.12  
mp = 122-123°C  
pKa = 4.2



ethyl 4-hydroxybenzoate  
formula C<sub>9</sub>H<sub>10</sub>O<sub>3</sub>  
from. wt = 166.17  
mp = 115-117°C  
pKa = 8.5



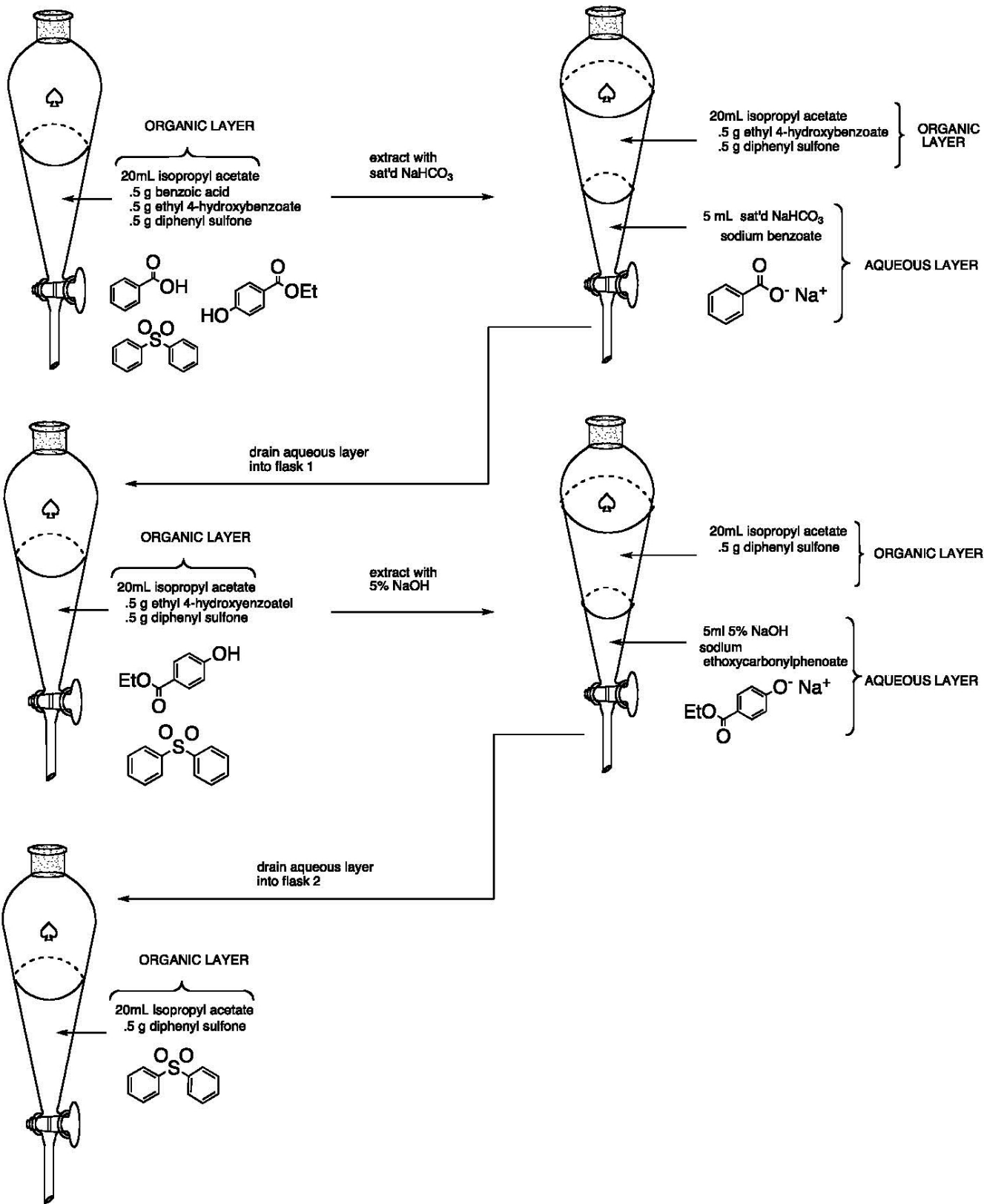
diphenyl sulfone  
formula C<sub>12</sub>H<sub>10</sub>O<sub>2</sub>S  
from. wt = 218.27  
mp = 126-128°C  
pKa = neutral

A 1.5-gram sample of a 1:1:1 (by weight) mixture of benzoic acid, ethyl 4-hydroxybenzoate and diphenyl sulfone was added to a 125 mL separatory funnel. Isopropyl acetate (20 mL) was added to the separatory funnel and the mixture swirled until all solids had dissolved. The solution was sequentially extracted with saturated aqueous NaHCO<sub>3</sub> solution (4 X 5 mL), then with water (1 X 5 mL); with the aqueous extracts from each extraction being added to a 50 mL beaker (beaker 1). [*The separatory funnel should be shaken for at least 1 minute during each of the four NaHCO<sub>3</sub> extractions. Venting of the funnel should be done every 20-25 seconds during each extraction. When draining off the aqueous layer in these and all subsequent extractions leave a two mm tall layer of aqueous solution in the separatory funnel. This greatly reduces the amount of organic layer that contaminates the aqueous extracts.*] Next the organic layer was extracted sequentially with 5% aqueous NaOH solution (3 X 5 mL) then with water (1 X 5 mL). Each aqueous extract was collected in a 50 mL beaker (beaker 2). [*The separatory funnel should be shaken for at least 1.0 minute during each NaOH extraction.*] The remaining organic layer is extracted with saturated aqueous NaCl solution (5 mL) and the aqueous layer is discarded [*Do not leave any water in the funnel after this extraction*]. The organic layer is transferred to a 50 mL Erlenmeyer flask (flask 3). The separatory funnel is washed with isopropyl acetate (2 X 2 mL) with each washing being added to flask 3. The organic solution in flask 3 is dried (Na<sub>2</sub>SO<sub>4</sub>) then decanted into a tared 50 mL Erlenmeyer flask (flask 4). The drying agent is washed with isopropyl acetate (2 X 1 mL) with each rinse being added to flask 4. The solvent in flask 4 is evaporated to give crude diphenyl sulfone as a white solid: 0.416 g, 83.2%, M. pt.=121-127°C. [*Evaporate the solvent using a hot plate set on a moderate (4) setting. You must be very careful not to overheat the product when all the solvent has boiled away. The only way to actually know when all of the solvent has been removed is to weight the flask at the point of "presumed dryness," then reheat for a few seconds and re-weigh the flask. If the weight does not change, the product is solvent free. An alternative, and probably better, procedure is to evaporate the isopropyl acetate until only 3-5 mL of solution remains, cool, add hexane (10 mL), chill in an ice bath then filter. Both procedures work well. If insufficient time remains to isolate this material on day 1, then store the dried isopropyl acetate solution in your drawer until the next lab period. The solvent will have evaporated by then. [Optional: tlc (alumina, 70/30 hexane/ethyl acetate) showed a single spot, R<sub>f</sub> = 0.58. The crude product is recrystallized from toluene to give the crude product; M. pt. = 125-127°C].*

The aqueous solution in beaker 1 was acidified (acid to litmus paper) by the addition of 6 M HCl solution to give a white precipitate. [*Caution! Foaming will occur due to liberation of CO<sub>2</sub>.*]

After cooling the resulting mixture in an ice bath for 10 minutes, the solid was isolated by vacuum filtration, washed with ice water (3 X 1 mL), and air dried to give crude benzoic acid as a white solid: 0.358 g, 71.6%, M. pt.= 115-120°C. [*OPTIONAL: tlc (alumina, 70/30 hexane/ethyl acetate) showed a single spot (R<sub>f</sub> = 0.03). This material was recrystallized from water to give pure benzoic acid; M. pt. = 118- 120°C.*]

The aqueous solution in beaker 2 was acidified (acid to litmus paper) by the addition of 6 M HCl to give a white precipitate. The resulting aqueous mixture was cooled in an ice bath for 10 minutes. The resulting white solid was isolated by vacuum filtration, washed with ice water (3 X 1 mL), and air dried to give the crude ethyl 4-hydroxybenzoate: 0.353 g, 70.6%, M.pt.= 113-117°C. [*Optional: tlc (alumina, 70/30 hexane/ethyl acetate) showed a single spot (R<sub>f</sub> = 0.42). The crude material was recrystallized from 1/1 toluene/hexane to give the pure ethyl 4-hydroxybenzoate as a white solid; M. pt.= 115-117°C.*]



## EXTRACTION part II

### Technique 12: Liq/liq extraction Phase 2

Additional instruction for recrystallization of flask 2 crude containing  
Ethyl 4-hydroxybenzoate. (E4HB)

Method description:

Technique: Hirsch vacuum filtration post crystallization

Solvent: Methylcyclohexane (MCH)

Molar mass: 98.186 g/mol

Boiling point: 101 °C

Formula: C<sub>7</sub>H<sub>14</sub>

Density: 0.77 g/mL

Procedure:

1. Accurately weigh your crude E4HB collected from flask 2 and record the weight.
2. Subsample 0.050 to 0.100 g of crude E4HB into a 10 mL Erlenmeyer flask and record the weight.
3. Obtain 5 mL of MCH in a 10 mL beaker.
4. Add 1 mL of MCH and heat the mixture to a gentle boil on a hotplate.
5. Stir continuously with a spatula.
6. Add MCH as necessary to obtain a saturated boiling mixture up to a total volume not to exceed 3.0 mL while continuously stirring.
7. Cool the mixture for 10 minutes to RT.
8. Cool the remaining MCH in an ice bath.
9. Cool the mixture for 5 minutes in an ice bath.
10. Collect the crystallized product on a Hirsch filter.
11. Wash the product with 2 x 0.5 mL ice cold MCH.
12. Air-dry the crystals for 5 minutes.
13. Transfer the crystals to a pre-weighed weigh boat and record the weight.
14. Describe and characterize the crystals. (e.g. appearance, shape, color, size, IR, NMR, mp, TLC/R<sub>f</sub>, etc.)
15. Keep the resulting product in the weigh boat for inspection by the instructor.
16. Report g and calculate % recovery of the crystallization step.

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