

Formal Lab 2: Synthesis and Recrystallization of Acetanilide

Introduction. Recrystallization is a widely-used technique to purify a solid mixture. The solid is dissolved completely in hot solvent and then cooled to ice temperatures. The desired product isolated from its impurities by differences in solubility. Insoluble impurities and colored impurities can be removed from hot solvent through the use of activated carbon and gravity filtration. After cooling, the recrystallized solid is isolated by vacuum filtration. Soluble impurities remain dissolved in the cold filtrate and are eliminated at the vacuum filtration stage. The desired product should be as soluble as possible in hot solvent and as insoluble as possible in cold solvent. The selection of solvent is, therefore, critical to the successful recrystallization.

The purpose of this report is to compare the recrystallization of impure acetanilide using two solvents (dichloromethane and water). Percent recovery was found for each solvent. Preparation of acetanilide from aniline and acetic anhydride provided another source of impure acetanilide. Purification was achieved through recrystallization from water.

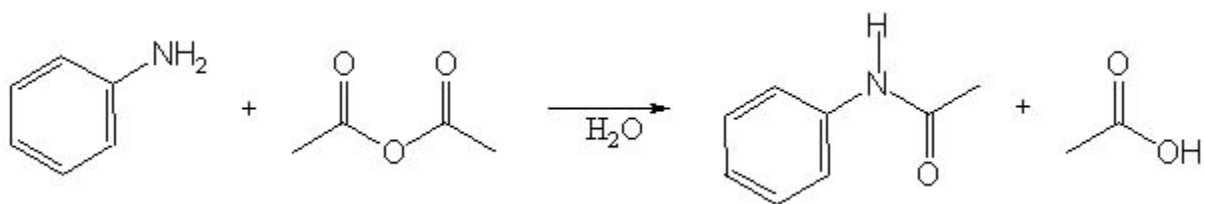
Materials and Hazards.

| <u>Compound</u> | <u>FW</u> | <u>BP</u> | <u>density (g/mL)</u> | <u>Hazards</u> |
|------------------|-----------|------------|-----------------------|--|
| Acetanilide | 135.17 | (mp)114 °C | --- | Toxic. |
| Dichloromethane | 84.93 | 40 °C | --- | Harmful. Possible Carcinogen. |
| Aniline | 93.13 | 184 °C | 1.022 | Highly Toxic: LD ₅₀ (oral rat) 250 mg/kg. |
| Acetic Anhydride | 102.09 | 138 °C | 1.082 | Toxic. Corrosive. Lachrymator. |

Data from *Aldrich Handbook of Fine Chemicals*, Milwaukee, WI: Sigma-Aldrich Co., 1998, and LD₅₀ from MSDS.

Procedures. from Bell, C. E. Jr.; Clark, A. K.; Taber, D. F.; Rodig, O. R. *Organic Chemistry Laboratory: Standard and Microscale Experiments, 2nd ed.*; Saunders/Harcourt Brace: Fort Worth, 1997.

Impure acetanilide was recrystallized by dissolving 2.08 g in 10-15 mL of hot dichloromethane, treatment with activated carbon, gravity filtration, and cooling with an ice-water bath. Large, white crystals (1.23 g) were collected by vacuum filtration and dried on a watchglass overnight. A similar procedure was used to recrystallize impure acetanilide (1.91 g) from hot water (about 100 mL) yielding 1.36 g of acetanilide after air-drying for a couple days.



Acetanilide was prepared according to the reaction shown above. The aniline (2.12 g, about 2 mL), 15 mL DI water, and 2.5 mL acetic anhydride were stirred together in an Erlenmeyer flask. Heat was given off as the reaction proceeded. The product was purified by recrystallization from hot water, as described above, yielding 2.33 g of crystalline acetanilide.

Data.

Table 1. Results from Recrystallizations of Acetanilide from Dichloromethane and Water.

| | <u>CH₂Cl₂</u> <u>Recrystallization</u> | <u>Water Recrystallization</u> |
|--|---|--------------------------------|
| melting point (measured) | 109 - 111 °C | 111 - 112 °C |
| melting point (corrected) ^a | 111 - 113 °C | 113 - 114 °C |
| initial mass | 2.08 g | 1.91 g |
| recovered mass | 1.23 g | 1.36 g |
| %recovery | 59.1 % | 71.2 % |

^aCorrection from Lab 1, *corrected* = 1.05(*measured*) - 2.7.

Table 2. Results from the Synthesis of Acetanilide and Recrystallization (from Water).

| | |
|--|---------------------|
| melting point (measured) | 111 - 112 °C |
| melting point (corrected) ^a | 113 - 114 °C |
| amount of aniline ^b | 2.12 g = 0.0228 mol |
| amount of acetic anhydride | 2.5 mL = 0.026 mol |
| theoretical yield | 3.08 g |
| product mass | 2.33 g |
| % yield | 75.6 % |

^aCorrection from Lab 1, *corrected* = 1.050(*measured*) - 3.1. ^bLimiting reagent.

Discussion. Recrystallization proved to be a somewhat effective method of purification for impure acetanilide, as indicated by the fine white crystals with a narrow melting point range (1-2 °C). The percent recovery was better for recrystallization from water than it was from dichloromethane. Both the percent recovery and purity were better from the water recrystallization. Water may have a greater ability to dissolve the impurities and it definitely has a greater temperature difference between boiling solvent and ice-water. This is likely to correspond to a greater difference between the solubility in hot and cold solvent. The crystals obtained from the water recrystallizations had a narrower range (1 °C) and were closer to the literature melting point of acetanilide (113-114 °C vs. literature: 114 °C), this is indicative of higher purity. Care was taken on the second trial (water) to reduce the amount of crystals formed on the fluted filter paper by pre-warming the funnel/filter paper and quickly filtering. The major disadvantage of water is that it takes much longer for the crystals to dry. A percent recover of 71% seems quite reasonable, especially considering that the initial composition was unknown. About 1-2 mL was spilled but this should account for a loss of only 1-2%.

Synthesis of acetanilide from aniline and acetic anhydride produces acetic acid as a byproduct. Since water was shown to be a good recrystallization solvent and the acetic acid byproduct is highly soluble in water, recrystallization from water seems appropriate. Another impurity that is expected in the crude product mixture is aniline because the reaction may not have gone to completion. However, the isolated yield (76%) is even

greater than the percent recovery in the earlier recrystallizations of acetanilide, thus, the reaction probably went nearly to completion. Compared to the earlier recrystallizations there was very little color to remove with activated carbon. Crystals were pure and dry as indicated by the narrow melting point range that is very close to the reported melting point of acetanilide (113-114 °C vs. literature: 114 °C).

Conclusion. Synthesis of acetanilide was accomplished in decent yield. Recrystallization from water proved to be an effective method of purification.