PW 01: recrystallization

I. Introduction

Recrystallization is a method used to **purify solids** based on their **different solubility in hot and cold solvents**. The product dissolves when hot but crystallizes when cooled, while impurities are removed either by hot filtration or remain dissolved.

II. Objectives

- Classify solvents by type (protic, polar aprotic, non-polar aprotic).
- Test miscibility of solvent pairs.
- Purify a crude solid by recrystallization.
- Use a binary solvent system for recrystallization.

III. Miscibility and Immiscibility of Solvents

Like dissolves like**: polarity determines solubility.**

- **Solvent types:**
    1. **Protic:** water, methanol, ethanol.
    2. **Polar aprotic:** acetone, DMF, DMSO.
    3. **Non-polar aprotic:** toluene, hexane, chloroform.
- **Miscibility:**
    - Complete: water/methanol.
    - Immiscible: water/mercury.
    - Partial: water/ether.

III.1. Experimental Procedure

III.1.1. Materiel and products

Products: H_2O, EtOH, DMSO, DMF, THF,CCl_4, CH_3CO_2H, toluene, acetone, ethyl acetate, ethylene glycol, CH_2Cl_2, $CHCl_3$, n-heptane, CH_3OH.

Materiel: test tube, Bunsen burner, test tube rack.

III.1.2. Procedure for the Classification of Solvents

Classify the following solvents according to the categories mentioned above:

H_2O, EtOH, DMSO, DMF, THF,CCl_4, CH_3CO_2H, toluene, acetone, ethyl acetate, ethylene glycol, CH_2Cl_2, $CHCl_3$, n-heptane, CH_3OH.

III.1.3. Procedure for the Study of Miscibility and Immiscibility of Solvents

Step 1 – Numbering solvents

Assign numbers from **1 to 15** to all solvents provided (for example: 1 = water, 2 = ethanol, etc.). Record the solvent list in your notebook.

Step 2 – Preparation of test tubes

- Take **14 clean and dry test tubes**.
- Label them from **Tube 2 to Tube 15** according to the solvent number being tested.

Step 3 – Addition of solvents

- Into each test tube, place **1 mL** of each solvent (from No. 2 to No. 15).
- Add 1 mL of solvent **No. 1** to each tube.

Step 4 – Mixing

- Shake each test tube gently to mix the two solvents.
- Record whether the mixture forms a **single homogeneous phase (miscible)** or separates into **two distinct layers (immiscible)**.

Step 5 – Heating if necessary

- For test tubes where **two phases are observed**, heat the tube gently in a water bath (never with a direct flame).
- Note whether miscibility improves upon heating (formation of one phase) or remains unchanged.

Step 6 – Recording results

- Create a table with columns: **Tube number | Solvent pair | Observation at room temperature | Observation after heating**.
- Classify each pair as **miscible, partially miscible, or immiscible**.

IV. Recrystallization

IV.1. Principles

- Impurities must remain soluble in the cold solvent; product should crystallize out.
- Large difference in solubility between hot and cold solvent is required.
- Cooling must be slow to avoid trapping impurities in crystals.
- Use a rubber pad to limit heat loss; refrigeration can improve yield if impurities don't crystallize.

IV.2. Choice of Solvent

- Solvent polarity should match the product's.
- Boiling point < product's melting point.
- Poor solubility at cold T°, good solubility at hot T°.
- Solvent must be inert (no reaction with product).
- Impurities should be soluble or insoluble but not co-crystallizing.
- Activated carbon may be used to remove colored/organic impurities.

IV.3. Troubleshooting

- No crystallization: wrong solvent or too many impurities.
- Sudden crystallization during filtration: receiving vessel must be preheated.
- Excess impurities: further purification (e.g., chromatography) may be required.

IV.4. Verification

- Measure melting points of crude vs purified product.
- Purity ↑ → sharper, higher melting point.

IV.5. Experimental Procedure

III.5.1. Materiel and products

Products: benzoic acid, distillated water.

Materiel: Erlenmeyer, filter paper, Buchner, ice bath.

IV.5.2. Procedure

1. Place ~**0.5 g** contaminated benzoic acid in a 25 mL Erlenmeyer flask with 5 mL water. Warm and add near-boiling water gradually until all solids dissolve.
2. Heat to reflux, adding solvent until complete dissolution.
3. If oil forms → indicates too much heat or not enough solvent.

4. Perform **hot filtration** to remove insoluble impurities.
5. Allow solution to cool slowly → crystals form.
6. Further cooling in ice bath maximizes yield.
7. If crystallization doesn't occur → induce by scratching glass, seeding, or strong cooling.
8. Filter and dry crystals.

Questions

1. How can a good recrystallization be carried out, and what conditions must be met?
2. To improve recrystallization, can the mixture be placed in the refrigerator?
3. Explain how recrystallization is performed using a mixture of two solvents.
4. Is it a good idea to use ethanol/water mixtures to recrystallize solid carboxylic acids?
5. Does an impurity decrease or increase the melting point?
6. How can impurities be separated from the final product?
7. How do you choose a recrystallization solvent?
8. What should you do if crystallization has still not occurred after several tens of minutes (the solution should then be at room temperature)?
9. How can the efficiency of recrystallization be determined?