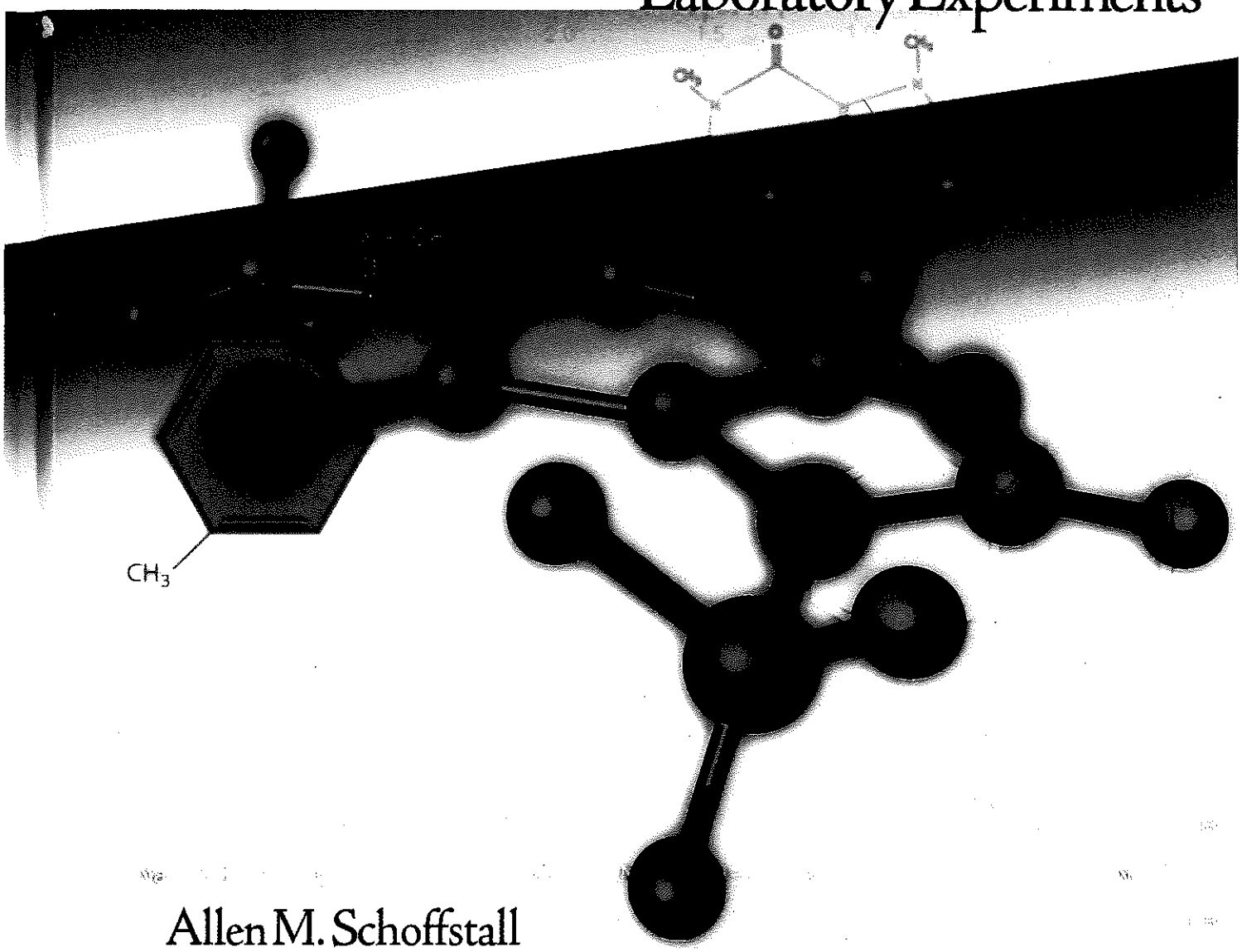
Microscale and Miniscale

ORGANIC CHEMISTRY

Laboratory Experiments



Allen M. Schoffstall
Barbara A. Gaddis
Melvin L. Druelinger

Second Edition

Results and Conclusions for Part B

1. Calculate the percent recovery for the recrystallization process. Explain why it is not 100%.
2. Explain and evaluate the effectiveness of the recrystallization solvent in terms of percent recovery and purity of the recrystallized solid.
3. Suggest other solvents or solvent pairs that might have been used for this recrystallization.

Cleanup & Disposal

Place the solvents used for recrystallization in a container labeled "nonhalogenated organic solvent waste." Aqueous solutions can be washed down the drain with water.

Critical Thinking Questions *(The harder one is marked with a ❖.)*

1. List the main criteria for selecting a recrystallization solvent.
2. When is it necessary to use a solvent-pair recrystallization?
3. Why should the recrystallization solvent have a fairly low boiling point?
4. ❖ Will the following pairs of solvents be suitable for doing a solvent-pair recrystallization? Explain.
   a. ethanol (bp 78.5°C) and water
   b. methylene chloride (bp 40°C) and water
   c. dimethylformamide (bp 153°C) and diethyl ether (bp 37°C)
5. If a solute is soluble in cold solvent, is it necessary to test the solubility of the solute in the same solvent when hot? Explain.
6. Arrange the following solvents in order of increasing polarity: ethanol, ethyl acetate, petroleum ether, toluene, and acetone.
7. Methylene chloride (CH_2Cl_2) is polar, whereas carbon tetrachloride (CCl_4) is nonpolar. Explain.
8. Carbon disulfide (CS_2) is sometimes used as a recrystallization solvent. Will this solvent dissolve polar or nonpolar compounds? Explain.

Experiment 3.5: Separations Based upon Acidity and Basicity

Extraction is a technique in which a solute is transferred from one solvent to another. In this experiment, you will investigate acid-base extraction. You will:

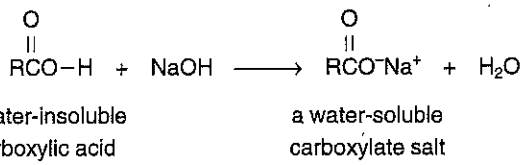
- determine the solubilities of an organic acid, an organic base, and a neutral organic compound.
- design a flow scheme to separate an organic acid, an organic base, and a neutral compound.
- use microscale extraction techniques to separate and isolate each component of a mixture of naphthalene, benzoic acid, and ethyl 4-aminobenzoate.

Techniques

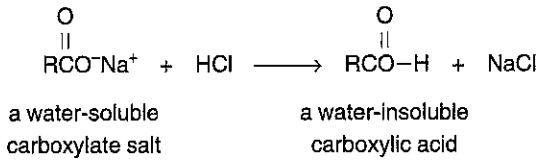
Technique C	Melting point
Technique F	Vacuum filtration
Technique I	Drying and extraction

Background

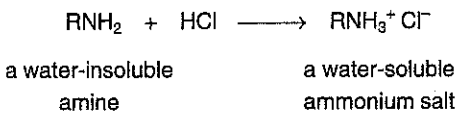
A water-insoluble, acidic organic compound such as a carboxylic acid or phenol can be easily separated from neutral and basic organic compounds by conversion to a water-soluble salt.



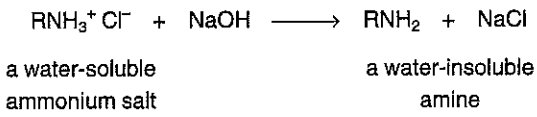
Neutral and basic organic compounds remain in the organic layer. The two layers can then be separated. Addition of HCl to the aqueous layer regenerates the water-insoluble carboxylic acid, which can then be filtered or extracted into an organic solvent:



A similar scheme can be used to separate a basic compound, such as a water-insoluble amine, from neutral or acidic organic compounds by conversion of the amine to a water-soluble salt:



Neutral compounds and acidic organic compounds remain in the organic solvent, where they can be removed. Addition of sodium hydroxide to the aqueous layer regenerates the amine, which is now insoluble in the aqueous solution. The amine can be filtered or extracted into an organic solvent.

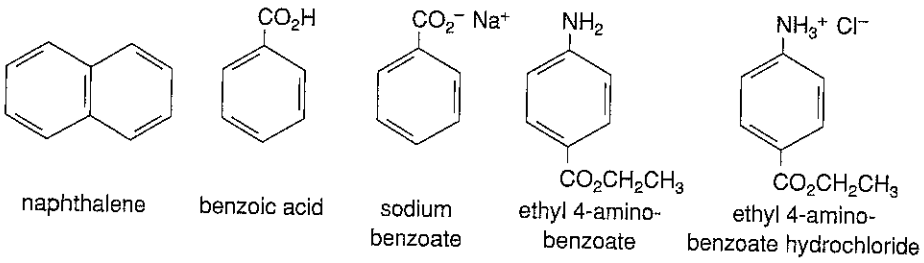


The neutral compound remains in the organic solvent, where it can be recovered by drying the solution to remove traces of water, filtering off the drying agent, and evaporating the solvent.

In this exercise, the solubilities of an organic acid (benzoic acid), an organic base (ethyl 4-aminobenzoate), a neutral compound (naphthalene), and the organic salts (ethyl 4-aminobenzoate hydrochloride and sodium benzoate) will be tested in methylene chloride and water.

From the solubilities, you will construct a flow scheme outlining the separation of naphthalene, benzoic acid, and ethyl 4-aminobenzoate. In Part B, you will use the flow

scheme to separate a mixture of naphthalene, benzoic acid, and ethyl 4-aminobenzoate in microscale. In Part C, you will use the flow scheme to separate a mixture of benzoic acid and ethyl 4-aminobenzoate in miniscale.



naphthalene — benzoic acid — sodium benzoate — ethyl 4-amino-benzoate — ethyl 4-amino-benzoate hydrochloride

The instructor may substitute other compounds for those shown here.

Prelab Assignment

1. Read Technique I on the theory and technique of extraction and do all assigned problems.
2. Construct a solubility table similar to Table 3.5-1 in the experimental section.
3. Identify the conjugate acid/conjugate base pairs for the structures above.
4. Write the reaction (if any) and give the products for the reaction of each pair of reagents below. If no reaction occurs, write NR. Indicate whether the product will be water-soluble or water-insoluble.
   a. benzoic acid with NaOH.
   b. sodium benzoate with HCl.
   c. ethyl 4-aminobenzoate with HCl.
   d. ethyl 4-aminobenzoate hydrochloride with NaOH.
   e. naphthalene and NaOH.
   f. ethyl 4-aminobenzoate with NaOH.
5. Determine whether each of the five compounds is predominantly ionically or covalently bonded. Based upon this answer, indicate whether the compound would be expected to be more soluble in water or more soluble in methylene chloride.

Experimental Procedure

Safety First!

Always wear eye protection in the laboratory.

1. Wear eye protection at all times in the laboratory.
2. Wear gloves when handling reagents in this experiment.
3. Methylene chloride is a toxic irritant and a suspected carcinogen. Do not breathe the vapors. Work under the hood or in a well-ventilated area.
4. NaOH and HCl are corrosive and toxic and can cause burns.

Part A: Determination of Solubilities

Obtain 20 small, dry test tubes or a spot plate. Place approximately 10–20 mg of benzoic acid into four of the test tubes or wells; place 10–20-mg of sodium benzoate into

The McGraw-Hill Companies

Mc Graw Hill Higher Education

MICROSCALE AND MINISCALE ORGANIC CHEMISTRY LAB EXPERIMENTS
SECOND EDITION

This book is printed on acid-free paper.

1 2 3 4 5 6 7 8 9 0 VNH/VNH 0 9 8 7 6 5 4 3

ISBN 0–07–242456–7

Publisher: *Kent A. Peterson*
Sponsoring editor: *Thomas D. Timp*
Senior developmental editor: *Shirley R. Oberbroeckling*
Senior marketing manager: *Tamara L. Good-Hodge*
Project manager: *Joyce Watters*
Lead production supervisor: *Sandy Ludovissy*
Senior media project manager: *Stacy A. Patch*
Senior media technology producer: *Jeffry Schmitt*
Senior coordinator of freelance design: *Michelle D. Whitaker*
Cover/interior designer: *Rokusek Design*
Cover image: *Rokusek Design*
Senior photo research coordinator: *Lori Hancock*
Compositor: *Precision Graphics*
Typeface: *10/12 Times Roman*
Printer: *Von Hoffmann Corporation*

All experiments contained in this laboratory manual have been performed safely by students in college laboratories under the supervision of the authors. However, unanticipated and potentially dangerous reactions are possible due to failure to follow proper procedures, incorrect measurement of chemicals, inappropriate use of laboratory equipment, and other reasons. The authors and the publisher hereby disclaim any liability for personal injury or property damage claimed to have resulted from the use of this laboratory manual.

Library of Congress Cataloging-in-Publication Data

Schoffstall, Allen M.
Microscale and miniscale organic chemistry laboratory experiments / Allen M. Schoffstall, Barbara A. Gaddis, Melvin L. Druelinger.—2nd ed.
p. cm.
Includes bibliographical references and index.
ISBN 0–07–242456–7 (acid-free paper)
1. Chemistry, Organic—Laboratory manuals. I. Gaddis, Barbara A. II. Druelinger, Melvin L. III. Title.

QD261 .S34 2004
547.0078—dc21

2003008663
CIP

www.mhhe.com