Wet Lab Unknown

In this lab you will be given an unknown solid. The solid will be either a phenol or a carboxylic acid. You will identify the unknown based on experiment and observation. If you have a phenol you are required to make a urethane derivative. If you have a carboxylic acid you are required to do a titration to determine the equivalent mass.

Melting Points: An important part of the characterization of the unknown is a precise and accurate melting point. Precision: Be sure that melting points are performed on small, well-packed samples. Be sure that the rate of heating near the melting point is 2 degrees per minute and be sure you keep in mind the calibration of your thermometer.

Solubility Tests: Start by testing solubility in water, followed by sodium hydroxide and sodium bicarbonate. Compounds that are water soluble generally have very low molecular weights. If the unknown is water soluble, test the resulting solution with pH paper. If the solution is acidic (turns blue pH paper red), the unknown is likely to be a carboxylic acid. If an unknown is water soluble, it will be likely be soluble in any aqueous solution, so the bicarbonate and hydroxide test are generally not informative. Water insoluble carboxylic acids are soluble in weak base (bicarbonate) and strong base (hydroxide). Water insoluble phenols are soluble in strong base (hydroxide), sometimes with a color change. In either case, we are talking about an enhanced solubility. Acids are more soluble in bicarbonate than in water; phenols are more soluble in hydroxide than in water or bicarbonate.

To perform a solubility test put approximately 10 mg of your unknown (a portion the size of a peppercorn) in a test tube, then add 1 mL of solvent according to the procedures below. Some compounds are only slightly soluble in the aqueous solvents, so pay attention to amount of solid you start with and whether you have the same amount or less after several minutes of swirling. It is important to use a small portion of solid otherwise you will not be able to tell if some or none of the solid dissolved.

Water Solubility – Add approximately 1 mL of water to the test tube containing your unknown. Shake the tube and/or stir with a glass stirring rod. A soluble unknown will form a homogeneous solution with water. You may add additional water, up to 1 mL, if your compound does not completely dissolve with the smaller amount.

5% NaOH Solubility - Add approximately 1 mL of 5% NaOH in small portions of about 6 drops each to the test tube containing your unknown. Shake the test tube vigorously after the addition of each portion of solvent. Solubility will be indicated by the formation of a homogeneous solution, a color change, or the evolution of gas or heat.

5% $NaHCO_3$ Solubility – Add approximately 1 mL of 5% $NaHCO_3$ in small portions of about 6 drops each to the test tube containing your unknown. Shake test tube vigorously after the addition of each portion of solvent. Solubility will be indicated by the formation of a homogeneous solution, a color change, or the evolution of gas or heat.

Ferric Chloride Test Most phenols react with ferric chloride to give colored complexes. The colors vary depending on the nature of the phenol, the solvent, concentration, and time of observation. Gray-purple is the most common color for a positive test. Red, blue or green coloration may also indicate a positive test. A orange/brown, ferric chloride-colored solution or precipitate is NOT a positive test.

Dissolve approximately 30-50 mg of your unknown in 1-2 mL of water, or a mixture of water and 95% ethanol if the compound is not water-soluble. When you have a homogenous solution, add several drops of 0.2M aqueous ferric chloride solution and observe for changes in color which are usually instant.

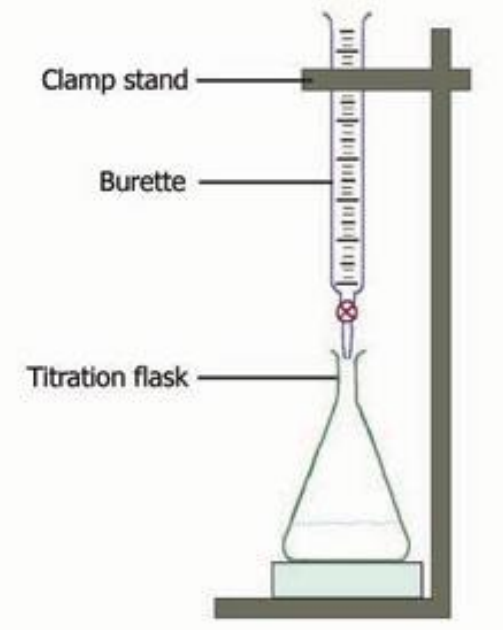
Determining the Equivalent Mass of an Acid An equivalent mass is the molar mass of a compound divided by the number of acidic hydrogens (i.e. HCO_2H – [46 g mol^{-1}/1 acid group] = 46 g/equiv; $HO_2C\text{-}CO_2H$ = [90 g mol^{-1}/2 acid groups] = 45 g/equiv). If you have an acid you can use titration to determine the mass per carboxylic acid group in the molecule. This is extremely useful as it will help you figure out the possible molar masses of your unknown. The moles of base it takes to titrate your compound is equal to the moles of acid in your sample. Since you know how many grams you started with and you now know the moles of acid groups you can figure out the equivalent mass.

$$\text{Equivalent mass} = \frac{\text{Grams of acid}}{\text{Volume of base (L)} \times \text{Concentration of base (mol/L)}}$$

If the equivalent mass came out to 81.34 g/equiv and there is one carboxylic acid in the molecule, the molar mass would be 81.34 g/mol. If there were two acid groups in the molecule the molar mass is 162.68 g/mol and so on. In other words, the molar mass of the unknown must be a multiple of the equivalent mass.

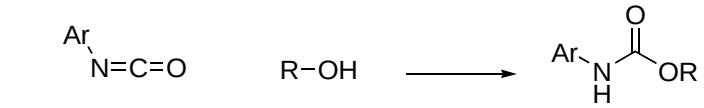
Accurately weigh about 0.2 g of the acid and dissolve it in about 50 mL of water is it is water soluble. If it is not water soluble, start by dissolving your unknown in 15 mL of 95% ethanol (it may be necessary to warm the mixture to dissolve the compound completely). Next, add water slowly until the solution until the total volume is about 50 mL. If during the addition of water, the solution becomes cloudy or a precipitate appears, stop adding water and add just enough additional ethanol to make the solution homogenous again. Add two drops of phenolphthalein indicator to the flask. Titrate the solution with a standardized sodium hydroxide* solution provided. Rinse the burette with two 5 mL portions of sodium hydroxide solution before filling the burette. Note the concentration on the bottle you are using. When a light pink color persists for at least 15 seconds the titration is complete. A diagram of the titration setup can be found below. Stir constantly using a magnetic stir bar during the titration. When finished with your titration setup, drain unused sodium hydroxide back into the bottle and rinse twice with water allowing some to flow through the tip (or pass your setup to another student who is ready for titration).

* Be sure that you are using standardized NaOH, NOT the 5% NaOH for solubility tests



Titration Setup

Urethane Derivative: A urethane derivative is made by reacting a phenol or alcohol with an aryl isocyanate. The reaction is sensitive to water so reagents and flasks must be kept very dry.



An aryl isocyanate An alcohol A urethane

This reaction, including the opening of reagent bottles should be done entirely in a hood.
Place 0.5 g of the unknown in a 25 mL round bottom flask and add 0.25 mL (measured in a clean, dry pipette) of phenylisocyanate in a fume hood. *Be sure to recap the bottle of isocyanate tightly to minimize the exposure of the reagent to atmospheric moisture.* Add 2-3 drops of pyridine as a catalyst. Attach a drying tube to the flask using a thermometer adapter – this prevents moisture in the air from entering the reaction flask. Warm the mixture in a water bath (~60^{o}C) for 5 minutes. Cool the mixture in an ice water bath and scratch the air-water interface with a glass stirring rod to induce crystallization. If necessary, recrystallize from high-boiling petroleum ether (also known as ligroin).

Chemicals: 5% sodium hydroxide, 5% sodium bicarbonate, ethanol, 0.2 M ferric chloride, standardized sodium hydroxide, phenylisocyanate, pyridine, ligroin.

List of Possible Unknowns

Carboxylic acids		
Chemical	mp	molar mass
Tetradecanoic acid (myristic acid)	57	228.3
Trichloroacetic acid	58	163.4
Chloroethanoic acid (chloroacetic acid)	63	94.5
Hexadecanoic acid (palmitic acid)	63	256.4
Octadecanoic acid (stearic acid)	71	284.4
E-2-Butenoic acid (crotonic acid)	72	86.1
2-Methoxybenzoic acid (o-anisic acid)	101	152
2-Methylbenzoic acid (o-toluic acid)	104	136
3-Methylbenzoic acid (m-toluic acid)	113	136
Benzoic acid	122	122.12
2,4-Dimethylbenzoic acid	126	150.2
3-Benzoylbenzoic acid	128	226.2
T-Cinnamic Acid	133	148
Sebacic Acid	134	202
Propanedioic acid (malonic acid)	135	104.1
3-Nitrobenzoic acid	141	167.12
2-Chlorobenzoic acid	142	156.6
2-Aminobenzoic acid (anthranilic acid)	147	137.14
2-Nitrobenzoic acid	146	167.1
Hexanedioic acid (adipic acid)	154	146
3-Chlorobenzoic acid	158	156.6
2-Hydroxybenzoic acid (salicylic acid)	158	138.1
1-Naphthoic acid	162	172.17
2,4-Dichlorobenzoic acid	164	191
3,5 Dinitrosalicylic acid	174	228
4-Methylbenzoic acid (p-toluic acid)	180	136
3,4-Dimethoxybenzoic acid (veratric acid)	181	182.2
2-Naphthoic acid	184	172.17
4-Aminobenzoic acid	186	137.13
4-Methoxybenzoic acid (p-anisic acid)	186	152.1
Succinic Acid	189	118
3-Hydroxybenzoic acid	201	138.1
3,5-Dinitrobenzoic acid	205	212
2,4-Dihydroxybenzoic acid	213	154.1
4-Hydroxybenzoic acid	215	138.1
4-Nitrobenzoic acid	241	167.1
4-Chlorobenzoic acid	243	156.6

Phenols		
Chemical	mp	Phenyl-urethane
2,4-Dimethylphenol	28	112
4-Propylphenol	22	129
2-Methylphenol (o-cresol)	31	142
4-Methylphenol (p-cresol)	36	115
Phenol	42	126
4-Chlorophenol	43	149
4-Ethylphenol	47	120
3,4-Dimethylphenol	65	120
4-Bromophenol	66	140
3,5-Dimethylphenol	68	151
2,4,5-Trimethylphenol	71	110
2,3-Dimethylphenol	75	193
2,5-Dimethylphenol	75	166
1-Naphthol	94	178
1,2-Dihydroxybenzene	105	169
1,3-Dihydroxybenzene	110	164
4-Nitrophenol	114	156
2-Naphthol	123	156
2-Hydroxybenzoic acid (salicylic acid	158	*
4-Phenylphenol	165	167.5
3,5 Dinitrosalicylic acid	174	*

* no derivative forms - contains both funtional groups perform a titration