TWO-BASE EXTRACTION OF BENZOIC ACID, 2-NAPHTHOL, AND NAPHTHALENE FROM UNKNOWN SAMPLE # 131

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Introduction: The purpose of this experiment was to separate a sample of benzoic acid, 2-naphthol, and naphthalene of unknown proportions using a two-base extraction method. The three components of the mixture will react differently to sodium bicarbonate and sodium hydroxide because each of the bases' conjugate acids has a different pK_a. The pK_a's of benzoic acid and 2-naphthol are 4.17 and 9.5, respectively, while naphthalene is a neutral compound. Since benzoic acid is much more acidic than 2-naphthol, the weak base, sodium bicarbonate, will be able to effectively remove benzoic acid's acidic hydrogen. It will take the much stronger base, sodium hydroxide, to remove the hydroxide hydrogen from 2-naphthol. Both of the sodium salts formed from the base extractions will be soluble in water, while naphthalene will only be soluble in the original solvent, diethyl ether. Introducing the two sodium salts to hydrochloric acid will effectively replace the original proton benzoic acid and 2-naphthol lost. In a chilled environment, both compounds will not be soluble in water, because the solubility of benzoic acid and 2-naphthol in water at 25˚C is 0.34g/100mL and 0.074g/100mL, respectively. They can be removed using vacuum filtration. After extraction and purification, the percent recovery and percentage composition of the unknown sample will be able to be calculated.

The unknown sample may not be separated using melting points because both benzoic acid and 2-naphthol have a melting point of 123˚C. The purity of the samples will be indicated by their melting points ranges. The purer the sample, the narrower the melting point range.

Experimental Procedure (Fig.1): An unknown sample of benzoic acid, 2-naphthol, and naphthalene (Table 1) was massed and the unknown number was recorded. The unknown sample was dissolved in 30mL of diethyl ether in a 125mL Erlenmeyer flask. The solution was transferred by funnel to a 125mL separatory funnel. The benzoic acid was extracted by adding 20mL of 10% aqueous sodium bicarbonate. The separatory funnel was swirled before inverting to allow any carbon dioxide gas produced to dissipate. The inverted separatory funnel was swirled with frequent venting until the fizzing carbon dioxide subsided. Afterwards, the inverted separatory funnel was shaken with frequent venting until the fizzing carbon dioxide subsided. The lower aqueous layer containing the benzoic acid was transferred to a labeled 125mL Erlenmeyer flask. Any remaining benzoic acid in the organic layer was extracted with another 20mL of 10% aqueous sodium bicarbonate following the same procedure as detailed above. The aqueous contents of both bicarbonate extractions were collected in the same 125mL Erlenmeyer flask.

The 2-naphthol was extracted from the organic layer by adding 20mL of cold 10% aqueous sodium hydroxide solution to the 125mL separatory funnel. The separatory funnel was inverted and shaken with frequent venting. The lower aqueous layer was transferred to a second, labeled 125mL Erlenmeyer flask.

The ether solution was transferred to a labeled 50mL Erlenmeyer flask and 0.7g of anhydrous sodium sulfate was added as a desiccant. The flask was corked to prevent evaporation.

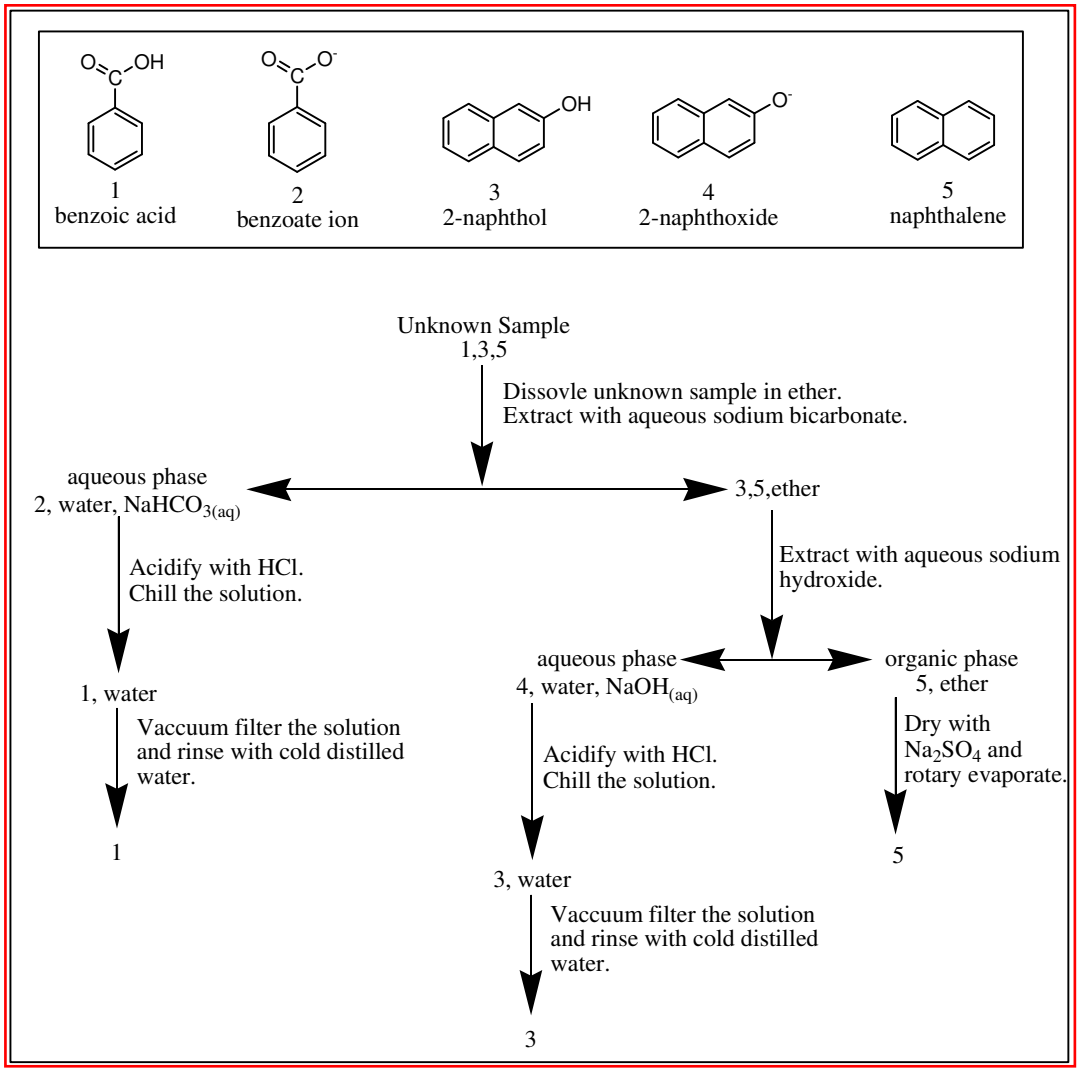

FIGURE 1 Flow chart for the two-base extraction of benzoic acid, 2-naphthol, and naphthalene.

Compound	Mol. Wt. (amu)	M.P. (˚C)	pK_a	Water Sol. (g/100mL, 25 ˚C)	Appearance
benzoic acid	122.12	123	4.17	0.34	wht. pwd.
2-naphthol	144.17	123	9.5	0.074	wht./brwn. pwd.
naphthalene	128.06	80	ntrl.	0.0031	clr./brwn. pwd.
$NaHCO_3$	--	--	6.37 (H_2CO_3)	--	--
NaOH	--	--	15.7 (H_2O)	--	--

TABLE 1 Table of reagents.

The aqueous bicarbonate extract containing the benzoic acid was acidified drop-wise with 3M hydrochloric acid until a blue litmus paper test turned pink. The solution was swirled while the acid was being added to allow the carbon dioxide gas formed to dissipate. The aqueous sodium hydroxide extract containing the 2-naphthol was acidified as described above, except the extract was chilled in an ice bath both prior and during the acidification process to prevent the 2-naphtol from turning to an oil. Both of the acidified aqueous extracts were chilled in an ice bath and the precipitates were individually isolated using a Büchner funnel with pre-weighed filter paper. Both the benzoic acid and 2-naphthol were rinsed with cold distilled water and they were allowed to dry for a week.

The ether solution containing the naphthalene was decanted into a pre-weighed, 100mL, round-bottom flask. A rotary evaporator was used to pull off the ether. The naphthalene was weighed and transferred to a vial to dry for a week.

The mass of the benzoic acid and 2-naphthol were recorded after a week of air-drying. Melting points were taken twice for all three chemicals on a Mel-Temp melting point apparatus. Mel-Temp #13 was used for all of the melting points. At 80ºC the calibration curve was 3.5ºC above the actual temperature, so 3.5ºC had to be subtracted from the measured melting points near 80ºC. Above 100ºC the calibration curve was 4.0ºC above the actual temperature, so 4.0ºC had to be subtracted from the measured melting points above 100ºC. All three samples were submitted for inspection.

Results and Observations: During the bicarbonate extraction, it was noted that the top ether layer was a light tan color. The bottom aqueous layer was clear. It was also noted that there was

hardly any carbon dioxide evolved. Very little pressure built up during the venting process. After the second bicarbonate extraction, there were a few white crystals dispersed throughout the Erlenmeyer flask. After the extraction with sodium hydroxide, the color of the layers changed. This time the top ether layer was clear, and the bottom aqueous layer appeared a little tan and cloudy.

It took 5ŌO drops of hydrochloric acid to acidify the aqueous bicarbonate solution to turn a piece litmus paper pink. A precipitate formed on the top of the solution. After chilling the solution in an ice bath, all of the precipitate dissolved, so another 30 drops of hydrochloric acid needed to be added. The addition of 480 drops of hydrochloric acid formed a thick, milky-white precipitate in the aqueous hydroxide solution.

Three distinct products were isolated after extraction and a week of drying. The benzoic acid was a very fine, white powder. The 2-naphthol was a fine, cream-colored powder. The naphthalene was an off-white/tan powder with some clear crystals that smelled like mothballs. Table 2 contains data corresponding to each of the isolated products.

Sample	Mass (g)	% Composition (%)	Melting Point (ºC) corrected	Color
unknown # 131	1.93	--	--	mixture of white and cream powders, flakes, and crystals
benzoic acid	0.28	16	122.0-123.2	white, fine powder
2-naphthol	0.42	25	122.2-124.0	cream, fine powder
naphthalene	1.00	59	82.0-82.6	off-white/tan powder and clear crystals

TABLE 2 Data table of the original unknown sample and the three isolated products.

The total mass of the isolated products was 1.70g. Dividing by the mass of the original unknown sample, 1.93g, yields a percent recovery of 88.1%. Dividing the mass of each of the isolated products by the total mass of the isolated products yields the percent composition of the recovered sample. The unknown sample consisted of 16% benzoic acid, 25% 2-naphthol, and 59% naphthalene.

Conclusions: The purpose of this experiment was to separate a sample of benzoic acid, 2-naphthol, and naphthalene of unknown proportions. The data supports that the separation of all three compounds was successful. The melting point ranges and colors of the products correspond to the physical properties of benzoic acid, 2-naphthol, and naphthalene. The melting points ranges show that the products are relatively pure since none of the ranges is greater than 1.8ºC.

The recovery of product from the original unknown sample was relatively high, 88.1%. A small portion of product was lost during the first inverting of the separatory funnel when a few drops of solution leaked out. Another small portion of product was lost during each separation of the aqueous and ether layers. A few drops from the interface of the two layers were discarded each time to prevent contamination of the products.

It was noted during the experiment that there was relatively little carbon dioxide produced during the bicarbonate extraction compared to some of the other lab groups' unknown samples. A percent composition of 16% benzoic acid supports that there was relatively little benzoic acid compared to the other components.

Answers to Assigned Questions: Page 146 (8,11)

8) Fig. 2 shows a flow chart for the separation of benzoic acid, 4-nitroaniline, and N-(4-nitrophenyl)benzamide. Benzoic acid will be extracted with an aqueous base, while 4-nitroaniline will be extracted with an aqueous acid. The neutral N-(4-nitrophenyl)benzamide will remain in the diethyl ether.

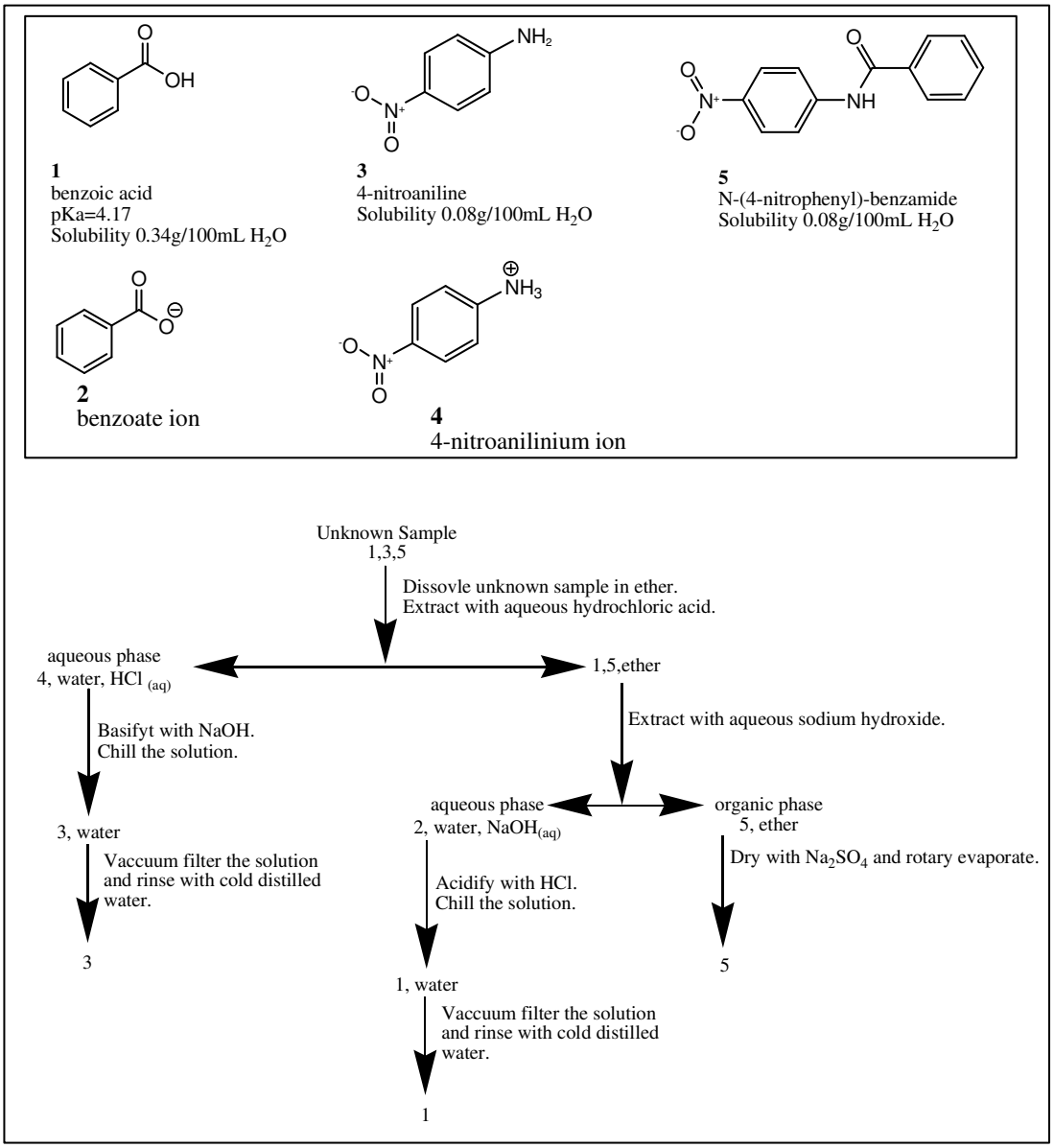

FIGURE 2 Flow chart for the two-base extraction of benzoic acid, 4-nitroaniline, and N-(4-nitrophenyl)benzamide.

11) The sequence of bases for the two-base extraction is critical to separating the benzoic acid from the 2-naphthol. Benzoic acid has a pKa of 4.17, while 2-naphthol has a pKa of 9.5. The conjugate acid of bicarbonate, H_2CO_3, has a pKa of 6.4. Since benzoic acid's pKa is lower than 6.4, it will deprotonate and become soluble in water, while 2-naphthol will remain in the ether because it won't deprotonate. If the sodium hydroxide were used first, both benzoic acid and 2-naphthol would deprotonate and become soluble in water, because they both have a pKa lower than water's pKa of 15.7.