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Contents

Comparison of Separation and Extraction Procedures 3
   Dustin Randy

Organic Chemistry Separation Techniques: Column Chromatography & Acid-Base Extraction 7
   Candido Tenorio
Comparison of Separation and Extraction Procedures

Dustin Randy

Abstract

Acid-base extraction and column chromatography used to isolate compounds from a mixture. NaHCO3 and HCl are used to ionize acetylsalicylic acid and benzocaine respectively, to then enter an aqueous layer and be separated by drainage from a separatory funnel. They are then reacidified and rebasified to reconstitute the original substances, and quantitative measurements obtained. A chromatography column filled with silica gel and heptane, and topped with sand, has the compound mixture added to it and a 25% acetone/75% heptane solution, later changed to 40% acetone/60% heptane, poured into it to drive the separation out the bottom of the column. From obtained data, neither procedure showed itself clearly superior, though the column appeared to be more easily controllable.

Introduction

In organic chemistry, chemical solutions often contain mixtures of different compounds, yet definitive qualitative and quantitative analysis of a chemical requires its isolation to eliminate variables in the testing. Once a chemical has been reliably isolated, the chemist can comfortably interpret testing results as being representative of the chemical in question, and this data can be compared to known data for the chemical for confirmation. To this end, various techniques are used to separate chemicals out from a solution, two of which were used in this experiment. Though the current methods of separation are more advanced than in the past, the need and procedure for separating compounds has been present for hundreds of years, and often used similar methods. The process can be as simple as simply finding something that can reliably bind to one reagent in a solution and precipitate, and then separating it out via filtration.

This experiment was conducted to compare the two methods of separation. The first process used in this experiment was acid-base extraction, which is a solvent-solvent extraction, whereby an acid or base is used to modify the structure of a chemical and make it either soluble or insoluble in water or solvent (Acid-base). This is done by either protonating or deprotonating the substance in question, creating an ion with polarity that will then interact with the aqueous layer. After separation, the reagent can be reformed by reversing the ion creating process.

The second technique was column chromatography. This procedure used a column filled with silica gel to separate out the chemicals from a solution by passing a solvent through the gel, which carried the chemicals out with it at different rates dependent upon their polarity, and the interactions with the silica gel and the solvent (Column). After separations were complete, quantitative data was obtained of the isolated products and compared to known values to determine effective isolation.
Results and discussion

The theory behind the acid-base extraction process seems sound. However, the results between experimenter groups conducting these experiments produced an aspirin precipitate with melting points that all fell within a few degrees of two numbers approximately 200°C apart. This was determined by the instructor to be caused by the differences in the bases used to extract the aspirin, as half the groups used sodium hydroxide, and the other half used sodium bicarbonate. The relatively stronger sodium hydroxide resulted in a nucleophilic attack on one of the carbonyl groups of the aspirin, resulting in a different molecule once the extraction was completed. The sodium bicarbonate merely deprotonated the aspirin, which was then re-protonated when acidified, rendering the original aspirin back ( Vaughan, Lab results). Though this difference in melting points was the only known effect between the two base groups, the data highlight the potential interference that can be caused depending on the chemicals used to carry out the extraction with this process.

Separating the layers using extraction involving draining the lower and denser layer out the bottom of the separatory flask. This introduced a potential for error, as there was no way to ensure that all of the bottom layer, and thus the chemical suspended in it, was extracted from the tube. As the stopcock was turned when the draining layer approached it, some small amount would sometimes be left behind above the stopcock, in addition to the amount below the stopcock before the bottom tip of the flask. This was mitigated by repeating the separation a second time to wash the mixture of any remaining targeted chemical, but the potential for some amount of chemical remaining behind may skew any subsequent quantitative analysis. Also, an unsteady hand may accidentally allow too much solution through the stopcock, letting some amount of the upper layer through while attempting to isolate the lower layer. Some amount of the aspirin was lost due to experimenter error when weighing it on paper after the acid-base extraction, which helps account for the high percentage error for aspirin recovery. There was also a large percentage error for the recovery of benzocaine due to unknown reasons.

The column chromatography method appeared to be more controlled, with the added benefit of being able to adjust solvents used to control the rate of extraction. This gives the option of speeding up the extraction process at the expense of potentially extracting multiple substances at once, or slowing the process down to ensure proper isolation. This may have played a factor in the acetyl salicylic acid appearing on the TLC plates at fraction 7, during the 5-9 fraction window that the benzocaine was extracting, so some amount of aspirin was extracted with the benzocaine. Collecting of isolated aspirin fractions did not begin until fraction 10, likely contributing to the large percentage errors for both the aspirin and benzocaine. The naphthalene recovered was not measured as per the professor’s instructions. Percent errors were obtained based on the professor’s approximation of each of the three compounds comprising approximately 33% of the mass of the initial solution ( Vaughan, Josh). There were no apparent explanations for these errors. All data contained in tables in experimental.

Experimental

Acid-base extraction.

IR spectra was obtained on a Perkin Elmer Spectrum 100 FT-IR. The procedure was carried out using a 125mL separatory funnel, Hirsch funnel, and rotary evap. All other materials were standard. All reagents, TLC plates, and the mixed compound were obtained from the
instructor without modification.

**Acetylsalicylic acid.** The initial compound mixture was a white, dry, crystalline solid that was weighed by difference and then dissolved in 25mL MTBE in a separatory funnel. 12mL of 1M NaHCO₃ was added to the funnel and agitated repeatedly, venting built-up pressure, and creating a heterogeneous solution. The bottom layer was drained into a 125mL Erlenmeyer flask, and the separatory funnel was washed with another 12mL of 1M NaHCO₃. The extract was acidified to litmus with 3M HCl, creating a white precipitate in solution. The solution was then dried using filter paper and a Hirsch funnel, washing the flask with water into the funnel. The resulting compound was a white crystalline solid with a mp 136oC, 0.12g (141.7% error). IR (ATR) cm⁻¹: 1678 (s, C=O), 1749 (s, C=O), 2660 (bd m, O-H), 2831 (bd m, O-H).

**Benzocaine.** 10mL of 1.5M HCl was added to the mixture in the separatory funnel remaining from the ASA extraction, agitated and vented, creating a heterogeneous solution. The lower layer was drained into a 125mL Erlenmeyer flask, and the funnel was washed with another 10mL of 1.5M HCl. The extract was basified to litmus with 3M NaOH, creating a white precipitate in solution. The solution was then dried using filter paper and a Hirsch funnel, washing the water into the funnel. The remaining compound was a white crystalline solid with a mp 81oC, 0.499g (-41% error).

**Naphthalene.** 15mL of brine solution was added to the remaining solution in the separatory funnel, agitated and vented, then the aqueous layer drained and discarded. The remaining solution was drained into a 125mL Erlenmeyer and anhydrous magnesium sulfate was added to excess and agitated vigorously. This solution was then filtered using filter paper and collected in a recovery flask, then the MTBE was evaporated using a rotary evapor. The remaining solution was a white, crystalline solid with a mp of 72oC. Figure 1: TLC of original and separated solutions. 25% acetone : 75% heptane

**Column chromatography extraction.**

The procedure was carried out using a chromatography column and silica gel, all other materials were standard. All reagents and materials were obtained from the instructor without further modifications. The original compound mixture was a white, dry, crystalline solid, which was then dissolved in 10mL MTBE. The chromatography column was packed with silica gel with cotton at the tip, and saturated with heptane until fully settled. Approximately 1cm of sand was added on top of the gel and the sides of the column were washed with methylene chloride. Excess heptane was siphoned off and the solution mixture was added to the column, draining heptane until the mixture was at sand level. 30mL of 25% acetone/75% heptane was added to the column and the stopcock opened, collecting all drained fluid into a sequential series of test tubes known as fractions. Approximately 2mL were collected in each fraction, and each was spot tested on a TLC plate under UV light to check for the presence of UV fluorescence.

**Naphthalene.** Naphthalene appeared on fractions 2-3. These tubes were combined and discarded, no mass obtained.

**Benzocaine.** Benzocaine appeared in fractions 5-9. These tubes were combined and rotary evaporated to produce a white crystalline solid, mp 82.1oC, 0.101g (-46.5% error).

**Acetylsalicylic acid.** Acetylsalicylic acid appeared in fractions 7-19. 40% acetone/60% heptane was added after fraction 10. Fractions 10-19 were collected and rotary evaporated to
produce a white, crystalline solid, mp 124.20C, 0.032g (68.8% error).

Figure 2: TLC of column chromatography fraction progression.

Table 1: Mass data with percent error from expected.

Acid-base extraction Column Chromatography Acetylsalicylic acid
Approximate original mass (33%) 0.292g 0.0545g Final isolated mass 0.12g 0.032g Percent error 141.7% 68.8% Experimental mp 136.0oC 124.2oC Known mp (Aspirin) 136.0 oC 136.0 oC Mp % error 0% 8.8% Benzocaine
Approximate original mass (33%) 0.292g 0.0545g Final isolated mass 0.499g 0.101g Percent error -41.9% -46.5% Experimental mp 81.00C 82.1oC Known mp (Benzocaine) 89-920C 89-920C Mp % error 9.9% 8.4%

References

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Organic Chemistry Separation Techniques: Column Chromatography & Acid-Base Extraction

Candido Tenorio

Abstract

Mixtures of naphthalene, benzocaine, and acetylsalicylic acid were separated using two techniques. The techniques used are column chromatography and acid-base extraction. These techniques are compared in relation to how well they separated the molecules and to factors that will favor one over the other. For this procedure the relative effectiveness and easiness of column chromatography makes this a better choice.

Introduction

Separations within organic chemistry are important tools that scientist use to isolate desired molecules. Moreover, these techniques can be compared in order to understand which are most useful in certain situations. For this report, the procedures that will be compared are column chromatography and acid-base extraction.

Column chromatography is a method that uses a solvent (with an adjusted amount of polarity) to remove molecules within a mixture; each molecule within the mixture has a different polarity, thus they will move down the column at different rates (these are taken in samples called fractions). Acid-base extractions utilizes the interaction of charged molecules to separate the individual molecules from the original mixture; this is done by reacting the neutral molecules with an acid or base; this creates a charged species which falls out of the neutral environment and interacts with the polar water that can be removed easily from the container.

Both experiments dealt with the separation of a mixture containing 1/3 naphthalene, 1/3 benzocaine, 1/3 acetylsalicylic acid; moreover, both experiments used thin layer chromatography to check for separation. The column chromatography had two runs: one with a 50:50 acetone/heptane solvent mixture, and a second that used a gradient for the acetone/heptane ratio; both of these will also be compared. For the acid-base extraction, the naphthalene needed no acid or base because it is unreactive; the acetylsalicylic acid was extracted using sodium bicarbonate; finally, the benzocaine was extracted using hydrochloric acid; these are reacted again to give the original molecule back, dried to remove the water, filtered to remove the hydrated magnesium sulfate, and evaporated to remove the solvent; different groups used a different base for the extraction of the acetylsalicylic acid and this will also be compared.

Results and Discussion

The column chromatography for the first run used a 50:50 acetone/heptane mixture; this was not the correct method for this technique because there was cross contamination; the purpose for column chromatography is to reduce this as much as possible. The correct method (which
was done in the second column chromatography trial) was to use a gradient for the solvent, which would allow the molecules to separate much more effectively (the gradients for this trial started at 75:25 heptane/acetone and then shifted to a 60:40 heptane/acetone ratio). Another difference that was noticed with the first and second trial is that the first trial was quicker than the second trial; this seems reasonable because the solvent was very polar; the large polarity of the solvent allowed the benzocaine to separate at the speed that the naphthalene did; moreover, it also allowed the acetylsalicylic acid to separate with the benzocaine, thus the entire process was a failure because of the high contamination. Though the second trial was noticeably slower the end results showed that it was much more effective at separating the mixture then was the first trial. However, some mistakes were made. For example, during the second run the benzocaine crystallized on the tip of the column and was not noticed until after two fractions were taken; this gave strong UV readings for the TLC plates of those fractions and afterwards there was a drastic drop in the uv reactivity of the spotted plates. Another mistake was the failure to attain rf values for both trials.

The acid-base extraction was separated into two different reactions for the acetylsalicylic acid; the reaction with sodium bicarbonate and sodium hydroxide. The groups that did the extraction with the base sodium bicarbonate attained a melting point that was closer to the melting point of pure acetylsalicylic acid; those that used the sodium hydroxide attained a melting point which was much higher than expected. Therefore, sodium bicarbonate was demonstrated to be the better base to use. Aside from this aspect, both groups ran the same experiment. Moreover, this experiment was quicker than the column chromatography, but the possibility to make mistakes is increased with the several steps involved with the procedure; furthermore, the contamination can be increased if improper separation is used (e.g., allowing the organic mixture to drain out with the aqueous mixture), or if improper reactants are used (e.g., the sodium hydroxide). A mistake for this procedure was the failure to attain an rf value for the TLC plate that would have been spotted by the pure extracted molecules, thus an uncertainty of how well the procedure worked in removing the molecules from each other is still present.

In comparing both the column chromatography and the acid-base extraction it seems that both are very effective techniques to use. However, in choosing one over the other would depend on somethings. Such as, the monetary aspect of the experiment; column chromatography is a very cheap procedure to carry out. Acid-base extraction is relatively cheap for some experiments that do not require expensive reagents; however, once this is not the case then it can begin to cost more. Moreover, if time is a restrictive factor then the ability to carry out a quick procedure becomes crucial. In this case, acid-base extraction would be a better option because it can be quickly done. Another factor to take into account is the molecules that are being extracted; molecules that are very close in terms of pH can be very hard to separate, if not, then impossible to do so because of their similar chemical behaviours. This procedure dealt with cheap reagents and time was not much of an issue; moreover, the molecules that were being extracted from the original mixture were quite different in their pH's; therefore, the best method of separation for this laboratory would be column chromatography.

**Experimental**

Column Chromatography measurements: Original mixture weight-156 mg, Acetylsalicylic acid melting point-111°C, Benzocaine melting point-86°C, Naphthalene melting point-82°C,
Acetylsalicylic acid weight post-evaporation-1 g, Benzocaine weight post-evaporation-1 g.

Acid-Base Extraction Measurements: Acetylsalicylic acid melting point-112°C, Benzocaine melting point-85°C, Naphthalene melting point-80°C.

Column Chromatography:
The mixture of naphthalene, benzocaine, and acetylsalicylic acid was acquired. This mixture was dissolved into methylene chloride.

The column is clamped onto the monkey bars and the amount of silica needed was measured using the column; this silica was poured into an Erlenmeyer flask and heptane was added to make the silica wet. The wet silica was poured into the column and tapped to allow the silica to pack well (i.e., removing any air pockets and making the silica even throughout the column). After all this, sand was added to the column.

The mixture was added into the column after the heptane line was just above the sand. More methylene chloride was used to add the remaining mixture into the column. The solvent for the separation was created using 30 mL of a 75:25 heptane/acetone ratio; this is increased to a 60:40 heptane/acetone ratio. This was added into the column, and it is mixed slightly.

Fractions are begun to be taken and capillary tubes are created to test for UV activation. Once all fractions are UV tested to check which molecules are present in which, then each fraction is added to each other in regards to what they contain. These separations are evaporated to remove the solvent and to isolate the pure molecule.

Acid-Base Extraction:
The mixture of naphthalene, benzocaine, and acetylsalicylic acid was obtained. This mixture was dissolved into 26 mL of MTBE. This was added to a separatory funnel; the funnel was shaken a few times and the placed upside down with the stopcock opened to remove pressure built up from the MTBE.

10 mL of sodium bicarbonate was added to the funnel. The funnel was shaken again and the gas pressure was allowed to vent; this is done twice. The water carrying the acetylsalicylic acid was removed from the funnel into an Erlenmeyer flask; the flask is placed somewhere out of the way.

10 mL of hydrochloric acid was added to the funnel. The funnel was shaken and the gas pressure was allowed to escape; this is done twice. The water is separated into another Erlenmeyer flask; this is placed somewhere safe.

The remaining organic material is drained into a third Erlenmeyer flask, and the funnel was washed using brine. The organic material is placed somewhere safe.

HCl was added to the acetylsalicylic acid to obtain the original acetylsalicylic acid back. A sodium bicarbonate was added to the benzocaine to acquire the original benzocaine. Water was separate from these flasks and anhydrous magnesium sulfate was added to remove any excess water; naphthalene only required the anhydrous magnesium sulfate. These are then evaporated using the rotovaps. Melting points are also taken.

References

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