Liquid/liquid Extraction of a Carboxylic Acid, Amine, and Neutral Unknown Mixture

Purpose:

An unknown mixture of a carboxylic acid, amine, and neutral compounds was dissolved in ether and then separated using microscale liquid/liquid extraction. The solid mixture was dissolved into ether and the carboxylic acid and amine components were separated by adjusting the pH of the solution using sodium hydroxide or hydrochloric acid. The carboxylic acid and amine components were then precipitated and filtered to obtain the solid form. The neutral compound was allowed to crystallize on a watch glass. Finally, the solid components were analyzed using melting point and 1H NMR spectral analysis to determine their identities.

Results, Discussion, and Conclusions:

The extraction was performed on the basis of acid/base reactions, pulling the organic component out of an organic solvent and isolating it in an aqueous solution. Acids and bases exist in their neutral form in an organic solvent. Acids can be deprotonated by the addition of a strong base, resulting in a negatively charged ion that is soluble in water and can therefore be separated. Similarly, bases can be converted into a positively charged ion that is water soluble by protonating with a strong acid. Once separated, the ionic form of the compound can be converted back into its original form by the adjusting the pH of the solution with addition of acid or base, causing the organic compound to precipitate.

Unknown number 104 was used in this experiment. The results of melting point and 1H NMR analysis were used to determine the identities of the the unknown components.

Based on the given possibilities, the neutral component could have been 4-acetylbenzonitrile or fluorenone. The measured melting point range of 53.2 ℃ - 57.5 ℃ best fits the melting point range of 4-acetylbenzonitrile, which is 56 ℃ - 59 ℃ (1). Therefore the neutral component was determined to be 4-acetylbenzonitrile. Out of the initial 100 mg solid neutral compound, 35 mg of solid neutral component was recovered, giving a percent yield of 35%. This was the highest percent yield out of any of the unknown compounds, but was still extremely low. The low percent yield could have been due to an incomplete decanting of the ether off of the sodium sulfate drying agent. If ether was left in between the sodium sulfate crystals at the bottom of the reaction tube, then some of the solid neutral compound would have been left in the reaction tube. In addition, more ether was needed to be added prior to the drying step because the ether level had dropped below 1.5 mL. The reaction started with 2 mL of ether, so more than 0.5 mL must have been lost in the carboxylic acid and amine extraction, which most likely was a result of overambitious attempts to draw out the entire aqueous layer. In each of these extraction steps, some of the organic ether layer must have been accidently drawn into the pipette, which would have taken the neutral component along, therefore decreasing the percent yield.

The carboxylic acid component was either benzoic acid or 3-methoxybenzoic acid. The experimentally determined melting point range of 122.4 ℃ - 124.9 ℃ points towards the melting point of benzoic acid, which is 121 ℃ - 125 ℃ (3). The 1H NMR spectrum of the carboxylic acid component also supports this determination. The spectrum shows characteristic monosubstituted aromatic splitting, with a 2 hydrogen doublet shifted downfield from a 3 hydrogen multiplet. 3-methoxybenzoic acid would have a large singlet with and integration value of 3 corresponding to the methoxy group coming off of the benzene ring, which this spectrum does not have, so it could not have been 3-methoxybenzoic acid. One problem with the spectrum is that it does not show a carboxylic acid peak, which may be because the single proton on the carboxylic acid functional group readily deprotonates. Or, the peak is so small and broad that it could not be viewed on the spectrum. Nevertheless, the combination of the melting point data and splitting pattern points only towards benzoic acid. Only 19 mg of the 100 mg of solid carboxylic acid was recovered, or a percent yield of 19%. This was the lowest percent yield out of any of the compounds. Some reasons for such a low yield could have been not adjusting the pH low enough to precipitate out all of the carboxylic acid. Since a carboxylic acid is very acidic, it requires a high concentration of protons to fully protonate it in an aqueous solution. If the pH of the aqueous solution is not low enough, then much of the carboxylic acid remains suspended in solution. Furthermore, during the precipitation step, much of the solid stuck onto the sides of the extraction tube, requiring it to be scraped out using a spatula into the vacuum filter apparatus. Not all of the solid could be completely scraped out, so a significant amount was left in the reaction tube (4).

The amine component was either 4′-aminoacetophenone or 3′-aminoacetophenone. The experimentally determined melting point range was 105.6 ℃ - 107.7 ℃, which best fits the melting point of 4′-aminoacetophenone, which is 103 ℃ - 107 ℃ (2). The 1H NMR spectrum also supports the melting point data. The spectrum shows characteristic para-substituted aromatic splitting, with two doublets both with an integration value of 2 in the aromatic shift region. Each doublet corresponds to equivalent hydrogens in 4′-aminoacetophenone on the benzene ring. 3′-aminoacetophenone would have three peaks at different chemical shifts for its aromatic hydrogens because each of its aromatic hydrogens are chemically distinct. The spectrum also displays a sharp singlet at a chemical shift of 2.5 and an integration value of 3.06, which corresponds to the methyl ketone group. Finally, the spectrum has a small peak at around a chemical shift of 4.2 and an integration value of 1.62, which corresponds to the para-substituted amine hydrogens. The integration value for this peak should be closer to 2 since the amine has 2 hydrogens. This discrepancy could be a result of minor deprotonation of the amine in the organic solvent. The combination of the melting point range and NMR spectrum indicate that the amine component was 4′-aminoacetophenone. Out of the initial 100 mg of solid amine component, only 33 mg was recovered after filtration, or a percent yield of 33%. Similar to the carboxylic acid, the low percent yield for the amine was most likely due to problems with the precipitation out of the aqueous solution. If not enough base was added, the pH would not have been high enough to deprotonate the amine and draw all of it out of the solution. In the precipitation step, much of the amine precipitate stuck to the sides of the reaction tube like the carboxylic acid precipitate did, causing much of it to be left behind during the transfer to the filtration apparatus (4).

3 unknown compounds were successfully separated using liquid-liquid extraction in this experiment. The identity of these compounds were also successfully deduced using melting point and 1H NMR analysis. The neutral compound was identified as 4-acetylbenzonitrile, the carboxylic acid was identified as benzoic acid, and the amine was identified as 4′-aminoacetophenone. Various sources of error were present in this experiment that could have contaminated the final samples. First, since this was a microscale extraction, precise use of the pipette was necessary to get the most accurate results. Small miscues could have left aqueous solution in the organic layer or drawn organic solution into the extracted aqueous layer. Second, the sticking of the amine and carboxylic acid precipitates to the sides of the reaction tube presented a huge problem because the metal spatula was not maneuverable enough to fully

scrape out all of the solid (4). This step in the procedure could have been improved in order to increase the percent yield.

Experimental:

300 mg of unknown 104 was weighed out and dissolved in 2 mL of ether in a reaction tube. First, the amine component was extracted using two, 1 mL treatments of 5% HCl solution. The two immiscible layers were mixed thoroughly each time then the lower layer was drawn off using a pipette and placed in a separate reaction tube. Next, the carboxylic acid component was separated using two, 1 mL treatments of 1M NaOH solution. The two layers were pipette mixed thoroughly each time then the lower layer was drawn off using a pipette and placed into a third reaction tube. Then, the neutral component was isolated with a treatment of 1 mL saturated NaCl solution, and removing the aqueous layer. The organic layer was dried with anhydrous sodium sulfate, then decanted onto a watch glass and allowed to dry. Afterwards, the amine component was isolated using a treatment of 1 M NaOH, which was added dropwise until the pH was basic. The pH was determined by dabbing solution onto litmus paper with a glass stir rod. The mixture was vacuum filtered to obtain the solid amine and allowed to dry on a watch glass. Subsequently, the carboxylic acid component was isolated using a dropwise treatment of concentrated HCl solution. The HCl was added until the pH of the solution was less than 4, again determined by dabbing onto litmus paper. The crystals were also vacuum filtered and transferred onto a watch glass. Finally, melting point analysis was performed on all of the compounds and 1H NMR analysis was performed on the carboxylic acid and amine components.

References

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