BChO [16]

Time for Chemistry!

16th Baltic States Chemistry Olympiad

Practical Examination Problems

English version

General directions

- You must wear protective glasses and a laboratory coat all the time during the practical examination. Put them on now, please! It is recommended to wear protective gloves.
- Do not hesitate to ask an instructor if you have any questions concerning safety issues.
- Write your identification code on each answer sheet.
- You have 5 hours to complete the problems and record your results on the answer sheets. You must begin only when the START command is given and stop immediately after the STOP command is given.
- Carefully read the text of the problems and study the layout of the answer sheets. All results must be written in the appropriate areas on the answer sheets.
- The English version of the problems and the answer sheets is available if you wish to see it.
- The number of significant figures in numerical answers must conform to the rules of evaluation of experimental errors.
- Chemicals and supplies are refilled or replaced if used up or broken.
- Use the appropriate waste containers for disposal of chemical and other waste materials.
- You must put the answer sheets into an envelope (do not seal) and give them to an instructor once you have finished the practical examination. Do not leave the examination room until you are allowed to do so.

Good luck!

Problem 1 – The determination of constants of an acid

Apparatus and Supplies

1. Laboratory stand
2. Glassware rack
3. Two sets of holders
4. 25 mL burette
5. Two 10 mL pipettes
6. Pipette filler bulb
7. 20 mL pipette
8. Small funnel
9. 50 mL volumetric flask
10. 100 mL separating funnel
11. Two 100 mL bottles *(labeled "A" and "B")*
12. Two 100 mL beakers *(labeled "A" and "B")*
13. 100 mL Erlenmeyer flask
14. 500 mL beaker *(labeled "Aqueous waste")*
15. 200 mL bottle *(labeled "1-octanol waste")*
16. Distillated water washer
17. Distillated water dropper
18. Cleaning paper roll *(shared among a few students)*
19. Blank sheets of paper
20. Ruler

Chemicals

The exact concentrations of the solutions are written on the bottles.

1. 150 mL of X acid solution *(labeled "X")*
2. 150 mL of ~0.25 M NaOH solution
3. 300 mL of ~0.03 M NaOH solution
4. 40 mL of 1-octanol (*labeled "1-octanol")*
5. 10 mL of 0.1% bromothymol blue solution (*labeled "BTB"; color transition yellow-blue at pH=7.2)*

Safety data

1-octanol

Formula $C_8H_{18}O$
Molar mass 130.2 g/mol
Melting point -15°C
Boiling point 195°C
Density 0.826 g/mL

R 36/38 Irritating to eyes and skin.
S 26 In case of contact with eyes, rinse immediately with plenty of water and seek medical advice.
S 37/39 Wear suitable gloves and eye/face protection.

X acid *(the identity of the compound can not be revealed)*

Melting point 57°C
Boiling point 196°C
Density 1.63 g/mL

R 35 Causes severe burns.
R 50/53 Very toxic to aquatic organisms, may cause long-term adverse effects in the aquatic environment.
S 26 In case of contact with eyes, rinse immediately with plenty of water and seek medical advice.
S 36/37/39 Wear suitable protective clothing, gloves and eye/face protection.
S 45 In case of accident or if you feel unwell, seek medical advice immediately (show the label where possible).
S 60 This material and its container must be disposed of as hazardous waste.
S 61 Avoid release to the environment. Refer to special instructions/safety data sheets.

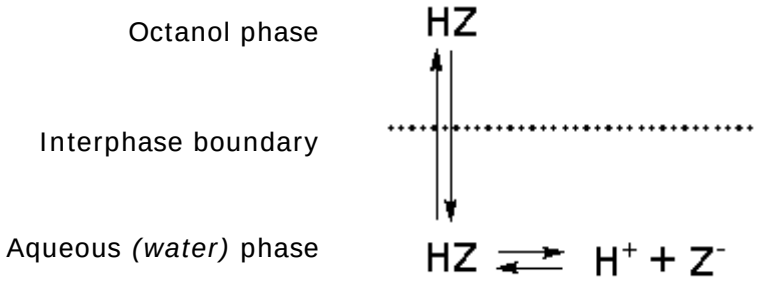
Sodium hydroxide

Formula NaOH
Molar mass 40.00 g/mol

R 35 Causes severe burns.
S 26 In case of contact with eyes, rinse immediately with plenty of water and seek medical advice.
S 37/39 Wear suitable gloves and eye/face protection.
S 45 In case of accident or if you feel unwell, seek medical advice immediately (show the label where possible).

Introduction

The system consists of two immiscible solvents *(1-octanol and water)* and an acid referred as HZ. Assume that HZ can move across an interphase boundary easily and the dissociation of HZ occurs in the aqueous phase only. Other reactions *(e.g. esterifaction)* are considered as insignificant.



The diagram of the distribution of HZ acid between two immiscible solvents

The distribution of HZ in all forms between the solvents is defined by two equilibriums:

- The ionization of HZ in the aqueous phase is defined by the ionization constant (K_a):
  $K_a = \frac{[H^+][Z^-]}{[HZ]}$ or $pK_a = -\log K_a$, where $[H^+]$, $[Z^-]$ and [HZ] are the concentrations of corresponding species in the aqueous phase.

- The partition of unionized HZ between the solvents is defined by the partition coefficient (P_{ow}):
  $P_{ow} = \frac{[HZ]_o}{[HZ]}$ or $\log P_{ow} = \log \frac{[HZ]_o}{[HZ]}$, where $[HZ]_o$ and [HZ] are the concentrations of unionized HZ in the octanol and aqueous phases respectively.

Consider two systems:

- The first system is identical to the one discussed before.

- The second system is almost identical to the one discussed before. Except it has the additional amount of strong base in the aqueous phase.

Taking into account the conservation of mass, the set of characteristic equations of the systems can be derived:

$$\begin{cases} K_a = \dfrac{[HZ]_1^2\ P_{ow}}{[HZ]_{o1}} + \dfrac{[HZ]_{o1}}{P_{ow}} - 2\ [HZ]_1 \\ K_a = \dfrac{[HZ]_2\ \left([HZ]_2 + [B]_2\right) P_{ow}}{[HZ]_{o2}} + \dfrac{[HZ]_{o2}}{P_{ow}} - \left(2\ [HZ]_2 + [B]_2\right) \end{cases},$$

where $[B]_2$ is the concentration of strong base in the aqueous phase of the second system. The subscripts of the parameters denote the system they belong.

However, the analytical solution of the set of characteristic equations is too clumsy. Contour plots representing numerical solutions are given in Appendix.

Task

You are provided with the solution of an unknown monoprotic acid. For convenience, this monoprotic acid will be referred as "X acid". In this problem you have to determine the molar mass, pK_a and log P_{ow} of X acid.

Procedures

1. Pour 20.00 mL of X acid solution to the 50 mL volumetric flask. Dilute the solution to 50.00 mL with H_2O. Pour the content of the flask to the 100 mL bottle labeled "A" and add 10.00 mL of 1-octanol. *(It is difficult to wash 1-octanol from glassware. So devote one 10 mL pipette to 1-octanol only.)*

2. Pour 20.00 mL of X acid solution and 10.00 mL of ~0.25 M NaOH to the 50 mL volumetric flask. Dilute the solution to 50.00 mL with H_2O. Pour the contents of the flask to the 100 mL bottle labeled "B" and add 10.00 mL of 1-octanol.

3. Seal both bottles tightly and shake well for 1 min. Repeat the same procedure every 10 min for one hour. Then leave to stand for the next hour for the solvents to separate. *(You can proceed to the other tasks while waiting.)*

4. Pour the content of the bottle A to the 100 mL separating funnel carefully *(don't shake the solvents again)*. Give ~5 min for the solvents to separate completely. Release the aqueous solution to the 100 mL beaker *(don't contaminate the aqueous solution with 1-octanol)*. The obtained aqueous solution will be referred as "solution A".

5. Transfer the 1-octanol solution from the separating funnel to the bottle labeled "1-octanol waste". Wash out 1-octanol from the separating funnel by shaking distilled water inside it for several times. Place the obtained emulsions to the bottle labeled "1-octanol waste".

6. Pour the content of the bottle B to the 100 mL separating funnel carefully *(don't shake the solvents again)*. Give ~5 min for the solvents to separate completely. Release the aqueous solution to the 100 mL beaker *(don't contaminate the aqueous solution with 1-octanol)*. The obtained aqueous solution will be referred as "solution B".

7. Fill the 25 mL burette with ~0.03 M NaOH solution *(the exact concentration is written on the bottle)*. Take 10.00 mL of solution A and titrate it using bromothymol blue as an indicator. Titrate slowly near the equivalence point. Give ~30 s for the color change *(yellow-blue)*. Repeat the titration for a few times to obtain reliable results. Place the wastes to the beaker labeled "Aqueous waste".

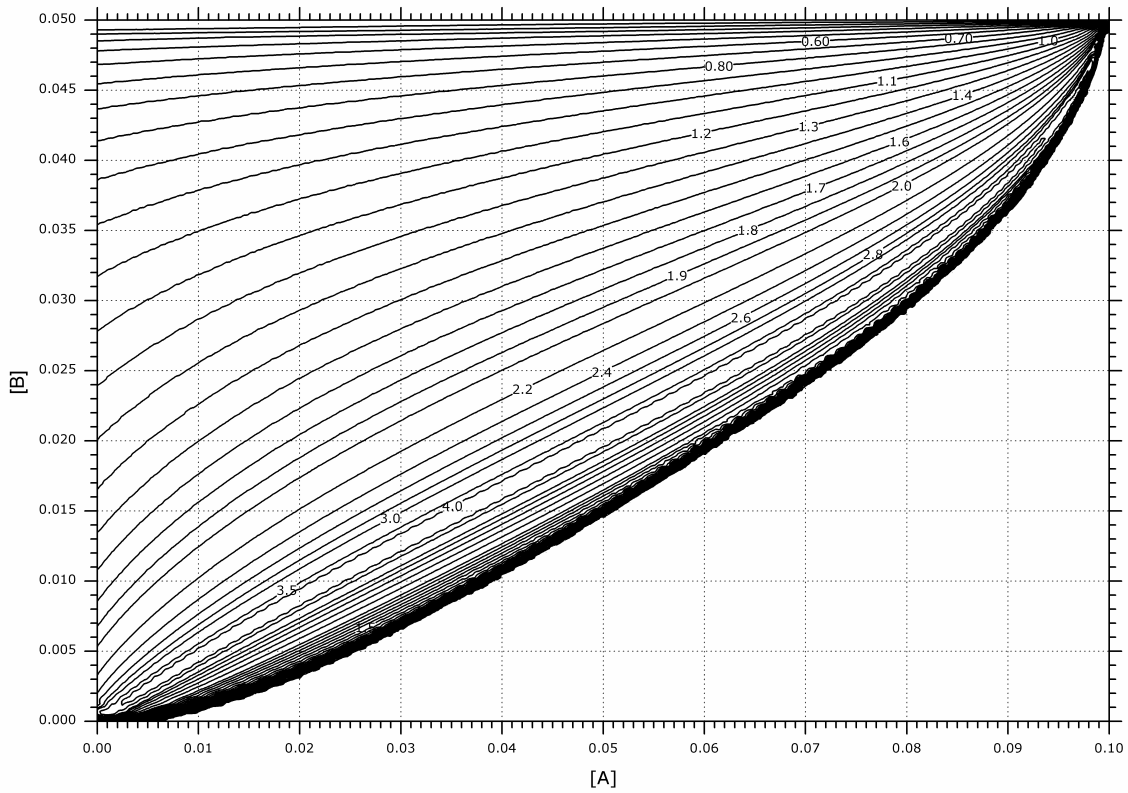
8. Fill the 25 mL burette with ~0.03 M NaOH solution *(the exact concentration is written on the bottle)*. Take 10.00 mL of solution B and titrate it using bromothymol blue as an indicator. Titrate slowly near the equivalence point. Give ~30 s for the color change *(yellow-blue)*. Repeat the titration for a few times to obtain reliable results. Place the wastes to the beaker labeled "Aqueous waste".

9. Calculate the concentrations of X acid in solutions A and B. Find the values of pK_a and log P_{ow} of X acid. *(Refer to the contour plots in Appendix.)*

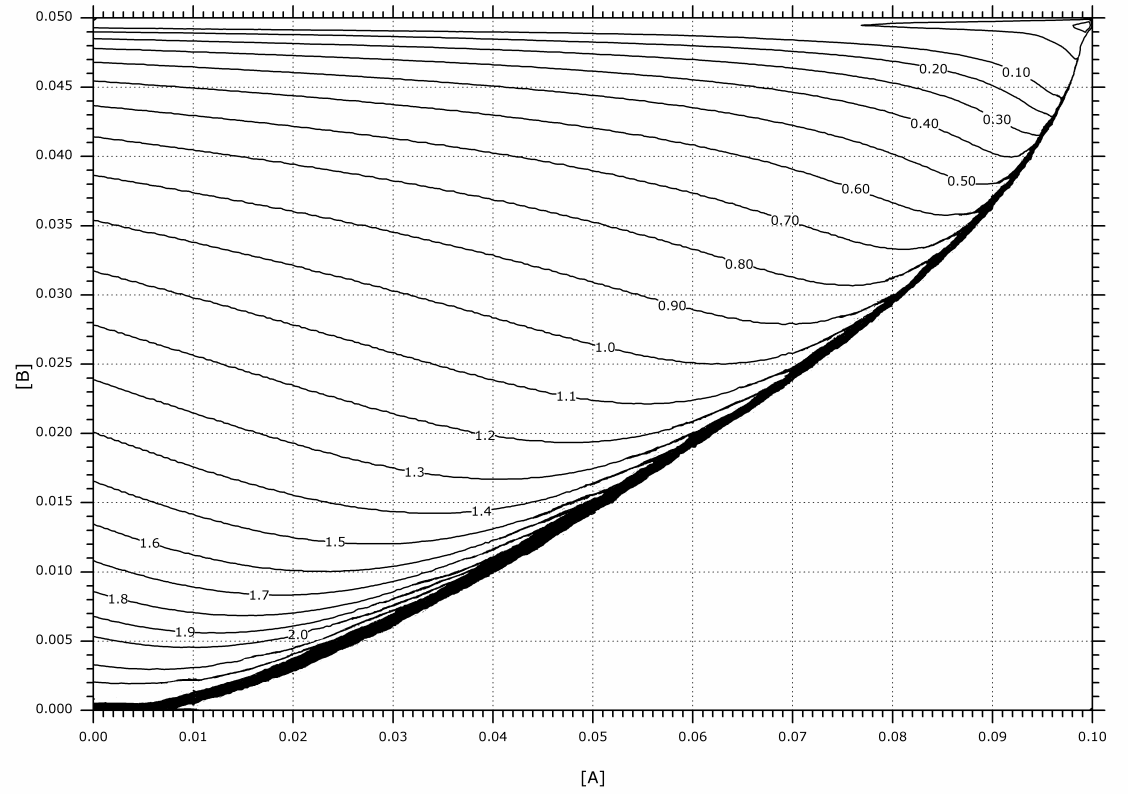
10. Fill the 25 mL burette with ~0.25 M NaOH solution *(the exact concentration is written on the bottle)*. Take 10.00 mL of X acid solution and titrate it using bromothymol blue as an indicator. Repeat the titration for a few times to obtain reliable results. Place the wastes to the beaker labeled "Aqueous waste".

11. Calculate the molar mass of X acid. (*The mass concentration of X acid solution is written on the bottle.)*

Appendix



The contour plot represents the dependence of pK_a of X acid on the concentrations of X acid in solutions A and B. The concentration of X acid in solution A is plotted on the x-axis *(labeled "[A]")*. The concentration of X acid in solution B is plotted on the y-axis *(labeled "[B]").*



The contour plot represents the dependence of log P_{ow} of X acid on the concentrations of X acid in solutions A and B. The concentration of X acid in solution A is plotted on the x-axis *(labeled "[A]")*. The concentration of X acid in solution B is plotted on the y-axis *(labeled "[B]")*.

Problem 2 – Synthesis of N-benzyl-3-nitroaniline

Apparatus and Supplies

1.	Erlenmeyer flask *(25 mL)*	1
2.	Erlenmeyer flask *(100 mL)*	1
3.	Sintered glass funnel	1
4.	Magnetic stirrer	1
5.	Magnetic stirring bar	1
6.	Plastic syringe *(1 mL)*	1
7.	Long needle	1
8.	Spatula	1
9.	TLC developing beaker	1
10.	TLC plate	1
11.	Plastic bag for TLC plate	1
12.	Tweezers	1
13.	Screw cap bottles *(labeled TLC1-TLC4)*	4
14.	Capillary tubes for TLC	4
15.	Measuring cylinder *(25 mL)*	1
16.	Petri dish	1
17.	Cooling bath	1
18.	Glass beaker for ice-cooled water	2
19.	Waste container *(for general use, labeled "Organic waste")*	
20.	Cleaning paper roll *(shared among a few students)*	
21.	Ice and ice-cooled water (*ask an instructor)*	
22.	UV-lamp (for general use)	

Chemicals

1. Meta-nitroaniline 1.1 g weighted in Erlenmeyer flask *(25 mL)*
2. Sodium borohydride 0.6 g weighted in capped glass vial *(labeled "$NaBH_4$")*
3. Benzaldehyde approx. 2-3 mL in caped glass vial *(labeled "Ph-CHO")*
4. Ethanol approx. 50 mL *(labeled "EtOH")*
5. TLC eluent *(labeled "EL")*
6. Acetone *(for general use, in a fume hood)*

Safety data

Acetone

Formula C_3H_6O
Molecular weight 58.08 g/mol
Melting point -94.9°C
Boiling point 56.5°C
Density 0.79 g/mL

R11 Highly flammable
S9 Keep container in a well ventilated place
S16 Keep away from sources of ignition
S23 Do not breathe vapour
S33 Take precautionary measures against static discharges

Ethanol

Formula C_2H_6O
Molecular weight 46.07 g/mol
Melting point -114.3°C
Boiling point 78.4°C
Density 0.79 g/mL

R11 Highly flammable
S7 Keep container tightly closed
S16 Keep away from sources of ignition

Ethyl acetate

Formula $C_4H_8O_2$
Molecular weight 88.11 g/mol
Melting point – 83.6°C
Boiling point 77.1°C
Density 0.89 g/mL

R11 Highly flammable
R36 Irritating to the eyes
R66 Repeated exposure may cause skin dryness or cracking
R67 Vapours may cause drowsiness and dizziness
S16 Keep away from sources of ignition
S26 In case of contact with eyes, rinse immediately with plenty of water and seek medical advice
S33 Take precautionary measures against static discharges

Hexane

Formula C_6H_{14}
Molecular weight 86.18 g/mol
Melting point - 95.0°C
Boiling point 69.0°C
Density 0.66 g/mL

R11 Highly flammable
R38 Irritating to skin
R48/20 Harmful: danger of serious damage to health by prolonged exposure through inhalation
R51/53 Toxic to aquatic organisms, may cause long-term adverse effects in the aquatic environment

R62 Possible risk of impaired fertility
R65 Harmful: may cause lung damage if swallowed
R67 Vapours may cause drowsiness and dizziness
S9 Keep container in a well-ventilated place
S16 Keep away from sources of ignition
S29 Do not empty into drains
S33 Take precautionary measures against static discharges
S36/37 Wear suitable protective clothing and gloves

***meta*-nitroaniline**

Formula $C_6H_6N_2O_2$
Molecular weight 138.14 g/mol
Melting point 114.0°C

R 23/24/25 Toxic by inhalation, in contact with skin and if swallowed
R33 Danger of cumulative effects
R52/53 Harmful to aquatic organisms, may cause long-term adverse effects in the aquatic environment
S36/37 Wear suitable protective clothing and gloves
S45 In case of accident or if you feel unwell seek medical advice immediately
S61 Avoid release to the environment. Refer to special instructions/safety data sheet

Benzaldehyde

Formula C_7H_6O
Molecular weight 106.13 g/mol
Melting point -26.0°C
Boiling point 178.1°C
Density 1.04 g/mL

R22 Harmful if swallowed
S24 Avoid contact with skin

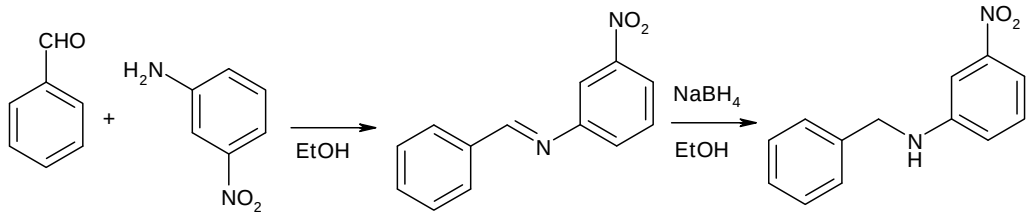
Sodium borohydride

Formula $NaBH_4$
Molecular weight 37.83 g/mol
Melting point 400°C

R15 Contact with water liberates extremely flammable gases
R24/25 Toxic in contact with skin and if swallowed
R34 Causes burns
S22 Do not breathe dust
S26 In case of contact with eyes, rinse immediately with plenty of water and seek medical advice
S36/37/39 Wear suitable protective clothing, gloves and eye/face protection

Introduction

Aromatic aldehydes react readily with anilines forming imines. The resulting imine can be reduced to the corresponding amine using sodium borohydride *($NaBH_4$)*. The overall reaction sequence is called reductive amination. It is possible to accomplish the same transformation in one pot using mild and selective reducing agent, sodium triacetoxyborohydride *($NaH(AcO)_3$)*. In this experiment you will carry out the synthesis of N-benzyl-3-nitroaniline according to the scheme:



Procedures

Step 1

Add 10 mL of ethanol to a 25 mL Erlenmeyer flask containing 1.1 g *meta*-nitroaniline. The starting material is moderately soluble in ethanol and only part of it dissolves. Add 1.5 mL of benzaldehyde to this mixture using a syringe. Let the flask stand for 20 minutes with occasional shaking by hand. Cool the flask in ice-water bath *(ask an instructor for an ice bath)*. On cooling a solid material separates. Collect it on a sintered glass funnel. Use the filtrate to transfer the solid remaining in the flask onto the filter. Dry it with suction. Set aside a small sample *(a few crystals on the tip of a spatula)* for thin-layer chromatography *(TLC, use the vial labeled **TLC3**)*.

Step 2

Transfer the solid substance obtained in **Step 1** from glass funnel into a 100 mL Erlenmeyer flask and add 20 mL of ethanol. *(Return your glass funnel to an instructor. You will get a cleaned one back later)*. Wash the spatula with acetone into the waste container in a fume hood and dry it with cleaning paper. Slowly add to this suspension 0.6 g of $NaBH_4$ in small portions *(approx. in 2-3 min)* with stirring. Continue stirring the flask for an additional 15 minutes, and then pour its content into 50 mL of ice-cold water *(ask an instructor for ice-cooled water)*. Collect the precipitate on a sintered glass funnel and wash with cold water. Dry the product with suction and transfer it to a weighted Petri dish. Take a small portion of the product to the vial labeled **TLC4**. The Petri dish with the synthesized compound must be left on your workplace.

TLC analysis

You are provided with four screw capped glass vials labeled **TLC1**, **TLC2**, **TLC3** and **TLC4**. The vials labeled **TLC1** and **TLC2** already contain m-nitroaniline and benzaldehyde solutions in ethyl acetate respectively. Dissolve the materials in the vials **TLC3** and **TLC4** in ethanol. Spot each solution on TLC plate *(remember to use separate capillary tubes for each solution)*. Add eluent *(labeled **EL** Ethyl acetate-Hexane (1:5, v/v)))* to the TLC beaker. Develop the TLC plate. Visualize the TLC plate under UV *(UV lamp, for general use, in a fume hood)* and mark the spots with pencil. Write your identification code on the top of the TLC plate with pencil and put it into a plastic bag.

Fill the answer sheets.