

# Materials and Life Sciences Lab. C 2019

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# I General notes and instructions

## I-1 General safety in the lab

1. Wear light clothing ~~which that~~ is suitable for conducting experiments safely. Shoes/boots with high heels and sandals (open-toed shoes etc) are prohibited. Suitable footwear, with relatively flat soles and closed toes should be worn. Tie back long hair and take other relevant precautions.
2. Wear safety spectacles at all times in the laboratory. Regular eyeglasses (provided they are not tinted) are also acceptable. Wear your "Safety Card".
3. Eating, drinking and smoking in the lab are prohibited.
4. Please take care not to touch/disturb any equipment/chemicals/experiments that are not related to your tasks.
5. Before plugging in any electrical device, ensure that the main power switch is OFF. Follow the instructions/manual there-after.
6. Please maintain good laboratory hygiene by keeping the benches and surrounding areas clean and free of clutter.
7. Be aware of the emergency procedures, evacuation routes, fire extinguishers and alarm locations.
8. In the event of an accident, inform TA/academic staff immediately.
9. In the event of a fire, announce it loudly and take appropriate measures.

## I-2 Lab hours and supervision

1. The laboratory hours are from 13:30 to 17:05 on Thursday and Friday. Manage your time so that the required tasks can be completed within the allotted period.
2. If you leave the laboratory without first obtaining permission, you may be marked as absent.
3. Know your supervisor. If you have any questions about the experiment and equipment, don't hesitate to ask.

## I-3 Preparation

1. Read the text for the appropriate experiment in advance (*not 5 minutes before!!*). Summarize the experimental flow in your notebook thoroughly, so that the actual experiment can proceed smoothly and on-time. Consult reference sources if some parts are unclear.
2. List of required equipment and chemicals are provided. If some of the required items are not present, inform the instructor/TA. Return any superfluous items. There is a written (paper) form that should be completed in the event of ~~Submit a "formal letter of apology" if there is~~ any negligent damage/loss.

## I-4 Important instructions and safety considerations during experiments

1. Common equipment should be used in the prescribed location (see experimental layout).
2. When borrowing equipment not available on the bench, fill in the necessary information and in principle return the item on the same day.
3. Write observations, experimental conditions and data directly in your notebook during the experiment. As a general rule, do not jot things on a separate piece of paper to be transferred later, to prevent transcription errors. Errors should be erased by crossing through.

4. For measurements that involve data collection over a reasonable time period (i.e. continuous time-dependent data collection), the recording of the data should be accompanied by plotting a graph on graph paper. In this way, the validity of each data point can be assessed *during* the experiment. This method allows significant errors to be identified during measurement.
5. Take special care when using a naked flame due to the presence of flammable chemicals in the laboratory.
6. Waste disposal: dispose of solid waste according to classification as either combustible or non-combustible. Dispose of liquid waste in the appropriate (designated) containers, as instructed.
7. Take care not to spill acid / base on your person/clothing. In the event of an emergency, immediately rinse thoroughly with running water.
8. Always wash apparatus after using. Be sure to replace any damaged or depleted items.
- ~~9. In general, use of the ovens (controlled temperature heating chambers) is limited to the laboratory hours. In exceptional cases, with the instructor's permission, overnight operation may be permitted provided an "Overnight Experiment" note is created with the student name(s), student number(s), date and experiment number. Such operation is not permitted over weekends/holidays.~~
- ~~10. Do not put laboratory equipment in the drawers of the laboratory benches.~~

## I-5 Before leaving

1. After the experiment, check that all of the equipment is in order, and request that the TA/instructor inspect the work area.
2. Be sure to close/switch off gas, water and power. Unplug power cords.
- ~~3. After ensuring that the work area is clean, let the TA/instructor know that you are leaving.~~
- ~~4. Failing to observe steps 1-3 above may result in an "absent" grading for the experiment.~~

## I-6 How to write reports

In this lab, the sections on purpose, principle, method etc are largely omitted. This allows more time for developing "discussion" and answering specific questions. For Experiments 4, 5 and 6, report forms are provided. In general, reports are structured as follows. In this laboratory session, omit sections on purpose, principles, and experimental methods to secure sufficient time for discussion, and write experimental results on the Report Form provided.

- I. Title of experiment
- II. Your name (student number), lab partner's name (student number)
- III. Submission date (~~dd/mm/yy~~), date(s) of experiment
- IV. ~~Date of experiment, ambient temperature, and atmospheric pressure on the day of experiment~~  
Temperature and pressure can affect the experimental data. Summary of experiment: summarise the experiment in one concise paragraph.
- V. ~~Purpose of experiment~~ Experimental results: summarise the progress of the experiment, observations and data. Include graphs where necessary.
- VI. ~~Principle of experiment~~ Discussion

~~The theoretical background required to achieve the purpose of the experiment should be described by clarifying the data you will directly observe (measure) and the analysis method. Describe the results together with any additional insights.~~

~~VII. Experimental method~~

~~The apparatuses used and their operating procedures should be described concretely, focusing as much as possible on the important information related to experimental results.~~

~~VIII. Measurement results~~

~~The directly measured data should be clearly organized and summarized in tables or graphs if necessary. The data should be analyzed and conclusions drawn on the basis of the purpose of the experiment.~~

~~IX. Discussion~~

~~The results obtained should be discussed considering the accuracy of the apparatuses used and the precision of the experimental procedure and method of analysis. If possible, the relationship between the experimental results and items other than those described in the purpose should also be discussed.~~

~~I–IV and VIII should be written on the Report Form provided, and IX and answers to exercises should be written on the writing sheets for experiments. Add graphs if required.~~

## II Tables of units

### II-1 SI base units

Quantity name	Quantity symbol	Unit name	Unit symbol
Length	<i>l</i>	metre	m
Mass	<i>m</i>	kilogram	kg
Time	<i>t</i>	second	s
Electric current	<i>I</i>	ampere	A
Thermodynamic temperature	<i>T</i>	kelvin	K
Amount of substance	<i>n</i>	mole	mol
Luminous intensity	<i>I<sub>v</sub></i>	candela	cd

### II-2 SI prefixes

Multiple	Prefix	Symbol	Multiple	Prefix	Symbol
10	deca	da	10 <sup>-1</sup>	deci	d
10 <sup>2</sup>	hecto	h	10 <sup>-2</sup>	centi	c
10 <sup>3</sup>	kilo	k	10 <sup>-3</sup>	milli	m
10 <sup>6</sup>	mega	M	10 <sup>-6</sup>	micro	μ
10 <sup>9</sup>	giga	G	10 <sup>-9</sup>	nano	n
10 <sup>12</sup>	tera	T	10 <sup>-12</sup>	pico	p
10 <sup>15</sup>	peta	P	10 <sup>-15</sup>	femto	f
10 <sup>18</sup>	exa	E	10 <sup>-18</sup>	atto	a

### II-3 SI derived units

Quantity name	Unit name	Unit symbol	Expressed in terms of SI base units
Frequency	hertz	Hz	s <sup>-1</sup>
Force	newton	N	m·kg·s <sup>-2</sup>
Pressure, stress	pascal	Pa	m <sup>-1</sup> ·kg·s <sup>-2</sup>
Energy, work, heat	joule	J	m <sup>2</sup> ·kg·s <sup>-2</sup>
Power	watt	W	m <sup>2</sup> ·kg·s <sup>-3</sup>
Electric charge	coulomb	C	s·A
Electric potential	volt	V	m <sup>2</sup> ·kg·s <sup>-3</sup> ·A <sup>-1</sup>
Electric capacitance	farad	F	m <sup>-2</sup> ·kg <sup>-1</sup> ·s <sup>4</sup> ·A <sup>2</sup>
Electric resistance	ohm	Ω	m <sup>2</sup> ·kg·s <sup>-3</sup> ·A <sup>-2</sup>
Electric conductance	siemens	S	m <sup>-2</sup> ·kg <sup>-1</sup> ·s <sup>3</sup> ·A <sup>2</sup>
Magnetic flux	weber	Wb	m <sup>2</sup> ·kg·s <sup>-2</sup> ·A <sup>-1</sup>
Magnetic flux density	tesla	T	kg·s <sup>-2</sup> ·A <sup>-1</sup>
Inductance	henry	H	m <sup>2</sup> ·kg·s <sup>-2</sup> ·A <sup>-2</sup>
Celsius temperature	degree Celsius	°C	K
Plane angle	radian	rad	1
Solid angle	steradian	sr	1

## II-4 Physical quantities

Quantity	Symbol	Value	Unit
Permeability of vacuum	$\mu_0$	$4\pi \times 10^{-7}$	$\text{N} \cdot \text{A}^{-2}$
Speed of light in vacuum	$c_0$	299 792 458	$\text{m} \cdot \text{s}^{-1}$
Permittivity of vacuum	$\varepsilon_0$	$8.854\,187\,817 \times 10^{-12}$	$\text{F} \cdot \text{m}^{-1}$
Elementary charge	$e$	$1.602\,176\,53(14) \times 10^{-19}$	C
Planck constant	$h$	$6.626\,0693(11) \times 10^{-34}$	J·s
Avogadro constant	$L, N_A$	$6.022\,1415(10) \times 10^{23}$	$\text{mol}^{-1}$
Rest mass of electron	$m_e$	$9.109\,3826(16) \times 10^{-31}$	kg
Rest mass of proton	$m_p$	$1.672\,621\,71(29) \times 10^{-27}$	kg
Faraday constant	$F$	$9.648\,533\,83(83) \times 10^4$	$\text{C} \cdot \text{mol}^{-1}$
Hartree energy	$E_h$	$4.359\,744\,17(75) \times 10^{-18}$	J
Bohr radius	$a_0$	$5.291\,772\,108(18) \times 10^{-11}$	m
Bohr magneton	$\mu_B$	$9.274\,009\,49(80) \times 10^{-24}$	$\text{J} \cdot \text{T}^{-1}$
Nuclear magneton	$\mu_N$	$5.050\,783\,43(43) \times 10^{-27}$	$\text{J} \cdot \text{T}^{-1}$
Rydberg constant	$R_\infty$	10 973 731.568 525(73)	$\text{m}^{-1}$
Gas constant	$R$	8.314 472(15)	$\text{J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}$
Boltzmann constant	$k, k_B$	$1.380\,6505(24) \times 10^{-23}$	$\text{J} \cdot \text{K}^{-1}$
Gravitational constant	$G$	$6.6742(10) \times 10^{-11}$	$\text{m}^3 \cdot \text{kg}^{-1} \cdot \text{s}^{-2}$
Standard acceleration due to gravity	$g_n$	9.806 65	$\text{m} \cdot \text{s}^{-2}$
Triple point of water	$T_{\text{tp}}(\text{H}_2\text{O})$	273.16	K
Zero of Celsius scale	$T(0^\circ\text{C})$	273.15	K
Molar volume of ideal gas (1 atm, 273.15 K)	$V_m$	$2.241\,3996(39) \times 10^{-2}$	$\text{m}^3 \cdot \text{mol}^{-1}$

## II-5 Greek letters

Letter		Name
A	$\alpha$	alpha
B	$\beta$	beta
$\Gamma$	$\gamma$	gamma
$\Delta$	$\delta$	delta
E	$\varepsilon$	epsilon
Z	$\zeta$	zeta
H	$\eta$	eta
$\Theta$	$\theta$	theta
I	$\iota$	iota
K	$\kappa$	kappa
$\Lambda$	$\lambda$	lambda
M	$\mu$	mu
N	$\nu$	nu
$\Xi$	$\xi$	xi
O	$\omicron$	omicron
$\Pi$	$\pi$	pi
P	$\rho$	rho
$\Sigma$	$\sigma$	sigma
T	$\tau$	tau
Y	$\upsilon$	upsilon
$\Phi$	$\phi$	phi
X	$\chi$	chi
$\Psi$	$\psi$	psi
$\Omega$	$\omega$	omega



### III Experiments

Assignment 1: Synthesis of 4-nitroaniline . . . . . 8~~9~~

Assignment 2: Synthesis of methyl orange . . . . . 14

Assignment 3: Polymer synthesis and viscosity measurement . . . . . 19~~18~~

Assignment 4: Dissociation constant (acidity constant) of formic acid 25~~23~~

Assignment 5: Reaction rate of sucrose hydrolysis~~-of suerose~~ . . . . . 33~~31~~

Assignment 6: Adsorption of acetic acid on activated carbon . . . . . 37~~35~~

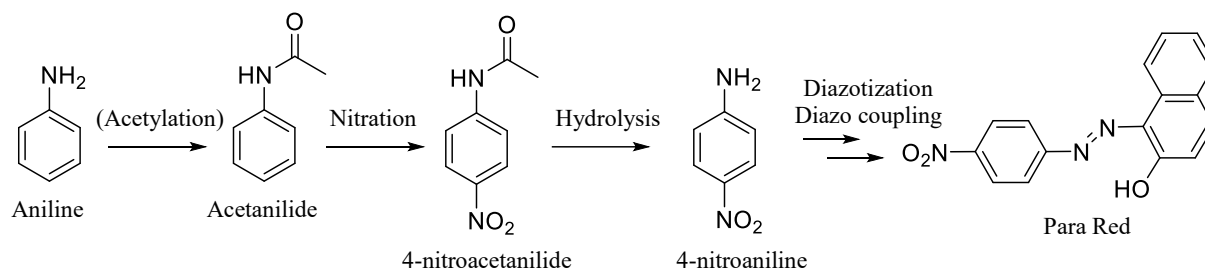
### III-1 Synthesis of 4-nitroaniline

#### [Objective]

The aim of this assignment is to learn laboratory operation procedures and basic techniques in organic chemistry through the synthesis, isolation, and purification of 4-nitroaniline (*p*-nitroaniline), an important aromatic compound that serves as a synthetic intermediate in the preparation of azo dyes. We will also learn how the properties of functional groups influence substitution reactions in the electrophilic substitution reaction of aromatic compounds.

#### [Overview]

4-Nitroaniline is synthesized via the nitration of acetanilide, which is obtained via the acetylation of aniline, in an electrophilic aromatic substitution reaction followed by hydrolysis of the acetyl group. Para Red (an azo dye) can be synthesized from this compound using diazotization and diazo-coupling reactions, which we will learn in (see Assignment 2).



In this experiment, we will use acetanilide as the starting material for the synthesis of 4-nitroaniline. (We have already performed the synthesis of acetanilide from aniline in “Basic Experiments in Science and Engineering”.)

#### [Pre-lab notebook organization]

- Write down the reaction formula for 4-nitroaniline synthesis from acetanilide.
- Create in advance a flow chart for 4-nitroaniline synthesis from acetanilide.
- Calculate in advance the amount of each reagent to be used.
- Create in advance a formula for calculating the synthesis yield.

[Required equipment and instruments]

Contents of container (container is shared with Assignment 2 and 3)			
Beaker (100 mL) ビーカー	1	Funnel 漏斗(ロート)	1
Beaker (300 mL) ビーカー	2	Komagome pipette (2 mL) 駒込ビペット	3
Erlenmeyer flask (100 mL) 三角フラスコ	1	Rubber dropper (2 mL) スポイトゴム	3
Erlenmeyer flask (300 mL) 三角フラスコ	1	Glass rod ガラス棒	1
Round-bottom flask (100 mL) ナス型フラスコ	1	Micro-spatula ミクロスパーテル	1
<del>Metric glass</del> Conical measuring cylinder (25 mL) メートルグラス	1	Measuring spoon (“medicine spoon”) 薬さじ	1
<del>Glass joint adapter</del> 異径管	1	Rubber adapter (black: large, small) ゴムアダプター(黒色:大, 小)	1 set
Büchner flask 吸引びん	1	Pipette stand ビペット台	1
Büchner funnel ブフナー漏斗	1		

On the bench and in common areas			
Aspirator (2 groups share, benchtop) アスピレーター	1	<del>磁器攪拌子</del> Stirrer bar (common) <del>磁器攪拌子</del>	1
Ice bath (benchtop) 氷浴	1	Filter paper (common) ろ紙	
Water bath (benchtop) ウォーターバス	1	Litmus paper (common) リトマス試験紙	
Plastic wash bottle (500 mL, benchtop) ポリ洗びん	1	Balance (common) 電子上皿天秤	
Stand (benchtop) スタンド	1	Melting point instrument (common) 融点測定器	
Clamp, <del>muff</del> clamp holder (benchtop) クランプ・ムッフ	1 set	Cover glass (common) カバーガラス	
TLC developing tank-(chamber) TLC展開層	1	UV lamp (common) UVランプ	
Work gloves (benchtop) 軍手	1 pair	TLC plates (common) TLC板	
Spot plate (reaction plate, benchtop) 呈色反応皿	1	Unglazed plate (melting point, common) 素焼き板	

In the <del>draft chamber</del> fumehood			
Aluminium block & hot-plate stirrer アルミブロック式加熱反応装置	1	Glass tubing ガラス管	
Reflux condenser 還流冷却器	1	Bunsen burner ブンゼンバーナー	
<del>冷却水用チューブ</del> Tube for cooling water	1	Ampoule cutter (glass cutter) アンプルカッター	

## [Experiment]

### A. Nitration of acetanilide (Synthesis of 4-nitroacetanilide)<sup>1</sup> (1<sup>st</sup> day)

The purities and the molecular weights of the reagents used in this experiment are as shown in Table 1.

1. Using a Komagome pipette, take 4.4 mL of concentrated sulfuric acid and dispense into a 100 mL Erlenmeyer flask. Add 2.0 g of acetanilide and stir well. Once most of acetanilide has dissolved, immerse the Erlenmeyer flask in an ice bath to lower the temperature of the reaction mixture to  $\leq 10$  °C. (Measure the temperature with a thermometer dipped in the liquid inside the flask.)
2. While keeping the Erlenmeyer flask immersed in the ice bath, add 2.3 mL of nitric acid drop by drop to the reaction mixture resulting from step 1, using a Komagome pipette. Shake well after adding each drop, being careful not to let the temperature of the reaction mixture exceed 20 °C.
3. Once all nitric acid has been added, remove the ice bath and leave the reaction mixture at room temperature for 30 minutes with occasional agitation (swirling).
4. Pour the reaction mixture into a 100 mL beaker containing ~~roughly~~ 30 mL of iced water, and stir well to precipitate crystals.
5. Collect the precipitated crystals by suction filtration using a Büchner funnel and Büchner flask. ~~(葉さじを使用し、全ての結晶を濾取する。)~~ (use a spoon to collect and filter all crystals). Wash with a *small amount* of ion-exchanged water until the crystals become white. (~~At this time~~Here, do not wash with a large amount of water.) Transfer the crystals in the Büchner funnel onto dry filter paper. (Keep roughly 0.5–1 mg wrapped in a piece of weighing paper, and use the remainder for the following Experiment part B.)

### B. Synthesis of 4-nitroaniline<sup>1</sup> (1<sup>st</sup> day)

1. Pour the crude nitroacetanilide into a 100 mL round-bottom flask and add 12 mL of 6.0 mol L<sup>-1</sup> hydrochloric acid. ~~磁器攪拌子を入れ,~~ Carefully add a stirrer bar, then connect a reflux condenser to the flask. ~~異径管と~~ (a glass joint adapter is needed to connect the two parts of different diameter) and heat for 20 minutes under reflux using an aluminum block<sup>2</sup>. *WARNING: this involves highly concentrated acidic solution at elevated temperature. Be careful.*
2. Remove the flask from the aluminum block and allow it to cool. Transfer the solution to a 300-mL beaker. While cooling the beaker in the ice bath, add 8% aqueous sodium hydroxide solution to neutralize the solution (confirm with litmus paper).
3. After crystals have precipitated, suction-filter the solution, and wash the crystals several times with a small amount of ion-exchanged water. Transfer all the crystals in the Büchner funnel onto a piece of filter paper, and then, using another piece of filter paper to cover and press the crystals, allow the filter paper to fully absorb moisture. After air drying, measure the crude mass and calculate the crude yield. (Transfer about 0.5–1 mg to a spot plate, and use the remaining in the next experiment C.)

### C. Purification of 4-nitroaniline (1<sup>st</sup> or 2<sup>nd</sup> day)

1. (1<sup>st</sup> day) Transfer the crude 4-nitroaniline to a 300 mL Erlenmeyer flask and add an appropriate amount of ion-exchanged water. While holding the mouth of the Erlenmeyer flask with a clamp, shake the flask by hand and heat it in a water bath. If the crystals do not dissolve completely, add ion-exchanged water in small amounts as appropriate until the crystals are completely dissolved. (Calculate the appropriate amount of ion-exchanged water from the crude yield and water solubility.)
2. (1<sup>st</sup> day) Quickly perform hot gravity filtration (use a funnel that has been heated beforehand and filter paper pre-moistened with hot water) to remove insoluble impurities. Transfer the filtrate to an Erlenmeyer flask, let it stand, and allow the temperature to drop to roughly room temperature.
3. (1<sup>st</sup> day) When crystals are formed, perform suction filtration. Vacuum until moisture disappears. Then, transfer all the crystals in the Büchner funnel onto a piece of filter paper, and place another piece of filter paper to cover and press the crystals to fully absorb moisture.
- 3-4. (2<sup>nd</sup> day) After drying well, transfer the crystals to a new sample bottle, weigh ~~the mass~~, and calculate the yield.

### D. Confirmation of 4-nitroaniline formation by melting point measurement and thin-layer chromatography (2<sup>nd</sup> day)

#### 《Melting point measurement》

1. Place ~~少量の~~ thea small quantity of crystals on an unused part of an unglazed plate and grind well with a micro-spatula to pulverize.
2. Place the finely ground crystals between two cover glasses and measure the melting point using the melting point apparatus. Record the temperature at the beginning and the end of melting. (Perform the measurement three times and take the average. Compare with the literature value.)

#### 《Thin-layer chromatography (TLC)》

1. On a TLC plate (pre-cut to an appropriate size), draw thin lines with a pencil 5 mm from the top and 5 mm from the bottom of the plate, and mark 4 spots with 'x' in equal distances on the starting line. Prepare two plates in this manner.
2. Add ~~crude~~ 4-nitroacetanilide, crude 4-nitroaniline, and pure 4-nitroaniline into different depressions of a spot plate. Add a few drops of ethyl acetate/hexane mixture (volume ratio 1:2) and dissolve each compound.
3. (First TLC plate) Take acetanilide in ethyl acetate/hexane solution (common reagent), crude 4-nitroacetanilide solution, and crude 4-nitroaniline solution using different capillary tubes (for each solution), and apply each of them on the different x marks one by one from the left end, letting the samples be absorbed on the plate. (Position the tip of the capillary tube containing the sample close to the plate perpendicularly, and lightly touch the silica gel surface. You can cut the capillary tube with an ampoule cutter and use it repeatedly.) Then, apply all the three samples (one-by-one) on the same (remaining) x mark at the right end, and let the samples be absorbed on the plate.
4. (First TLC plate) Place the TLC plate in the developing chamber containing ethyl acetate/hexane solution

(volume ratio 2:1), i.e., the developing solvent, and let it stand against the wall with the starting line at the bottom. Leave it with the lid on. (Make sure that the level of the developing solvent is below the starting line.) When the top of the developing solvent reaches the upper line, remove the TLC plate and let it dry.

5. (First TLC plate) Irradiate the plate with UV light, observe sample spots, mark their positions with a pencil, and record the distances traveled.
6. (Second TLC plate) Using different capillary tubes for each solution, take standard 4-nitroaniline in ethyl acetate/hexane solution (common reagent), crude 4-nitroaniline solution, and purified 4-nitroaniline solution, and put each of them on the different x marks one by one from the left end. Then apply all the three samples (one-by-one) on the same (remaining) x mark at the right end, and let the samples be absorbed on the plate. Develop the TLC plate in the same manner as with the first plate, and record the distance traveled by each sample spot.

#### E. Preparation of glass capillary tubes

1. Curl your hand and fingers lightly, with the back of the hand facing up. With your fingers, support one end of a soft glass capillary tube, roughly 1 cm in thickness and cut into an appropriate length, and rotate it with your thumb and forefinger (support the end of the capillary tube on the opposite side with the other hand in a supplementary fashion) to heat the capillary tube uniformly in the range of about 2 cm with a burner so that it becomes softened.
2. Remove the capillary tube from the flame, and after a short pause, pull it from side to side, starting slowly and gradually increasing speed, while rotating it with both hands. (The capillary tube will break if you pull it while being heated.) Before the glass hardens, pinch the capillary tube with two fingers and pull it firmly from side to side so that it is extended in a straight line.
3. Scratch the capillary tube surface with an ampoule cutter, hold both sides of the capillary tube near the scratched area using the fingers of both hands, and break the capillary tube by pulling it as if you are opening up the scratched surface outward. Prepare two capillary tubes measuring 15 to 20 cm in length and roughly 1 mm in diameter per person. (The cut surface should not be sharp. Cut the capillary tube so that the surface is flat and perpendicular to the side of the capillary tube.)

#### [Notes]

1. All glassware should be washed thoroughly with a brush and detergent, cleaned thoroughly, and stored in a container (they may still be wet with tap water). There is no need to wash with ion-exchanged water.
2. The filtrate after suction filtration is collected as organic waste liquid. Follow the instructions of the faculty staff or TA (never discard it into the sewage system).

#### [References]

1. Chemical Society of Japan, Ed., "The fifth series of experimental chemistry 1 - Basic edition I Basics of experiment and information," Maruzen, 58–66 (2007).
2. Kagaku-Dojin Publishing, Ed., "Supplementary volume: How to carry out experiments safely - Basic

operations/basic measurements, 4th edition," (2017).

[Reference: Physical properties of 4-nitroaniline]

- Molecular weight:  $138.12 \text{ g mol}^{-1}$
- Melting point:  $146 \text{ }^{\circ}\text{C}$
- Boiling point:  $332 \text{ }^{\circ}\text{C}$
- Solubility in water:  $22 \text{ g L}^{-1}$  ( $100 \text{ }^{\circ}\text{C}$ );  $0.57 \text{ g L}^{-1}$  ( $25 \text{ }^{\circ}\text{C}$ ).

Table 1 Purities, molecular weights, and formula weights of reagents.

Reagent	Purity (%)	Molecular weight / formula weight ( $\text{g mol}^{-1}$ )
Acetanilide	99.0	135.16
Concentrated sulfuric acid	98	98.08
Concentrated nitric acid	98	63.01

## III-2 Synthesis of methyl orange

### [Objective]

In this assignment, you will perform the synthesis of methyl orange (sodium 4-[(4-dimethylamino)phenylazo]-benzenesulfonate), which is used in acid-base titrations as an indicator. Diazotization and diazo-coupling reactions will be carried out using the basic organic chemistry laboratory operations and techniques you have learned thus far. You will gain an understanding of the chemical properties of methyl orange, and how its structure and color changes with solution pH.

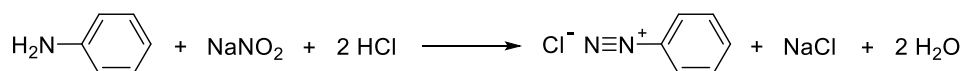
### [Overview]

Methyl orange, an azo compound, has an azo group  $-N=N-$ . Many synthetic dyes (azo dyes), including methyl orange, are synthesized via diazotization and diazo-coupling reactions.

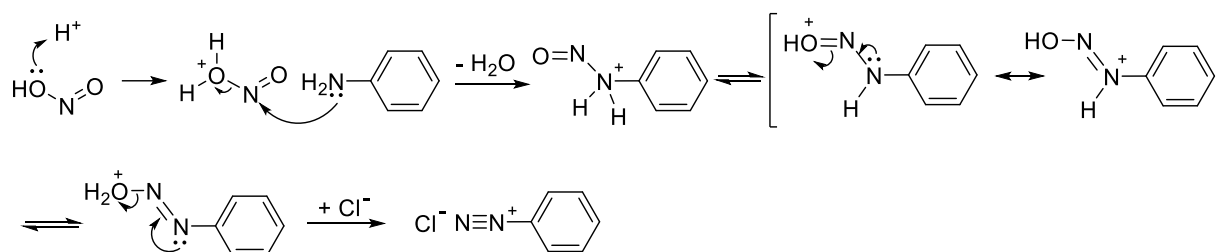
#### Diazotization reaction (synthesis of diazonium salt)<sup>1,2</sup>

A diazonium salt is formed via a reaction of a primary amine compound, such as aniline, with sodium nitrite and hydrochloric acid.

<Reaction formula for diazotization of aniline>



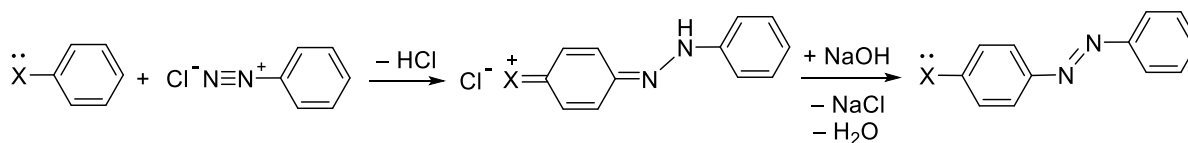
<Reaction mechanism>



#### Diazo-coupling reaction<sup>1</sup>

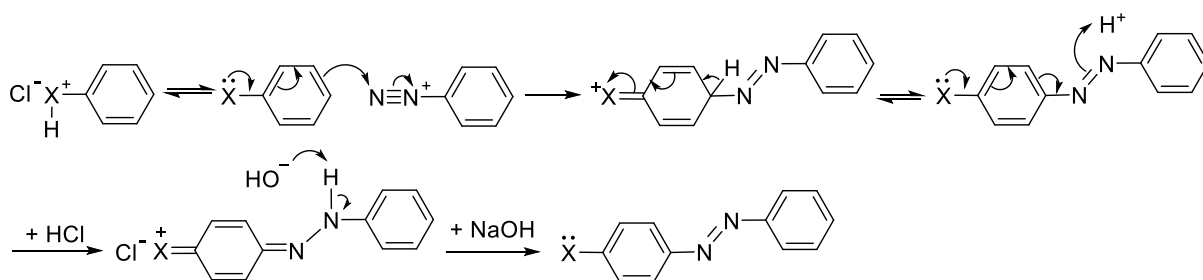
After reacting the diazonium salt with *N,N*-dimethylaniline, for example, in an acidic solution, the reaction solution is rendered alkaline, and an azo compound is obtained.

<General formula>





<Reaction mechanism>



In this experiment, we will synthesize a diazonium salt via the diazotization of sodium sulfanilate (sodium salt of sulfanilic acid), which is then diazotized with dimethylaniline to yield methyl orange.

[Pre-lab notebook organization]

- Check (and draw) the structural formulas of sulfanilic acid, *N,N*-dimethylaniline, and methyl orange.
- Calculate in advance the required amounts of reagents listed above.
- Write down the reaction formula for methyl orange synthesis.
- Prepare a flowchart for methyl orange synthesis.
- Create in advance a formula for calculating the synthesis yield.
- Check the color change range (pH) of methyl orange.

[Required equipment and instruments]

Contents of container (container is shared with Assignment 1 and 3)			
Beaker (100 mL) ビーカー	1	Komagome pipette (2 mL) 駒込ビペット	2
Beaker (50 mL) ビーカー	2	Rubber dropper (2 mL) スポイトゴム	2
Erlenmeyer flask (200 mL) 三角フラスコ	2	Glass rod ガラス棒	2
Test tube 試験管	1	Measuring spoon (“medicine spoon”) 薬さじ	1
Measuring cylinder (20 mL) メスシリンダー	1	Rubber adapter (black: large, small) ゴムアダプター (黒色: 大, 小)	1 set
Büchner flask 吸引びん	1	Thermometer 温度計	1
Büchner funnel ブフナー漏斗	1	Pipette stand ビペット台	1
Funnel 漏斗 (ロート)	1		

On the bench and in common areas			
Aspirator (2 groups share, benchtop) アスピレーター	1	Work gloves (benchtop) 軍手	1 pair
Ice bath (benchtop) 氷浴	1	Filter paper (common) ろ紙	
Water bath (benchtop) ウォーターバス	1	Litmus paper (common) リトマス試験紙	
Stand (benchtop) スタンド	1	Balance (common) 電子上皿天秤	
Clamp, <u>muff-clamp holder</u> (benchtop) クランプ・ムッフ	1 set	pH meter (common) pHメーター	
Plastic wash bottle (500 mL, benchtop) ポリ洗びん	1		

## [Experiment]

### A. Synthesis of methyl orange<sup>1</sup> (1<sup>st</sup> day)

The purities and the molecular weights of the reagents used in this experiment are as shown in Table 2. Reagents are accurately weighed to 2 digits after the decimal point (g).

- (As Operations a to d described below are all independent tasks, it is not necessary to carry out these tasks in the order listed.)
  - Add 2.0 g of sulfanilic acid and 5.0 mL of 2.5 mol L<sup>-1</sup> sodium hydroxide aqueous solution into a 100 mL beaker. Heat the mixture (70 to 80 °C) while stirring with a glass rod to dissolve sulfanilic acid, and then cool in an ice bath.
  - Add 0.80 g of sodium nitrite into a 50-mL beaker. Then, add 5.0 mL of ion-exchanged water to dissolve sodium nitrite, and cool the mixture in an ice bath.
  - Pour 12.5 mL of 2.0 mol L<sup>-1</sup> hydrochloric acid into a test tube and cool the solution in an ice bath. (Hold the test tube with a clamp.)
  - Add 1.25 g of *N,N*-dimethylaniline and 10 mL of 1.0 mol L<sup>-1</sup> hydrochloric acid into another 50-mL beaker and stir the mixture well using a glass rod until *N,N*-dimethylaniline dissolves completely. After complete dissolution, cool the solution in an ice bath (If *N,N*-dimethylaniline does not dissolve, add small amounts of 1.0 mol L<sup>-1</sup> hydrochloric acid until complete dissolution is achieved).
- Add the sodium nitrite solution prepared in step 1-**b** to the reaction solution prepared in step 1-**a** while maintaining the temperature in the range of 0 to 5 °C. Stir the mixture well. Add the 2.0 mol L<sup>-1</sup> hydrochloric acid solution cooled in step 1-**c** to the above mixture solution and stir well in an ice bath.
- Paying attention to the solution temperature, quickly add all the solution prepared in step 1-**d**, while stirring, to the reaction solution resulting from step 2. Cool the mixture in an ice bath and stir for approximately 10 minutes.
- Slowly add 1.0 mol L<sup>-1</sup> sodium hydroxide aqueous solution to the reaction solution resulting from step 3 to make it strongly alkaline (check using pH paper). Stir the reaction solution until it becomes yellow-brown.
- Add 約around 1 g of sodium chloride to the reaction solution in step 4. While heating in a hot water bath,

stir the mixture well for approximately 1 minute until sodium chloride is completely dissolved.

6. After cooling the solution, collect the precipitated crystals of methyl orange by vacuum filtration using a Büchner funnel and Büchner flask. Remove the remaining crystals in the beaker using a medicine spoon and rinse them with a small amount of cold water (prepared by placing a wash bottle containing ion-exchanged water directly in an ice bath). At this point, do NOT rinse with a large amount of water. Transfer the crystals from the funnel onto dry filter paper and remove the crystals attached to the wet filter paper (that was used for filtration) using a medicine spoon. Sandwich the crystals between two pieces of dry filter paper to absorb moisture from the crystals.

#### B. Purification of crude methyl orange by recrystallization (2<sup>nd</sup> day)

1. After measuring the crude yield, purify the dried crude crystals by recrystallization, as follows. Transfer the crude methyl orange crystals to a 200 mL Erlenmeyer flask and add an appropriate amount of ion-exchanged water. Hold the neck of the flask with a clamp and heat the flask in a hot water bath with constant shaking by hand. If the crystals do not dissolve completely, add ion-exchanged water in small amounts as appropriate to achieve complete dissolution. (At this time, be careful not to add too much ion-exchanged water.)
2. Quickly perform hot gravity filtration (use a funnel that has been heated beforehand and filter paper pre-moistened with hot water) to remove insoluble impurities. Place the filtrate in an Erlenmeyer flask, let it stand, and allow it to cool to room temperature.
3. Collect precipitated crystals by vacuum filtration. Vacuum-dry the crystals until moisture is completely eliminated, and transfer all the crystals from the Buchner funnel onto filter paper. Cover the crystals with another piece of filter paper to absorb moisture. Dry the crystals thoroughly and transfer them into a sample bottle. Measure the mass and calculate the yield.

#### C. Confirmation of methyl orange formation by titration (2<sup>nd</sup> day)

1. Pour 10 mL of 1.0 mol L<sup>-1</sup> ammonia water into a 10 mL beaker, add methyl orange, and add 1.0 mol L<sup>-1</sup> hydrochloric acid by dropping into the solution. When the color of the indicator changes, stop the titration.
2. Measure the pH of the solution using a pH meter, and record it.

#### [Notes]

1. All glassware should be washed thoroughly with a brush and detergent, cleaned thoroughly, and stored in a container (they may still be wet with tap water). There is no need to wash them with ion-exchanged water.
2. The filtrate after suction filtration is collected as organic waste liquid. Follow the instructions of the faculty staff or TA (never discard it into the sewage system).

#### [References]

1. Seiichi Asada, Shigeru Uchide, and Motohiro Kobayashi, "New organic chemistry experiments with illustrations and flowcharts," Hiroshi Fukutomi, Ed., Gihodo Shuppan Co., Ltd., 58-61 (1979).
2. Chemical Society of Japan, Ed. "The first series of experimental chemistry, volume 20 - Synthesis of organic

compounds II-," Maruzen, 347-349 (1957).

[Reference: Physical properties of methyl orange]

- Molecular weight: 327.3 g mol<sup>-1</sup>
- Melting point: ≥300 °C
- Solubility in water: 5 g L<sup>-1</sup> (20 °C)

Table 2 Purities, molecular weights, and formula weights of reagents.

Reagent	Purity (%)	Molecular weight / formula weight (g mol <sup>-1</sup> )
Sulfanilic acid	99.5	173.19
<i>N,N</i> -dimethylaniline	99.0	121.18
Sodium nitrite	98.5	69.00

### III-3 Polymer synthesis and viscosity measurement

#### [Objective]

Polymer materials, such as plastic, fiber, and rubber, have become an indispensable part of our daily lives. In this assignment, we will perform experiments on some of these polymer materials, namely, nylon and polyacrylic acid. Around 1927, Wallace Hume Carothers, a researcher at DuPont in the US, attempted to synthesize artificial fiber that resembled silk. However, it was not easy to synthesize polymers in the way he had envisioned because the moisture generated in the reaction of diamine and dicarboxylic acid would stop the polymerization reaction. He continued to modify the reaction conditions and persisted in his investigation for approximately one year. Finally, he succeeded in synthesizing a fiber that could be put to practical use. The fiber is nylon-6,6. Today, several types of nylons are available, enriching our lives. In this assignment, we will learn the synthesis of nylon-6,10 and polyacrylic acid. In addition, to better understand the characteristics of polymer compounds, we will measure the intrinsic viscosity of polyvinylpyrrolidone and the electrical conductivity of poly(3-hexylthiophene).

#### [Overview]

Polymer compounds are synthesized from monomers via polymerization reactions. The polymerization of monomers gives rise to an oligomer that comprises several polymerized monomer units, and if polymerization proceeds further, a polymer is formed. The process through which monomers are polymerized, as shown below, involves the linking of more and more molecules (A) as the synthesis (polymerization) proceeds. First, starting molecule A (monomer A) reacts with another monomer A, forming a dimer; this dimer then reacts with another monomer A, forming a trimer, which further reacts with another monomer A to form a tetramer. The repetition of reactions in this manner leads to the formation of oligomers and polymers.



The polymerization reactions of polymer compounds can be broadly divided into sequential polymerization and chain polymerization. Depending on the type of monomer reaction, sequential polymerization can be classified as (i) polycondensation or (ii) polyaddition, and chain polymerization can be classified as (i) addition polymerization or (ii) ring-opening polymerization. The mechanisms of monomer reactions can be classified according to the electronic properties of the monomer into, e.g., cationic, anionic or radical polymerization.

In this experiment, we will synthesize nylon-6,10 via interfacial polycondensation. A mixed solution of hexamethylenediamine and sodium hydroxide will be placed in a container, into which a hexane solution of sebacic acid dichloride (sebacoyl dichloride) will be added slowly. You will observe the formation of film-like nylon-6,10 at the interface of the two solutions.

#### [Pre-lab notebook organization]

- Understand the experiment and preparation to be performed on Day 1 and on Day 2.
- Prepare in advance the flow charts for the syntheses of nylon-6,10 and polyacrylic acid.
- Look up the chemical reaction formulae for the syntheses of nylon-6,10 and polyacrylic acid.
- Check each experimental procedure.
- Create ahead of time a table in which the results of intrinsic viscosity measurement can be recorded.

## [Required equipment, instruments, and chemicals]

Contents of container (container is shared with Assignment 1 and 2)			
Beaker (50 mL) ビーカー	5	Petri dish シャーレ	1
Beaker (100 mL) ビーカー	2	Test tube 試験管	1
Stoppered Erlenmeyer flask (100 mL) 共栓三角フラスコ	2	Glass rod ガラス棒	1
Measuring cylinder (100 mL) メスシリンダー	1	Funnel 漏斗(ロート)	1
Measuring cylinder (20 mL) メスシリンダー	1	Tweezers ピンセット	1
Graduated pipette (10 mL) メスピペット	1	Plastic bottle (100 mL) ポリ瓶	4
Volumetric pipette (5 mL) ホールスピペット	1	Dropper (10 mL) スポイトゴム	1
Volumetric pipette (25 mL) ホールスピペット	1	Measuring spoon (“medicine spoon”) 薬さじ	1
Komagome pipette (10 mL) 駒込スピペット	1	<del>Pipette stand</del> <del>ビペット台</del>	<del>1</del> <del>+</del>
Volumetric flask (50 mL) メスフラスコ	1	<del>Pipette stand</del> <del>ビペット台</del>	<del>+</del>
On the bench and in common areas			
Stand (benchtop) スタンド	1	Slide glass (common) スライドガラス	
Clamp, <del>muff-clamp holder</del> (benchtop) クランプ・ムッフ	1 set	Conductivity measurement device (common) 導電率測定装置	
Ring clamp (benchtop) リングクランプ	1	Stopwatch (common) ストップ・ウォッチ	
Plastic wash bottle (500 mL, benchtop) ポリ洗びん	1	Glass cutter (common) ガラスカッター	
Protective eyewear (common) 保護メガネ		Kim towel (common) キムタオル	
UV lamp (common) ブラックライトブルー蛍光ランプ		Bamboo skewer (common) 竹串	
Ostwald (U-tube) viscometer (common) オストワルド粘度計		Filter paper (common) ろ紙	

## [Experiment]

### A. Synthesis of nylon-6,10

The purities and the molecular weights of the reagents used are as described in Table 3.

1. (Day 1) Weigh out 0.6 g of purified hexamethylenediamine in a 50-mL beaker and dissolve it by adding 10 mL of 0.5 mol L<sup>-1</sup> sodium hydroxide solution prepared separately. (Hexamethylenediamine has a melting

point of approximately 40 °C, and is in the solid state at room temperature. In this experiment, melted hexamethylenediamine is measured using a Komagome pipette and directly transferred into a beaker.)

2. (*Day 1*) Obtain from your TA a sample bottle containing 10 mL of hexane solution into which sebacoyl dichloride is dissolved (1.2 g of sebacoyl dichloride is dissolved in the 10-mL hexane solution mentioned above).
3. (*Day 1*) Using a graduated pipette, slowly and gently dispense the 10-mL solution prepared in (2) down the wall of the beaker containing the solution prepared in (1) (do not do this in reverse). A film will form at the interface of the two solutions (it is important to add gently to prevent any ripples at the interface). With a pair of tweezers, immediately pick up the center of the film formed at the interface and wind it at a constant speed around a test tube.
4. (*Day 1*) The wound nylon should be washed with ion-exchanged water as it still contains unreacted raw materials. Unwind the nylon from the test tube and wash it well in a 100-mL beaker filled with ion-exchanged water. Pick up the nylon with tweezers and place it on Kimtowel. Sandwich the nylon with Kimtowel to remove the moisture sufficiently, and leave it to air-dry.
5. (*Day 2*) Measure the yield of the dried nylon.

#### B. Photopolymerization: ~~synthesis~~ of polyacrylic acid

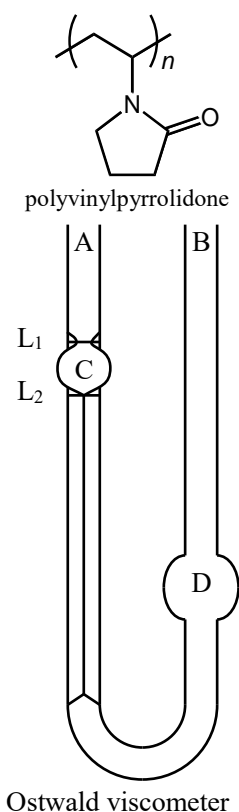
The purities and the molecular weights of the reagents used in this experiment are as shown in Table 4.

1. (*Day 1*) Into ~~a separate~~ 50 mL beakers, add ~~and dissolve~~ 4.0 mL ~~each~~ of methyl methacrylate, ethyl methacrylate, and hydroxyethyl methacrylate (one reagent per beaker). Add and dissolve 100 mg of 1-hydroxycyclohexyl phenyl ketone, which serves as the polymerization initiator.
2. (*Day 1*) Be sure to wear UV protection glasses in the following experiment. In a fume hood, irradiate the solution with a black light blue fluorescent lamp (365 nm). Check the degree of curing by turning off the lamp and touching the top of the reaction solution with a bamboo stick. Record the time (duration) of photo curing.
3. (*Day 2*) Add 10 mL of ion-exchanged water into the reaction beaker and wash the polymer obtained. Repeat this operation three times, and observe the hydrophilicity of the polymer.

#### C. Measurement of intrinsic viscosity of polyvinylpyrrolidone

1. (*Day 1*) Weight out 0.5 g of polyvinylpyrrolidone and place it in an Erlenmeyer flask. Into this, add 50 mL of ion-exchanged water. Dissolve it completely by stirring with a glass rod. The resulting solution is used as the original solution.
2. (*Day 1*) Dilute the original solution with ion-exchanged water to prepare a series of solutions whose concentrations are 1/2, 1/4, and 1/8 of the original concentration (use a volumetric pipette to dilute the solvent). Store the prepared solutions in 100 mL plastic bottles.

- (Day 1 or 2) Using a clamp, set an Ostwald viscometer vertically on a stand, and introduce 5 mL of ion-exchanged water into side B of the viscometer with a transfer pipette. Attach a syringe to side A, and suck the liquid up until the surface is above line L<sub>1</sub> on side A of the viscometer. Measure the time (sec) required for the liquid surface to pass lines L<sub>1</sub> and L<sub>2</sub>. Repeat this operation three times, and use the average value ( $t_0$ ) as the measurement value.
- (Day 1 or 2) In a similar manner, measure liquid flow time ( $t$ ) for the four different concentrations of polymer solution. Note: Before measuring the next sample, be sure to pre-wash the viscometer using the sample solution to be measured. Also, proceed with the measurement from less concentrated solutions.
- (Day 1 or 2) Perform the measurement described above for the samples at each concentration to determine the specific viscosity and the intrinsic viscosity. In addition, based on the intrinsic viscosity, determine the average molecular weight of this polymer.
- (Day 1 or 2) Rinse the viscometer and the transfer pipette with ion-exchanged water at least 10 times.



#### D. Reprecipitation, film formation, and electrical conductivity of poly(3-hexylthiophene)

- (Day 1) Weight out 0.2 g of poly(3-hexylthiophene) and place it in ~~an~~ a 100 mL Erlenmeyer flask. Into this, add slowly purified dichloromethane to prepare a saturated solution. (Be careful not to over-dilute the solution.)
- (Day 1) Add slowly the solution prepared in (1) into purified methanol (10 times the volume of the solution) and stir for 5 minutes. Filter the resulting solid, put it on a piece of filter paper, and wash twice with 10 mL of purified methanol.
- (Day 1) After drying sufficiently on the filter paper, weigh (for reprecipitation yield calculation), then dissolve poly(3-hexylthiophene) in purified dichloromethane to prepare a saturated solution. (Be careful not to over-dilute the solution.)
- (Day 1) Place several pieces of Kimwipe on a petri dish, and place two clean slide glasses. Without spilling, drop the same amount of the saturated solution onto the two slide glasses and let them air-dry. This operation is to be repeated approximately five times until a cast film of poly(3-hexylthiophene) is formed on the surface of each slide glass.
- (Day 2) Measure the electrical conductivity of the poly(3-hexylthiophene) cast film using a digital multimeter connected with a 4-point probe. Use one cast film to measure electrical conductivity as is; the other cast film is to be immersed in the prepared iodine hexane solution (distributed by the TA) for 30 seconds, so that you can observe changes in the film. Then, air-dry the cast film, and when dry, measure its electrical conductivity.

[Notes]



1. If necessary, air-dry the cast films using a hot plate installed in the fume hood.
2. Solutions used for the interfacial polycondensation of nylon and the synthesis of polyacrylic acid, as well as the primary wash solution and the polyvinylpyrrolidone solution, will be collected as organic waste liquid. Follow the instructions of your instructor or TA (never discard the solutions into the sewer/sink).

### [References]

1. Chemical Society of Japan, Ed., "Interesting Chemistry Laboratory II," Tokyo Kagaku Dojin, 15 (1995).
2. Chemical Society of Japan, Ed., "The fourth series of experimental chemistry 1 - Basic operations I," Maruzen, 104 (1996).
3. J. Brandrup, E. H. Immergut, E. A. Grulke, Eds, "Polymer Handbook," Fourth Edition, John Wiley & Sons, Inc., 1999.
4. T. Seki, Y. Okahata, "Chemistry and Education," Vol. 34, 1986, p. 492.

### [Supplement: Relationship between viscosity and average molecular weight of polymer]

The time required for a certain amount of liquid to flow through a capillary tube is proportional to the viscosity of the liquid. The rate of increase in viscosity ( $\eta_{sp}$ : specific viscosity) as a result of polymer dissolution is expressed by Equation (1), where  $\eta$ ,  $t$ , and  $\rho$  are the viscosity, the liquid flow time, and the density of the polymer solution; and  $\eta_0$ ,  $t_0$ , and  $\rho_0$  are those of the solvent, respectively.

$$\eta_{sp} = \frac{\eta - \eta_0}{\eta_0} = \frac{\rho t - \rho_0 t_0}{\rho_0 t_0} \approx \frac{t - t_0}{t_0} \quad (1)$$

The intrinsic viscosity of the polymer solution  $[\eta]$  is defined by Equation (2) ( $C$  is the concentration of the solution).

$$[\eta] = \lim_{C \rightarrow 0} \left( \frac{\eta_{sp}}{C} \right) \quad (2)$$

Thus, the relationship shown in Equation (3) is established between  $[\eta]$  and  $M$ , the average molecular weight of the polymer ( $K$  and  $a$  are constants depending on the polymer, the solvent, and the temperature), and is referred to as the Mark-Houwink-Sakurada equation. Table 5 shows the  $K$  and  $a$  values for representative polymers.

$$[\eta] = KM^a \quad (3)$$

Table 3 Purities, molecular weights, and formula weights of reagents.

Reagent	Purity (%)	Molecular weight / formula weight (g mol <sup>-1</sup> )
Sebacoyl dichloride	95.0	239.1
Hexamethylenediamine	95.0	116.2
Sodium hydroxide	96.0	40.0

Table 4 Purities, molecular weights, and formula weights of reagents.

Reagent	Purity (%)	Molecular weight / formula weight (g mol <sup>-1</sup> )
Methyl methacrylate	98.0	100.1
Ethyl methacrylate	99.0	114.1
Hydroxyethyl methacrylate	95.0	130.1
1-Hydroxycyclohexyl phenyl ketone	97.0	204.3

Table 5  $K$  and  $\alpha$  values used in the Mark-Houwink-Sakurada equation.

Polymer	Solvent	Temperature / °C	$K/10^{-4}$	$\alpha$	Molecular weight range / $10^4$
Polyvinylpyrrolidone (PVP)	Water	25	1.9	0.68	2.2 ~ 100
Polystyrene	Benzene	25	0.95	0.74	3 ~ 61
Polyvinyl acetate	Acetone	25	1.76	0.68	19 ~ 72

### III-4 Dissociation constant (acidity constant) of formic acid

#### [Objective]

The aim of this assignment is to determine the dissociation constant (acidity constant) of formic acid from changes in hydrogen ion concentration. You will also learn the principle of pH measurement using a glass electrode, and the actual measurement procedures.

#### [Principle]

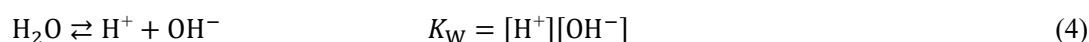
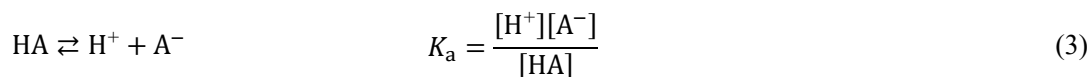
The dissociation constant of formic acid is defined as follows (Equation 1). This constant takes different values depending on the temperature, pressure, and ionic strength (when the ionic strength is not too high,  $K_a$  increases with increasing ionic strength).

$$K_a = \frac{[H^+][HCOO^-]}{[HCOOH]} \quad (1)$$

The ionic strength is defined by Equation (2), and is used to assess the interaction between ions in an electrolyte solution.

$$I = \frac{1}{2} \sum_i z_i^2 c_i \quad \left( z_i \text{ and } c_i \text{ are the charge number and molar concentration of ion } i, \text{ respectively.} \right) \quad (2)$$

Let us consider a titration of a monoprotic weak acid (HA), such as formic acid, with a strong base (MOH). As we can assume that MOH and its salt (MA) are completely dissociated in an aqueous solution, the chemical species present in the solution are HA,  $A^-$ ,  $M^+$ ,  $H^+$ ,  $OH^-$ , and  $H_2O$ . The relationships between these chemical species and their molar concentrations are expressed by Equations (3) to (7).



$$C_A = [HA] + [A^-] \quad (5)$$

$$C_M = [M^+] \quad (6)$$

$$[A^-] + [OH^-] = [H^+] + [M^+] \quad (7)$$

$C_A$  and  $C_M$  are the concentrations of HA and MOH, respectively, in the solution during titration. These values can be calculated from the amounts used in the titration. Equation (7) can be derived easily given the fact that the solution has equal positive and negative charges. From Equations (3) to (7), the following Equation (8) can be obtained by eliminating unknown numbers other than the concentration of hydrogen ions and the acid dissociation constant.

$$[H^+]^3 + (C_M + K_a)[H^+]^2 + (K_a C_M - K_a C_A - K_W)[H^+] - K_a K_W = 0 \quad (8)$$

The volume of the mixed solution necessary for the calculation of  $C_A$  and  $C_M$  can be approximated as  $V_{HA} + V_{MOH}$ , where  $V_{HA}$  is the volume of HA solution at a molar concentration of  $C_{HA}$ , and  $V_{MOH}$  is the volume of MOH solution used for titration, having a molar concentration of  $C_{MOH}$  (this is a sufficiently good approximation, if  $C_{HA}$  and  $C_{MOH}$  are approximately  $1 \text{ mol L}^{-1}$  or less). Accordingly,  $C_A$  and  $C_M$  can be calculated as follows:

$$C_A = \frac{C_{HA} V_{HA}}{V_{HA} + V_{MOH}} \quad (9)$$

$$C_M = \frac{C_{MOH} V_{MOH}}{V_{HA} + V_{MOH}} \quad (10)$$

By substituting Equations (9) and Equation (10) into Equation (8), the following Equation (11) can be obtained.

$$K_a = -\frac{\beta}{\alpha} = -\frac{[H^+]^2 + \frac{C_{MOH} V_{MOH}}{V_{HA} + V_{MOH}} [H^+] - K_W}{[H^+] + \frac{(C_{MOH} V_{MOH} - C_{HA} V_{HA})}{V_{HA} + V_{MOH}} - \frac{K_W}{[H^+]}} \quad (11)$$

As suggested by Equation (11), acid dissociation constant  $K_a$  is the slope of the straight line plotted with  $-\alpha$  on the horizontal (x) axis and  $\beta$  on the vertical (y) axis. Thus, it is possible to determine  $K_a$  from the concentration of hydrogen ions measured in the mixed solution as the amount of titrant (MOH solution) added,  $V_{MOH}$ , is increased, by calculating  $\alpha$  and  $\beta$  and obtaining the slope by the least squares method. If measurements are performed properly, a straight line passing through the origin should be obtained.

#### [Required equipment, instruments, and chemicals]

Contents of container			
Beaker (100 mL) ビーカー	4	Conical beaker (200 mL) ニカルビーカー	3
Beaker (500 mL) ビーカー	1	Volumetric flask (100 mL) メスフラスコ	3
Volumetric pipette (10 mL) ホールピペット	2	Graduated pipette (1 mL) メスピペット	1
Volumetric pipette (20 mL) ホールピペット	1	Pipette bulb ピペッター (ゴム球)	2
Wide-mouthed plastic bottle (100 mL, dry) 広口ポリビン	5	Pipette stand ピペッター台	1
Wide-mouthed plastic bottle (250 mL, dry) 広口ポリビン	1	Small funnel ロート小	1
Wide-mouthed plastic bottle (500 mL, dry) 広口ポリビン	1	Weighing bottle 秤量ビン	3
Komagome pipette (5 mL) 駒込ピペット	2	Plastic beaker ポリビーカー	5
Glass rod ガラス棒	2	Measuring spoon (stainless) 薬さじ (ステンレス)	2

On the laboratory bench			
pH meter pH計	1	Glass electrode, thermometer and stand ガラス電極およびスタンド	
Burette (25 mL) ビュレット	1	Burette stand and clamp ビュレット台 & ビュレットばさみ	1
Plastic wash bottle (500 mL, benchtop) ポリ洗びん	1		

## [Experiment]

### A. Reagent preparation

As the dissociation constant of formic acid changes depending on the ionic strength, in the following experiment, the ionic strength of the solution is kept nearly constant by adding sodium chloride, which does not interfere with the reactions.

1. Using a graduated pipette, remove the supernatant of saturated aqueous sodium hydroxide solution prepared in the fume hood (dissolve sodium hydroxide in approximately 0.8 fold by mass of ion-exchange water), and pour out  $0.8\text{ cm}^3$  into a  $250\text{ cm}^3$  plastic bottle (determine the amount of liquid to be dispensed according to the difference indicated by the scales of the graduated pipette).
2. Weigh out approximately 6.6 g of sodium chloride using a two-pan balance (down to two decimal places, in grams), dissolve it in ion-exchanged water in an appropriate beaker, and add this to the aforementioned plastic bottle to prepare a  $250\text{ cm}^3$  aqueous solution with ion-exchanged water. This solution is referred to as Solution A hereafter. Try not to expose this solution to air to the extent possible.
3. Accurately weigh out approximately 0.12 g of potassium hydrogen phthalate using a weighing bottle dried in a drying oven and dissolve it in an appropriate amount of ion-exchanged water. Transfer the solution to a  $200\text{ cm}^3$  conical beaker and add a few drops of phenolphthalein. Prepare three of these. Wash the weighing bottle with ion-exchanged water immediately after use and allow it to dry by placing inside the drying oven.
4. Pour Solution A into a burette that has been pre-washed with a small amount of Solution A. Be sure to remove the funnel used at this time from the burette after pouring. Perform titration with Solution A three times, and report immediately the result of Solution A standardization to the instructor or TA.
5. Prepare  $500\text{ cm}^3$  of  $0.5\text{ mol L}^{-1}$  aqueous sodium chloride solution using a  $500\text{ cm}^3$  plastic bottle.
6. Weigh out  $0.8\text{ cm}^3$  of concentrated hydrochloric acid in a  $100\text{ cm}^3$  plastic bottle using a graduated pipette. Weigh out approximately 2.3 g of sodium chloride using a two-pan balance (down to two decimal places), dissolve it in ion-exchanged water in an appropriate beaker, and add this to ion-exchanged water to prepare a  $100\text{ cm}^3$  aqueous solution. Hereafter, this solution is referred to as Solution B<sub>1</sub> (the concentration of hydrochloric acid is approximately  $10^{-1}\text{ mol L}^{-1}$ ).
7. Using a volumetric pipette, transfer  $10\text{ cm}^3$  of Solution B<sub>1</sub> into a  $100\text{ cm}^3$  volumetric flask, and add  **$0.5\text{ mol L}^{-1}$  aqueous sodium chloride solution prepared in Step 5** to prepare a  $100\text{ cm}^3$  aqueous solution. Hereafter, this solution is referred to as Solution B<sub>2</sub> (its concentration is approximately  $10^{-2}\text{ mol L}^{-1}$ ). In the same manner, prepare Solution B<sub>3</sub> and Solution B<sub>4</sub> of hydrochloric acid having concentrations of approximately  $10^{-3}\text{ mol L}^{-1}$  and  $10^{-4}\text{ mol L}^{-1}$ , respectively. Store each of the three prepared aqueous solutions in  $100\text{ cm}^3$  plastic bottles.
8. In a  $200\text{ cm}^3$  conical beaker, add  $10\text{ cm}^3$  of Solution B<sub>1</sub> measured with a volumetric pipette, add a few drops of phenolphthalein, and titrate with Solution A. Perform titration only once. Assuming that accurate dilutions have been performed, calculate the concentrations of Solutions B<sub>2</sub>, B<sub>3</sub>, and B<sub>4</sub> from the concentration of Solution B<sub>1</sub>.
9. Measure  $0.2\text{ cm}^3$  of formic acid using a graduated pipette and dispense it into a  $100\text{ cm}^3$  plastic bottle.

Prepare a 100 cm<sup>3</sup> aqueous solution using **0.5 mol L<sup>-1</sup> aqueous sodium chloride solution prepared in Step 5.** Hereafter, this solution is referred to as Solution C.

#### B. Preparing the pH meter and constructing a calibration curve for $h$

The pH meter must be calibrated each time as the zero point and span shift every time the power is turned on. It should also be noted that the value displayed on the pH meter ( $h$  value) is different from the defined pH value in a strict sense, so it needs to be converted into the defined pH value by constructing a calibration curve.

1. Calibrate the pH meter according to “How to use the pH meter.” [\(page 29 of this document\)](#)
2. Wash plastic beakers thoroughly with ion-exchanged water and transfer Solutions B<sub>1</sub> to B<sub>4</sub> into each beaker after pre-washing with the respective solutions. Clearly label the plastic beakers to indicate the type of solution contained.
3. Measure the  $h$  value and the temperature of each solution, starting from B<sub>4</sub> and then B<sub>3</sub>, B<sub>2</sub>, and B<sub>1</sub>. Before each measurement, thoroughly wash the sensing part with ion-exchanged water, wipe off water, and rinse with the sample solution.
4. Draw a graph on a piece of graph paper with the obtained  $h$  values on the x axis and  $-\log_{10}([H^+]/\text{mol L}^{-1})$  of each solution on the y axis. As hydrochloric acid is completely ionized, the concentration of hydrogen ions can be determined from the molar concentration of each solution. If measurements are done properly, a straight line with a slope of 1 should be obtained. If the calibration curve significantly deviates from the straight line, redo the operations in 3. Be sure to predetermine the slope and the intercept of the straight line using the least squares method.
5. Wash the sensing part thoroughly with ion-exchanged water and wipe off water.

#### C. Measuring a titration curve

With this measurement, we will obtain a titration curve, as shown in Figure 1. As the range indicated by the double-headed arrow in Fig. 1 (approximately 0.1 to 0.9 of the volume required until the equivalence point is reached) will be used for the calculation of  $K_a$ , the volume of the titrant to be added should be adjusted so that there are at least 10 points (approximately) in this region that can be used for calculation. In addition, the measurement should be continued beyond the equivalence point, so that the overall shape can be visualized.

1. Measure 40 cm<sup>3</sup> of Solution C using a volumetric pipette and dispense it into a dry plastic beaker.
2. Rinse the sensing part with Solution C and then dip it in the plastic beaker.
3. Start adding Solution A to the plastic beaker from the burette in small drops, measuring each time the  $h$  value and the temperature of the solution. The amount of each drop can be estimated as follows: 1 cm<sup>3</sup> until around  $h = 4$ , 0.5 cm<sup>3</sup> in the range of  $h = 4 \sim 4.5$ , 0.2 cm<sup>3</sup> in the range of  $h = 4.5 \sim 4.8$ , and 1 drop thereafter until the equivalence point is reached. After passing the equivalence point, the amount of each drop should be increased, in reverse, from 1 drop  $\rightarrow$  0.2 cm<sup>3</sup>  $\rightarrow$  0.5 cm<sup>3</sup>  $\rightarrow$  1 cm<sup>3</sup>. Once approximately 4 cm<sup>3</sup> of titrant has been added, you may add approximately half the volume of Solution A that has been added to the solution

up to that point, divided into several portions. While performing the measurement, simultaneously plot a graph on a piece of graph paper, as shown in Fig. 1, and make sure that the measurement is performed properly.

4. Ask your instructor or TA to check your data, and if they are OK, start cleaning up.
5. The burette should be washed well, and the stopcock should be removed.
6. Wash the sensing part of the pH meter thoroughly with ion-exchanged water, and attach the cap containing saturated potassium chloride solution to the tip. Put the cap on the filling hole for the internal solution, and turn the power off.
7. If you have time, follow procedures in “Data analysis” to calculate each value.

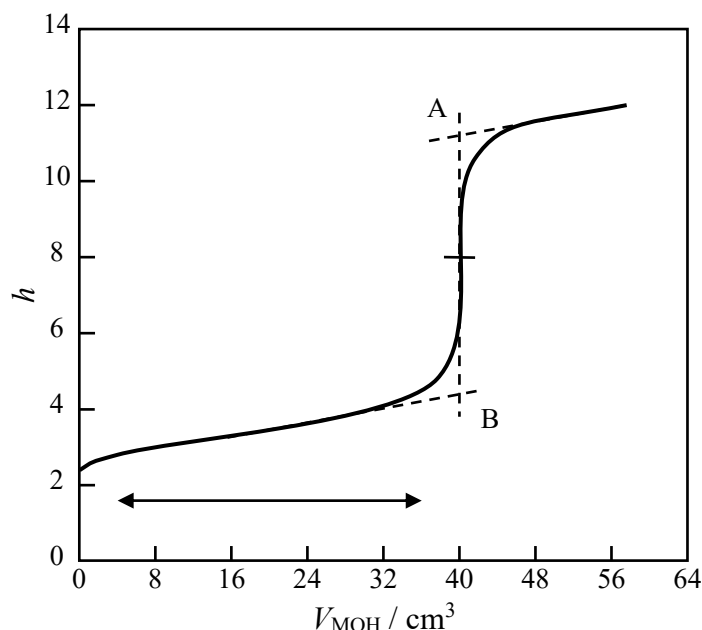


Fig. 1 Titration curve and how to determine the equivalence point.  
(schematic diagram, measurement points are omitted)

### [Data analysis]

#### A. Molar concentration of formic acid in Solution C

1. As shown in Fig. 1, extrapolate the (almost) flat portion of the curve around the equivalence point and determine points A and B at which the extrapolated line intersects with tangent lines drawn at points that appear to be inflection points.
2. The x-axis coordinate at the midpoint of line AB is defined by  $V_{\text{MOH}}$  at the equivalence point.

#### B. Determining dissociation constant $K_a$ of formic acid

1. Select approximately 10 measurement points from the first half of the titration curve (the range indicated by the double-headed arrow in Fig. 1). If any of the measured  $h$  values deviates from the smooth curve, either avoid the outlier or connect all points with a smooth curve and read the y-axis coordinates on the curved line.

2. Using the  $h$  calibration curve, determine  $[H^+]$  from the measured  $h$  values at each point.
3. Using Equation (11) and  $K_W = 1.0 \times 10^{-14} \text{ mol}^2 \text{ L}^{-2}$ , calculate  $\alpha$  and  $\beta$  for each point and determine the slope of the straight line plotted with  $-\alpha$  on the x axis and  $\beta$  on the y axis, i.e.,  $K_a$ , by the least squares method. At this time, set the intercept of the straight line to 0 (zero). As these calculations will be complicated, we suggest using Excel.

### [How to use the pH meter]

1. Record the following items in your notebook and reflect them in your report: the temperature of the sample solution at the time of measurement; the manufacturer, name, and product number of the pH meter; the form and type of electrode; and the name, manufacturer, lot number, date of manufacture, quality, and standard of the pH meter used for calibration.
2. Remove the cap of the internal solution filling hole of the glass electrode and turn on the pH meter. Do not turn off the power until all experiments are finished.
3. Make sure that the height of the electrode stopper is appropriate (the tip of the glass electrode should not touch the bottom of the beaker).
4. Write down the type of pH buffer on the plastic beaker and wash the beaker with ion-exchanged water. After pre-washing three times with the pH buffer to be added, add a sufficient amount of the pH buffer into the plastic beaker, enough to completely immerse the electrode liquid junction.
5. Follow the steps below to perform zero point calibration.
  - A1. Using a wash bottle, spray ion-exchanged water over a large beaker to wash the sensing part (the tip of the glass electrode) from all sides; repeat this a few times. Blot the electrode dry with Kimwipe (do not rub) to remove excess water droplets. You do not have to completely wipe the droplets off.
  - A2. Rinse the sensing part with a small amount of neutral phosphate buffer solution pH 7.00 in the plastic beaker by pouring it over a large beaker.
  - A3. Immerse the sensing part and a thermometer in the plastic beaker containing the neutral phosphate buffer solution, and shake the beaker gently two to three times. At this time, make sure that no bubbles are attached to the electrode (especially the liquid junction part). In addition, be careful not to bump the electrode against the plastic beaker.
  - A4. Measure the temperature of the neutral phosphate buffer solution. If the instrument has a temperature compensation dial, set the value of the scale to the temperature of the buffer solution.
  - A5. Turn the zero adjustment dial so that the displayed value is the pH value corresponding to the temperature of the neutral phosphate buffer solution (Table 6). Values at temperatures not listed in Table 1 can be determined by smooth interpolation.
6. Follow the steps below to perform span calibration.
  - B1. Wash the sensing part thoroughly with ion-exchanged water, and wipe off water.
  - B2. Rinse the sensing part with a small amount of phthalate buffer solution pH 4.00 by pouring it from a plastic beaker.
  - B3. Immerse the sensing part and a thermometer in the plastic beaker containing the phthalate buffer solution and shake the beaker gently two to three times.
  - B4. Measure the temperature of the phthalate buffer solution. If the instrument has a temperature compensation dial, set the value of the scale to the temperature of the buffer solution.
  - B5. Turn the span adjustment dial so that the displayed value is the pH value corresponding to the temperature of the phthalate buffer solution (Table 6). Values at temperatures not listed in Table 1 can



be determined by smooth interpolation.

7. Going back to step 5 again, perform zero point calibration and span calibration one after the other, and if the displayed value obtained at the stage of span calibration while the electrode is immersed in the solution is within  $\pm 0.01$  of the pH value corresponding to the temperature of the phthalate buffer solution, you may consider the calibration to be completed. The operations of zero point calibration and span calibration should be completed after repeating the calibrations twice or so, but if not, it is highly likely that the operations are inappropriate or the pH meter is out of order; please notify your instructor or TA.
8. Wash the sensing part repeatedly with ion-exchanged water, and after wiping off water, move to the next step.

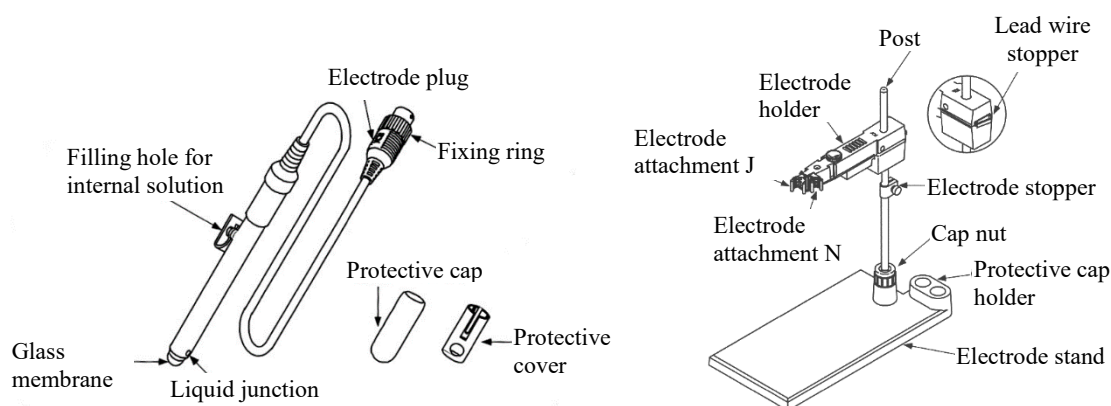


Fig. 2 Typical pH meter electrode and its stand.

#### [Notes]

1. Saturated aqueous sodium hydroxide solution severely affects the skin and will cause blindness if it gets into the eyes. Please handle with great caution.
2. The tip of the glass electrode is fragile and may easily break when hit by something. Take extra care when handling.

Table 6 pH values of JIS standard pH buffer solutions at ~~each~~-various temperatures\*

Standard number	K0018		K0019		K0020		K0023		K0021		K0022
	Oxalate		Phthalate		Neutral phosphate		Phosphate		Borate		Carbonate
Temperature /°C	First class	Second class	First class	Second class	First class	Second class	First class	Second class	First class	Second class	Second class
0	1.666	1.67	4.003	4.00	6.984	6.98	7.534	7.53	9.464	9.46	10.32
5	1.668	1.67	3.999	4.00	6.951	6.95	7.500	7.50	9.395	9.40	10.24
10	1.670	1.67	3.998	4.00	6.923	6.92	7.472	7.47	9.332	9.33	10.18
15	1.672	1.67	3.999	4.00	6.900	6.90	7.448	7.45	9.276	9.28	10.12
20	1.675	1.68	4.002	4.00	6.881	6.88	7.429	7.43	9.225	9.22	10.06
25	1.679	1.68	4.008	4.01	6.865	6.86	7.413	7.41	9.180	9.18	10.01
30	1.683	1.68	4.015	4.02	6.853	6.85	7.400	7.40	9.139	9.14	9.97
35	1.688	1.69	4.024	4.02	6.844	6.84	7.389	7.39	9.102	9.10	9.92
38	1.691	1.69	4.030	4.03	6.840	6.84	7.384	7.38	9.081	9.08	—
40	1.694	1.69	4.035	4.04	6.838	6.84	7.380	7.38	9.068	9.07	9.89
45	1.700	1.70	4.047	4.05	6.834	6.83	7.373	7.37	9.038	9.04	9.86
50	1.707	1.71	4.060	4.06	6.833	6.83	7.367	7.37	9.011	9.01	9.83
55	1.715	1.72	4.075	4.08	6.834	6.83	—	—	8.985	8.98	—
60	1.723	1.72	4.091	4.09	6.836	6.84	—	—	8.962	8.96	—
70	1.743	1.74	4.126	4.13	6.845	6.84	—	—	8.921	8.92	—
80	1.766	1.77	4.164	4.16	6.859	6.86	—	—	8.855	8.88	—
90	1.792	1.79	4.205	4.20	6.877	6.88	—	—	8.850	8.85	—
95	1.806	1.81	4.227	4.23	6.886	6.89	—	—	8.833	8.83	—

\*Values specified by the JIS standard are pH values at 25 °C; pH values at other temperatures are listed in the specification as “Reference” values.

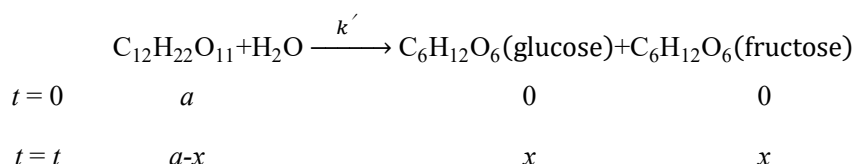
### III-5 Reaction rate of ~~hydrolysis of~~ sucrose hydrolysis

#### [Purpose]

You will measure the reaction rate for the hydrolysis of sucrose in the presence of hydrochloric acid (HCl) and determine the rate constant. The activation energy of the reaction will also be determined from the change in rate constant with temperature.

#### [Principle]

When the amount of water in a reaction system is large, the concentration of an aqueous solution of sucrose can be regarded as being unchanged after the reaction. Therefore, the hydrolysis of sucrose in an aqueous solution can be treated as a pseudo-first-order reaction. Now, assume the concentrations of each chemical species at times  $t = 0$  and  $t = t$  are as follows.



Assuming that  $k'[H_2O] = k$ , the rate of generation of glucose is given by

$$\frac{dx}{dt} = k(a - x) \quad (1)$$

By integrating Eq. (1), we obtain

$$\ln(a - x) = -kt + C_1 \quad (C_1 = \ln a) \quad (2)$$

Therefore, the rate constant  $k$  can be determined by tracing the change in  $x$  with time.

Sucrose is dextrorotatory (+), whereas the product of sucrose hydrolysis (a mixture of glucose and fructose) is levorotatory (-). The change in the angle of optical rotation ( $\alpha$ ) is proportional to the progress of the reaction and  $\alpha$  has an additivity. Therefore, the terms for sucrose concentration in Eq. (2) can be replaced by the changes in  $\alpha$ . Namely, by denoting  $a = |\alpha_0 - \alpha_e|$  and  $a - x = |\alpha_t - \alpha_e|$ , Eq. (2) can be rewritten as

$$\ln|\alpha_t - \alpha_e| = -kt + C_2 \quad (C_2 = \ln|\alpha_0 - \alpha_e|) \quad (3)$$

Here, the subscripts 0,  $t$ , and e indicate the start of the reaction, the time, and the equilibrium state, respectively. Therefore,  $k$  can be determined from the slope of the straight line obtained by measuring the time course of the angle of optical rotation ( $\alpha_t$ ) and plotting  $\ln |\alpha_t - \alpha_e|$  against  $t$ .

## [Laboratory apparatus, instruments, and reagents]

Contents of container			
Beaker (100 mL) ビーカー	2	Measuring cylinder (20 mL) メスシリンダー	1
Stoppered Erlenmeyer flask (100 mL) 共栓三角フラスコ	4	<del>Weights (O-shape)</del> <del>おもり</del> <del>Measuring cylinder (250 mL)</del> <del>メスシリンダー</del>	<del>4</del> <del>+</del>
Stoppered Erlenmeyer flask (300 mL) 共栓三角フラスコ	2	Plastic bottle (500 mL, acid waste) ポリビン	1
Komagome pipette (10 mL) 駒込ピペット	2	Rubber dropper スポイトゴム	2
Measuring spoon 薬さじ	1	Glass rod ガラス棒	1
Polarimeter cell 旋光計セル	2	Thermometer 温度計	1
<del>Weights (O-shape)</del> <del>おもり</del>	<del>4</del>	<del>Vinyl tubing</del> <del>ビニール管</del>	<del>+</del>
Stopwatch ストップ・ウォッチ	2	<u>Vinyl tubing</u> <u>ビニール管</u>	<u>1</u>

On the laboratory bench			
Polarimeter 旋光計	1	Thermostated water bath 恒温槽	1
Plastic wash bottle (500 mL, benchtop) ポリ洗びん	1		

## [Experimental procedures]

1. Set the temperature of the thermostat to 30, 35, 40, or 45°C (refer to Note 1).
2. Prepare a 1.5 mol dm<sup>-3</sup> HCl aqueous solution, and store it in a 300 cm<sup>3</sup> stoppered Erlenmeyer flask (this solution will be used for both days). The specific gravity of the common (highly concentrated) HCl solution is  $d = 1.19$ .
3. Dissolve 20 g of sucrose in a sufficient amount of water to make a 100 cm<sup>3</sup> sucrose aqueous solution (turbid solution should be filtered). Store it in a 300 cm<sup>3</sup> stoppered Erlenmeyer flask.
4. Pour ion-exchange water into the cells and measure its angle of optical rotation, adjust the polarimeter to the zero-point (refer to Notes 2, 3).
5. Divide 10 cm<sup>3</sup> of HCl and sucrose aqueous solutions in 100 cm<sup>3</sup> stoppered Erlenmeyer flasks, respectively.
6. Pour the sucrose aqueous solution with the equivalent volume of water in the cell, and measure the angle of optical rotation. The angle of optical rotation should be assumed as  $\alpha_0$ , because the reaction will not proceed without HCl.
7. Re-rinse the polarimeter cells with water. After attaching an optical window, place the cells in the thermostat. Take care not to allow the water (in the thermostat) to be included in the cells.
8. Quickly mix the sucrose aqueous solution with the equivalent volume of the HCl aqueous solution, pour the mixed solutions into the heated cells. Measure the initial angle of optical rotation of the mixed solution ( $\alpha_i$ ).

After measuring, immediately place the cells back in the thermostat. Assume the time of mixing the solutions to be  $t = 0$ , and measure the time course of the angle of optical rotation.

9. The interval between measurements should be varied because the amount of change in  $\alpha_t$  depends on the temperature and reaction time. In the measurements immediately after the start of reaction, the interval should be 1–1.5 min for higher temperatures and 2–3 min for lower temperatures. In the later measurements, adjust the time interval appropriately at your own discretion.
10. Determine the value of  $\alpha_t$  when it becomes constant, which should be regarded as the angle of optical rotation at equilibrium ( $\alpha_e$ ) (refer to Note 4).
11. Plot  $\ln |\alpha_t - \alpha_e|$  against  $t$  in the extent of reaction of 0–90% using the measured values.
12. Repeat steps 5–10 to determine the change in  $k$  with temperature and calculate the activation energy.

### [How to use polarimeter]

Fig. 3 shows a schematic of a polarimeter. Light from the light source S is guided into a Nicol prism (polarizer, P) and the resulting polarized light passes through another Nicol prism (analyzer, A). When the directions of polarization through P and A are perpendicular to each other, the light does not reach the eyepiece lens  $L_2$ . When the directions are parallel, the maximum amount of light reaches  $L_2$ .

When an optically active sample is placed in the section between P and A (denoted as C), the light reaches  $L_2$  even if the directions of polarization through P and A are perpendicular. In this case, the angle of optical rotation of the sample can be measured by rotating A until the field of view becomes dark.

However, it is difficult to determine the direction of A when the field of view becomes dark. Therefore, an auxiliary prism N is inserted between P and C so that two sources of light, i.e., one passing through P alone and the other passing through both P and N, reach C and A. When N is only slightly tilted with respect to P, rotating A to have the same angle with respect to both N and P makes the light from both sources equal and achieves a uniform brightness over the field of view (Fig. 3, ii). Rotating A from this direction clockwise or counterclockwise generates a difference in brightness over the field of view. When the direction of A becomes perpendicular to that of N or P, half the field of view becomes dark (Fig. 3, i or iii).

The angle of optical rotation can be determined as follows. Put an optically inactive substance (distilled water in this experiment) into the cell and set the scale plate D so that it indicates zero under the conditions shown in Fig. 3 (ii). Next, put a sample into the cell and read the value on the polarimeter when the brightness of the left part of the field of view is equal to that of the right part. This value indicates the angle of optical rotation and is proportional to the distance the light traveled when passing through the sample solution. The angle of optical rotation per 10 cm of distance traveled is generally defined as the specific angle of optical rotation.

### [Notes]

1. Experiments in 40, 45°C will be conducted on the first day and for 30, 35°C on the second day. Two thermostats set to different temperatures will be shared with the other group. Experiments for both temperatures will be done in tandem.
2. The operation of polarimeters differs according to their model type. Read the manual on the laboratory bench

before operation. If you have any questions, do not operate the polarimeter but ask the staff member for clarification.

3. Some polarimeters have an offset function. In that case, press the ZERO SET button after measuring the angle of optical rotation of the ion-exchange water (Fig. 3, ii).
4. Ask the staff member to check whether the reaction has reached equilibrium. Do not determine this by yourself.
5. When pouring the sample solution into the cell, take care not to allow air bubbles to be included in the cell. Also, in order to prevent scattering of light during measuring with the polarimeter, thoroughly wipe any water soaked in the optical window at both ends of the polarimeter.
6. The lamp of the polarimeter requires about 5-10 min to stabilize after it is turned on. Polarimeters that have an LED lamp will automatically turn off if no operation is made for more than 5 min, so press the shift – temperature button while measuring.
7. Pay constant attention to keep the temperature of the sample solution constant. The temperature of the sample solution is not always equivalent to the temperature of the thermostat. Always insert the thermometer directly to the sample solution.
8. Ensure that the temperature of the thermostat constantly keeps the preset value.

#### [Checklist]

1. Do you understand how to calculate and analyze the rate constant for first-order reactions from the change in measured concentration with time?
2. Do you understand how to calculate and analyze the activation energy from the change in calculated rate constant with temperature?
3. What is a pseudo-first-order reaction? Why should sucrose hydrolysis be treated as such a reaction?
4. Is it possible to calculate the rate constant for  $n$ th-order reactions from the change in concentration with time?
5. What roles does HCl play in this experiment?

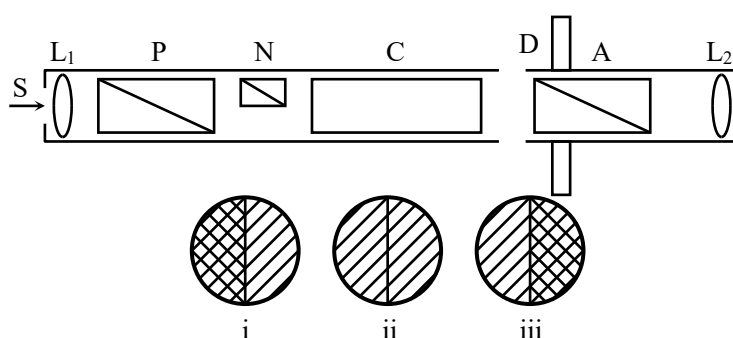


Fig. 3 Schematic diagram of polarimeter.

### III-6 Adsorption of acetic acid on activated carbon

#### [Purpose]

You will measure the amount of acetic acid adsorbed on activated carbon in an aqueous solution and examine the applicability of the Freundlich adsorption isotherm.

#### [Principle]

Porous materials such as activated carbon have a large surface area and are used as adsorbents. Adsorption with respect to a solid adsorbent is related to the temperature and concentration of an adsorbate, and several adsorption isotherms have been theoretically and empirically proposed. The adsorption isotherm empirically derived by Freundlich is most common and is given by Eq. (1) in a concentration range when adsorption reaches equilibrium.

$$\frac{x}{m} = kC^n \quad (1)$$

Here,  $m$  is the mass of the adsorbent,  $x$  is the mass of the adsorbate,  $C$  is the concentration of the adsorbate in solution, and  $n$  is a positive constant.

The constants  $k$  and  $n$  can be determined by measuring the amount of adsorbate on the adsorbent (amount of adsorption) while varying the concentration of the solution. In addition, an isotherm for monomolecular adsorption theoretically derived by Langmuir is given by

$$\frac{x}{m} = \frac{\alpha C}{1 + \beta C} \quad (2)$$

Here,  $\alpha$  and  $\beta$  are the constants and can also be determined by measuring the amount of adsorption while varying the concentration. When  $C$  is sufficiently large, Eq. (2) can be simplified as

$$\frac{x}{m} = \frac{\alpha}{\beta} \quad (3)$$

which indicates that the amount of adsorption is constant regardless of the concentration. When  $C$  is sufficiently small, Eq. (2) can be simplified as

$$\frac{x}{m} = \alpha C \quad (4)$$

which indicates that the amount of adsorption is proportional to the concentration. However, only a limited number of liquid-phase adsorption systems follow the Langmuir adsorption isotherm, and many systems deviate considerably from the isotherm.

## [Laboratory apparatus, instruments, and reagents]

Contents of container			
Erlenmeyer flask (200 mL) 三角フラスコ	8	Weights (O-shape) おもり	8
Stoppered Erlenmeyer flask (300 mL) 共栓三角フラスコ	4	Rubber stopper ゴム栓	8
Conical beaker (100 mL) コニカルビーカー	2	Plastic bottle (500 mL, for NaOH) ポリビン	2
Volumetric flask (100 mL) メスフラスコ	1	Small funnel ロート (小)	2
Volumetric pipette (5, 10, 50 mL) ホールピペット	2,1,1	Pipette bulb and pipette pump (scroll type) ピペッター (ダイヤル式, ゴム製)	1 set
Measuring spoon 薬さじ	1	Glass rod ガラス棒	1
Büchner funnel ブフナーロート	1	Büchner flask 吸引ビン	1
Filter paper ろ紙	1	Petri dish シャーレ	1
Litmus paper (red, blue) リトマス紙	1 set		

On the laboratory bench			
Burette (25 mL) ビュレット	2	Aspirator アスピレーター	1
Water bath 恒温槽	1	Desiccator デシケーター	1
Plastic wash bottle (500 mL, benchtop) ポリ洗びん	1		

## [Experimental procedures]

- Set the temperature of the thermostat to be 30 or 40°C. (The thermostat should have already been turned on; confirm the preset temperature.)
- Accurately prepare about 0.025 mol dm<sup>-3</sup> aqueous solution of oxalic acid.
- Standardize the concentration of the about approximately 0.1 and 0.01 mol dm<sup>-3</sup> aqueous solutions of NaOH (already prepared by the previous experimenter) using the oxalic acid aqueous solution prepared in step 2.
- Thoroughly rinse about 26 g activated carbon with ion-exchange water during suction filtration. If the rinsing solution is alkaline, neutralize the activated carbon using dilute HCl and rinse the activated carbon with water until no HCl is detected. Then place the activated carbon into a Petri dish and dry it in a drier (for 2–3 h).
- Prepare about 300 cm<sup>3</sup> aqueous solutions of acetic acid with concentrations of 0.4, 0.3, 0.2, and 0.1 mol dm<sup>-3</sup> and store them in stoppered Erlenmeyer flasks. The specific gravity of acetic acid is  $d_4^{20} = 1.04922$ .
- Accurately transfer each 100 cm<sup>3</sup> of the aqueous solutions of acetic acid prepared in step 5 into two Erlenmeyer flasks using a volumetric pipette and seal them with rubber stoppers. You should have two



solutions with four different concentrations, that is, a total of eight solutions.

7. Standardize the concentrations of the four acetic acid solutions prepared in step 5 (that remained in step 6) using the NaOH solutions.
8. Cool the dried activated carbon in a desiccator containing silica gel.
9. After cooling, accurately measure 3 g of activated carbon, and put that quantity into each of the eight solutions prepared in step 6, seal the flasks, place each set of four flasks with different concentrations in two thermostats at different temperatures (four solutions with different concentrations at 30 °C; other four solutions at 40 °C), and allow them to stand overnight. Place a weight on each flask to hold the stopper in place. (Share the two thermostats with an adjacent group that has a thermostat with a preset temperature different from yours.)
10. Using a volumetric pipette, accurately withdraw the supernatant from the solution left to stand overnight and measure the concentration of acetic acid in the supernatant.
11. Prepare about 0.1 and 0.01 mol dm<sup>-3</sup> NaOH solutions for the next experimenter.
12. The amount of adsorbate on 1 g of the adsorbent,  $x_n$  (mol g<sup>-1</sup>), is given by  $x_n = x/m = V(C_b - C_a)/1000m$ , where  $m$  (g) is the mass of the activated carbon,  $V$  (cm<sup>3</sup>) is the volume of the acetic acid aqueous solution, and  $C_b$  and  $C_a$  (mol dm<sup>-3</sup>) are the concentrations of the solutions before and after adsorption, respectively.
13. Plot  $\log x_n$  against  $\log C_a$  and determine  $k$  and  $n$  using Eq. (1).
14. Plot  $1/x_n$  against  $1/C_a$  and determine the amount of adsorption at saturation  $x_s = \alpha/\beta$  using Eq. (2).

#### [Notes]

1. Phenolphthalein will be provided by your instructor. Be sure to return it after use.
2. Take great care when neutralizing and drying the activated carbon. In particular, shake the Petri dish containing the activated carbon occasionally during drying to completely dry it.
3. Dispose of the activated carbon after use into the container for the used activated carbon located in the hood.

#### [Checklist]

1. To what range of concentrations can Freundlich's empirical equation be applied?
2. What is the effect of temperature on adsorption?
3. Under what conditions does the Langmuir adsorption isotherm hold?
4. What does the amount of adsorption at saturation mean?

# Report Submission Checklist Materials and Life Sciences Lab. C 2019

ID number	Name

Laboratory session	Start and end dates	Check for completion Day 1	Check for completion Day 2	Report submission date	Report receipt
III-1 Synthesis of 4-nitroaniline	~				
III-2 Synthesis of methyl orange	~				
III-3 Polymer synthesis and viscosity measurement	~				
III-4 Dissociation constant (acidity constant) of formic acid	~				
III-5 Rate of hydrolysis of sucrose	~				
III-6 Adsorption of acetic acid on activated carbon	~				

Publisher	Department of Materials and Life Science, Faculty of Science and Technology, Sophia University
Publication date	27 Sep. 2019

ID number \_\_\_\_\_ Name \_\_\_\_\_