THE BUNSEN REACTION IN THE PRESENCE OF ORGANIC SOLVENT IN H₂S SPLITTING CYCLE

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By

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ABSTRACT

This research project is a part of our endeavor to developing a new hydrogen sulfide (H_2S) splitting cycle for hydrogen production. In view of that the Bunsen reaction is the key step for the overall efficiency, the objective of this research is to develop an effective and efficient process to carry out the Bunsen reaction in the presence of organic solvents. Organic solvents can help dissolve iodine crystal, lower the reaction temperature and reduce the corrosiveness accompanying the reaction. Through screening of the ordinary organic solvents, aromatic hydrocarbons stood out and toluene was used in this project.

In order to study the Bunsen reaction rate in the presence of toluene, the iodine solubility in HI solution was extensively explored at room temperature. Although the iodine solubility in water is small (0.3404g/L at 25℃), it was found that the iodine solubility in HI solution increases greatly as the [HI] increases. At lower [HI] (0~0.238 M), the iodine solubility is linear to [HI] with a relationship of [iodine solubility] = 0.57[HI] + 0.0030; at higher [HI] (0.238 ~7.6 M), the relationship of the iodine solubility and [HI] conforms to [iodine solubility]/[HI] = 0.190[HI] + 0.58.

In the second part, the iodine distribution behavior between HI solution and toluene phase was studied at room temperature. It was determined that the iodine distribution coefficient (D = $[I_2]_{HI\ solution}$/$[I_2]_{toluene}$) increases as the increase of [HI]. At lower [HI] (0~1.89 M), the distribution coefficient has a quadratic relationship with [HI] as D = $1.4027[HI]^2$ + 0.8638[HI] + 0.0088; at higher [HI] (1.89~7.54 M) the distribution coefficient is linear to [HI] with a relationship of D=5.5937[HI]-3.5632.

On the basis of the above work, in a semi-batch reactor, the Bunsen reaction rate in the presence of toluene was measured. In a mixture of toluene and water, iodine prefers to stay in

toluene phase. The Bunsen reaction was readily initiated by feeding SO_2 into water phase. Experimental results indicated that the rate of the Bunsen reaction in the presence of toluene is equal to the molar flow rate of feeding SO_2 when the iodine concentration is higher than a certain value. This specific value depends on the reaction conditions, such as the interface area between water and toluene phase, the dispersion efficiency and the flow rate of SO_2.

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First, I am heartily thankful to my supervisor Dr. Hui Wang, for his continuous support during last two years and especially the time when my leg was broken. It was his perseverance and enthusiasm that encourages me to finally finish this project.

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TABLE OF CONTENTS

LIST OF TABLES

LIST OF FIGURES

NOMENCLATURE

A or ABS   Absorbance of ultraviolet–visible spectrophotometer

c   Concentration of the absorbing species in materials

D   Distribution coefficient of iodine between hydroiodic acid and toluene phase,

               $[I_2]_{HI\ solution} / [I_2]_{toluene}$

ε Molar extinction coefficient, L mol^{-1} cm^{-1}

HSC   The name of the program, which is based on the fact that calculation modules automatically utilize the same extensive thermochemical database which contains enthalpy (H), entropy (S) and heat capacity (Cp) data for more than 25000 chemical compounds.

I_0 and I The intensity of incident light and that of transmitted light, respectively

l   Path length that light will go through, cm

M   Molarity, mol L^{-1}

SCCM   Volume flow rate of SO_2, Standard cubic centimeter per minute

TMFM   Thermal mass flow meter

UV-Vis   Ultraviolet-visible spectrophotometer

[ ]   Molarity, mol L^{-1}

1. INTRODUCTION

1.1 H₂S splitting cycle

In oil sands bitumen upgrading, a huge amount of hydrogen is desired to convert organic sulfur-containing compounds into hydrogen sulfide (H_2S), which is further oxidized into sulfur and water in sulfur removal and recovery units such as the Claus plant. The hydrogen used here is mainly produced by steam reforming of natural gas. This process not only consumes clean fossil fuels but also releases greenhouse gas CO_2. Furthermore, hydrogen produced by this way finally goes into water and is difficult to recycle. In view of the adverse effect as mentioned above, a novel hydrogen production by H_2S splitting cycle was proposed for the first time by Wang[1], which contains reactions (1) , (2) and (3) as follows.

H₂S splitting cycle

$$H_2S + H_2SO_4 \leftrightharpoons S + SO_2 + 2H_2O \ (120°C) \tag{1}$$

$$SO_2 + 2H_2O + I_2 \leftrightharpoons 2HI + H_2SO_4 \ (120°C) \text{ (the Bunsen Reaction)} \tag{2}$$

$$2HI \leftrightharpoons H_2 + I_2 \ (300 - 450°C) \tag{3}$$

The overall reaction is:

$$H_2S \rightarrow H_2 + S \tag{4}$$
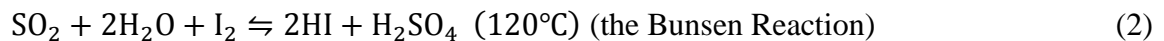
This new H_2S splitting cycle allows the conversion of H_2S into H_2 and elemental S with two working reagents I_2 and H_2SO_4 recycled. Further, if the sulfur produced by reaction (1) is continued to be oxidized into SO_2 by reaction (5), reactions (2) and (3) would occur in a double scale because two moles of SO_2 are produced. As a result, the overall reaction becomes reaction

(6) instead of (4). In this way, another new cycle called H_2S-H_2O splitting cycle was further proposed:

H_2S-H_2O splitting cycle

$$H_2S + H_2SO_4 \leftrightharpoons S + SO_2 + 2H_2O \ (120℃) \tag{1}$$

$$O_2 + S \rightarrow SO_2 \tag{5}$$

$$2SO_2 + 4H_2O + 2I_2 \leftrightharpoons 4HI + 2H_2SO_4 \ (120℃) \ (\text{the Bunsen Reaction}) \tag{2}$$

$$4HI \leftrightharpoons 2H_2 + 2I_2 \ (300-450℃) \tag{3}$$

The overall reaction is:

$$H_2S + 2H_2O + O_2 \rightarrow 2H_2 + H_2SO_4 \tag{6}$$
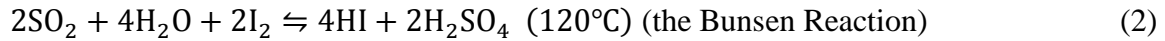
This new cycle produces two moles of hydrogen and one mole of sulfuric acid from only one mole of H_2S. Both H_2S and H_2S-H_2O splitting cycles are sustainable processes to recycle hydrogen for oil sands bitumen upgrading without CO_2 emission. The engineering objective of both cycles is to develop processes integrating all of the above reactions.

H_2S or H_2S-H_2O splitting cycle arose from two areas of research work. One area is the gas-liquid reaction system of H_2S and H_2SO_4 (reaction 1), which has been studied by Wang and Chuang[2,3,4,5,6]. The other area is the well-known thermochemical sulfur-iodine (S-I) water splitting cycle[7,8] as follows:

S-I water splitting cycle

$$H_2SO_4 \leftrightharpoons 0.5O_2 + SO_2 + H_2O \ (830-900℃) \tag{7}$$

$$SO_2 + 2H_2O + I_2 \leftrightharpoons 2HI + H_2SO_4 \ (120℃) \ (\text{the Bunsen Reaction}) \tag{2}$$

$$2HI \leftrightarrows H_2 + I_2 \ (300 - 450°C) \tag{3}$$

The overall reaction is:

$$H_2O \rightarrow H_2 + 0.5O_2. \tag{8}$$
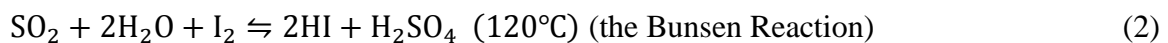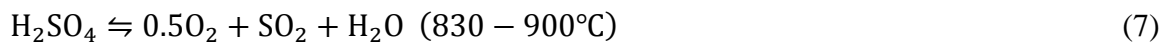
Since the only difference between S-I water splitting cycle and the H_2S splitting cycle is reactions (1) and (7), the research progresses achieved in the former area can be applied to the latter. The current research on S-I water splitting cycle indicates that the Bunsen reaction is the key reaction to determine the overall efficiency, because its products, H_2SO_4 and HI, mixture have to be purified to feed reactions (7) and (3), and this purification process is the most energy-consuming step[7,8]. This situation is the same for H_2S or H_2S-H_2O splitting cycle. Therefore, in order to optimize the H_2S or H_2S-H_2O splitting cycle, it is important to develop an effective and efficient way to carry out the Bunsen reaction. A literature review about the current routes of operating the Bunsen reaction will be introduced in Chapter 2.

1.2 Organization of this thesis

In this thesis, Chapter 1 introduces the background of the H_2S splitting cycle. Chapter 2 is a literature review on the operations of the Bunsen reaction. After the review, the knowledge gap was revealed and the research objective of this project was proposed. Chapter 3 describes the experimental procedures, which consists of analytical methods such as the determinations of the iodine solubility in HI solution, iodine distribution coefficient between HI solution and toluene, and the rate of the Bunsen reaction in a semi-batch reactor. Chapter 4 presented the results and discussions. In Chapter 5, the conclusions and future work were discussed.

2.   LITERATURE REVIEW

The Bunsen reaction has been extensively studied in the S-I water splitting cycle and is also the key step to decide the efficiency of the H_2S splitting cycle. For the introduction of the research background, a literature review is introduced in this chapter.

2.1 Survey of the Bunsen reaction routes to improve its energy efficiency

2.1.1 General Atomic stoichiometry

The operation of General Atomic stoichiometry on the Bunsen reaction was proposed by General Atomics[9] in the study of the S-I water splitting cycle. This method is operated in the liquid water media in a large excess of iodine to separate two product acids into two immiscible liquid phases: a heavy HIx phase and a light sulfuric acid phase. The heavy HIx phase is a combination of hydrogen iodide, iodine and water and the light phase is sulfuric acid shown in the following equation[10,11]:

$$SO_2 + 16H_2O + 9I_2 \rightarrow$$
$$(2HI + 10H_2O + 8I_2)_{HIx\ phase} + (H_2SO_4 + 4\,H_2O)_{Sulfuric\ acid\ phase}(120℃) \qquad (9)$$
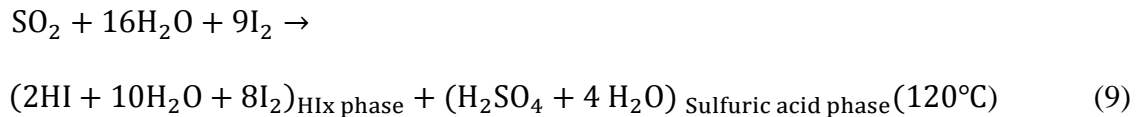
In this method, although the HI and H_2SO_4 are separated physically, the excess amount of water and iodine requires a great deal of energy to extract and recycle prior to the decomposition subunits. More specifically, sulfuric acid phase is only 57(wt) % H_2SO_4 and needs to be concentrated via a series of evaporators. The molar ratio of HI: H_2O is 1:5 in HI_X phase, which is

very close to ratio (1:5.36) of the azeotrope of HI and H_2O at atmospheric pressure. Both extractive distillation for HIx phase using H_3PO_4 [12]and reactive distillation[13] were believed to be the most expensive and energy-intensive steps. All these purification processes make the Bunsen reaction the bottleneck of the overall cycle's efficiency.

Furthermore, this method of the Bunsen reaction is operated at 120℃, which is slightly above the iodine melting point, 113.7℃ at atmospheric pressure. This not only leads to the severe corrosiveness caused by the evaporation of iodine, but also makes the following two side reactions feasible[14], which consume the formed HI and H_2SO_4.

$$H_2SO_4 + 8HI \leftrightharpoons H_2S + \ 4I_2 + 4H_2 \qquad (10)$$

$$H_2SO_4 + \ 6HI \leftrightharpoons S + 3I_2 + \ 4H_2 \qquad (11)$$

Currently, lots of relevant researches on the Bunsen reaction are devoted to reduce the usage of I_2 and H_2O and therefore decrease the energy burden caused. Recent progresses of the Bunsen reaction operations are reviewed as below.

2.1.2 The Bunsen reaction in organic solvents

The Bunsen reaction in organic solvents was first discussed by De Beni et al.[15]. Organic solvents can dissolve the reactants I_2, SO_2 and H_2O, and the product HI. Thus, HI stays in organic phase and so is separated from H_2SO_4 which stays in the water phase. For example, tributylphosphate (TBP) was selected for the Bunsen reaction due to its good solubility for SO_2. The resulting TBP and SO_2 mixture can dissolve a sufficient but smaller amount of I_2 and H_2O

5

for the Bunsen reaction. The simplified process is illustrated in Figure 2.1, where the product H_2SO_4 stayed in water phase and HI in TBP phase. Although this method reduced greatly the excess amount of iodine, the HI recovery from the organic solvent was still difficult.
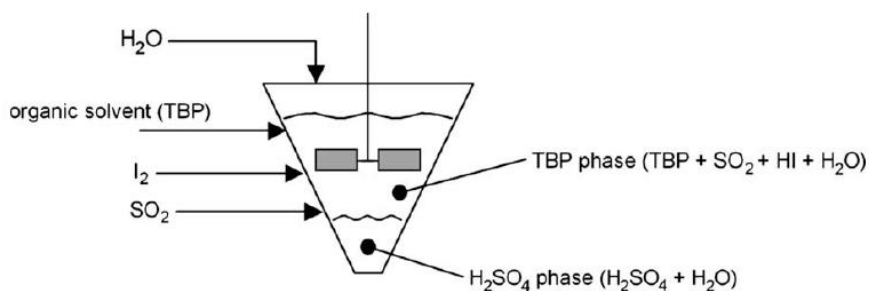
Figure 2.1 Scheme of the Bunsen reaction in TPB

2.1.3 The Bunsen reaction with a precipitating agent formation

Metathesis reactions with formation of insoluble solid salts lead to liquid-solid separation instead of original liquid-liquid separation of hydroiodic acid and sulfuric acid[16]. For example, lead sulfate was used in this method as shown in Figure 2.2. The accompanying reactions are:

$$PbSO_4(s) + 2HI(aq) \rightarrow PbI_2(s) \downarrow + H_2SO_4(aq) \ (20\text{-}120\ \text{°C}) \tag{12}$$

$$PbI_2(s) + 2HPO_3(aq) \rightarrow 2HI(g) + Pb(PO_3)_2 \ (420\text{-}450\ \text{°C}) \tag{13}$$

$$Pb(PO_3)_2 + H_2SO_4(aq) + 2H_2O \rightarrow PbSO_4(s) + 2H_3PO_4(aq) \ (20\text{-}80\ \text{°C}) \tag{14}$$
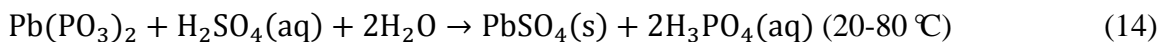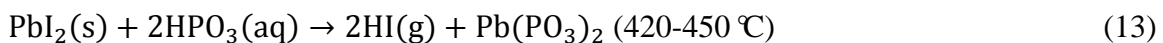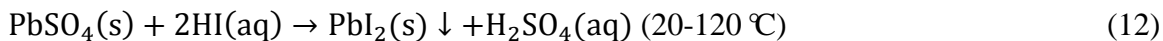
Reactions (13) and (14) regenerate $PbSO_4$ and recycle it to the process. This route drastically decreases the recirculation rate of recycling agents (water and iodine) and avoids energy-

intensive HIx processing, but it is disadvantageous to use solid material and concentrate dilute phosphoric acid.
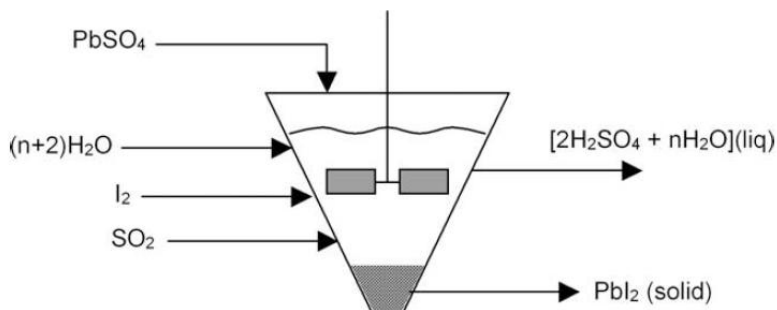
Figure 2.2 Scheme of the Bunsen reaction with insoluble lead sulfate

2.1.4 The Bunsen reaction in a electrochemical membrane reactor

The application of electrochemical membrane reactor (Figure 2.3) for the Bunsen reaction was proposed by Nomura et al.[17,18].

Anode side reaction: $SO_2 + 2H_2O \rightarrow H_2SO_4 + 2H^+ + 2e^-$ (15)

Cathode side reaction: $I_2 + 2H^+ + 2e^- \rightarrow 2HI$ (16)
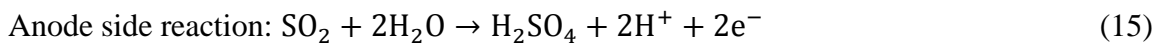
In this method, two acids are physically separated by the electrochemical membrane reactor and the excess use of iodine is avoided. But the product is diluted acids because large excess amount of water is required for the permeation of proton through the exchange membrane (Figure 2.3). Thus, more efforts are needed to improve this method.

7
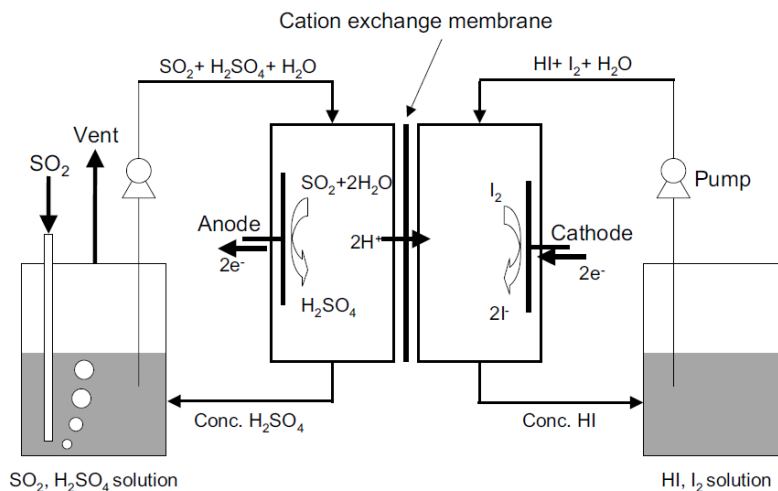
Figure 2.3 Schematic diagram of an electrochemical membrane reactor

2.2 The proposal of the Bunsen reaction in organic solvents

From the above literature review, it can be learned that one challenge in the Bunsen reaction operation is to reduce substantially the excess use of I_2 and H_2O. The other challenges are to lower the reaction temperature and facilitate the purification of HI and H_2SO_4 aqueous mixture. Wang proposed a new method of carrying out the Bunsen reaction in organic solvents[19]. The idea is to use organic solvents to dissolve the solid iodine and then add stoichiometric water into it. When SO_2 is introduced into this organic solution, the Bunsen reaction is initiated. Because only the stoichiometric amount of water was used, HI gas product (highly water-soluble) would be released directly and H_2SO_4 should stay in the reactor. This suggestion can be illustrated in Figure 2.4. Thus, the Bunsen reaction does not have to occur at 120°C for melting solid iodine and the usage of iodine and water is greatly reduced. The most important advantage of this method is that HI and H_2SO_4 can separate directly without huge energy burden. However, the validity and possible modification of this proposal needs to be explored.
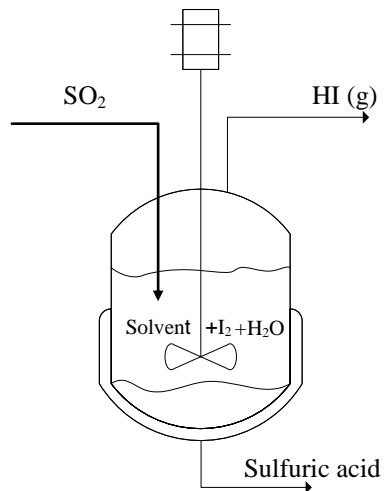
Figure 2.4 Schematic diagram of the proposal of the Bunsen reaction in organic solvents

2.3 Iodine solubility in ordinary organic solvents

The purpose of the introduction of organic solvents in the Bunsen reaction is to dissolve the solid iodine. Therefore the organic solvents which have higher solubility for iodine should be reviewed. Hildebrand and Benesi et al.[20] studied the iodine solubility in the ordinary organic solvents (Table 2.1), from which the suitable organic solvents for the Bunsen reaction will be screened out later in section 4.2.

Table 2.1 Iodine solubility in the ordinary organic solvents

Organic solvent	Iodine solubility, molar fraction, 25℃
benzene	0.0488
toluene	0.0639
o-xylene	0.0786
p-xylene	0.0760
m-xylene	0.0825
1,2,3-trimethylbenzene	0.0993
1,2,4-trimethylbenzene	0.0915
1,3,5-trimethylbenzene	0.1058
1,2,3,4-tetramethylbenzene	0.1167
ethylbenzene	0.0586
n-propylbenzene	0.0589
cumene	0.0561
n-butylbenzene	0.0548
isobutylbenzene	0.0480
tert-butylbenzene	0.0501
chlorobenzene	0.0333
bromobenzene	0.0549
n-C_6H_{14}	0.00456
n-C_7H_{16}	0.00679
CCl_4	0.0115
$CHCl_3$	0.0228
CS_2	0.0546
cyclohexane	0.0092
ethyl alcohol	0.0471
ethyl ether	0.0896

2.4 Iodine solubility in water and the solubilizing effect of HI on iodine in water

For the above proposal of the Bunsen reaction in organic solvents, the reaction mixture is a combination of an organic solvent, iodine, water, HI and H_2SO_4. Aside from the iodine will dissolve in organic solvents, will it have solubility in other species? To know about it, the following literature was reviewed.

Iodine solubility in pure water is very small (0.3404g/L at 25℃)[21]. However, the existence of iodide (I^-) and proton (H^+) will greatly increase the iodine solubility in water. One reason is that iodine crystals can dissolve rapidly in an iodide aqueous solution by forming soluble triiodide ions (I_3^-)[22]. The other reason is that polyiodine species, I_{2X}, where x=1, 2, 3, 4 etc., will be stabilized by H^+ in the solution[22]. Iodine solubility in concentrated hydroiodic acid solution (45.9-66.7wt% HI) was summarized in Table 2.2[23].

Table 2.2 Iodine solubility in concentrated hydroiodic acid

HI ,wt%	Gravity ,25℃	I_2 ,kg/L	I_2 ,kg/kg	I_2,mol/HI, mol
66.7	1.946	5.22	2.68	2.03
64	1.877	4.72	2.52	1.98
54.4	1.644	3.47	2.11	1.95
50.2	1.557	2.84	1.825	1.83
45.9	1.486	2.28	1.853	1.68

2.5 Knowledge gap

According to above literature review and the proposal of the Bunsen reaction in organic solvents, the knowledge gaps are concluded as follows:

1. Up to date, neither General Atomic stoichiometry nor other new methods are available to run the Bunsen reaction in an efficient way. One of new attempts to explore the Bunsen reaction is to run the reaction in organic solvents. However, this proposal has not been tested.

2. The suitable organic solvents for the Bunsen reaction have not been screened thoroughly.

3. The iodine solubility in less than 57wt% hydroiodic acid solution (the azeotropic mixture of HI and water) has not been investigated sufficiently.

4. The iodine distribution coefficient between HI solution and toluene has not been studied.

5. The reaction rate of the Bunsen reaction in the two phases of organic solvent and water has not been reported.

2.6 Research objectives

The goal of this project is to develop a novel process to operate the Bunsen reaction by use of organic solvent at room temperature. The research objectives can be described as follows:

1. At first, different water-insoluble organic solvents will be screened and toluene will be chosen to run the Bunsen reaction in a two-phase mixture.

2. The iodine solubility in HI solution with different concentrations in the absence and the presence of H_2SO_4 will be determined. The relationship of the iodine solubilities and the concentrations of hydroiodic acid solution will be investigated.

3. The distribution coefficient of iodine between HI solution and toluene will be determined.

4. The rate of the Bunsen reaction in the two-phase mixture of the HI solution and toluene will be determined in a semi-batch reactor.

3. EXPERIMENTAL

3.1 Chemicals and instruments

All chemicals used for experiments are ACS grade and used without further purification as received: iodine (Acros Organics), sodium hydroxide (EMD), sodium thiosulfate anhydrous (Fisher), potassium iodide (BDH), and toluene (BDH). All solutions were prepared with deionized water.

The UV-Vis absorption spectroscopy was determined using UV mini 1240 UV-Vis spectrophotometer from Shimadzu and Mandel 10mm path length quartz cuvettes.

3.2 Analytical methods

Toluene is chosen for the Bunsen reaction in this work according to the screening results over organic solvents.

For the Bunsen reaction in the presence of toluene, a set of corresponding analytical methods should be chosen and established. In this thesis, the protons concentration in water phase was determined by acid-base titration method; the iodine concentration in toluene phase was determined by iodometry method; the iodine in toluene phase and the iodide ions in the water phase were determined by UV-Vis spectrometry (see details in Appendix D).

NMR was used to see if there is reaction between toluene and iodine (Appendix C)

3.3 The semi-batch reactor for the Bunsen reaction

The semi-batch reactor used for the Bunsen reaction is shown as Figure 3.1. The reactor is a three-necked Pyrex flask (9), which is connected with the SO_2 feeding system and a condenser for gas escape. Iodine was dissolved in the solvents in the reactor. The SO_2 was introduced evenly into the aqueous phase through a gas dispersion tube (8) and the flow rate of SO_2 was controlled by the thermal mass flow meter (5). For the benefit of mass balance, washing bottle (11-a) filled with toluene was used to trap iodine vapor. Methyl orange was added into the water in washing bottle (11-b) to detect the escape of SO_2.
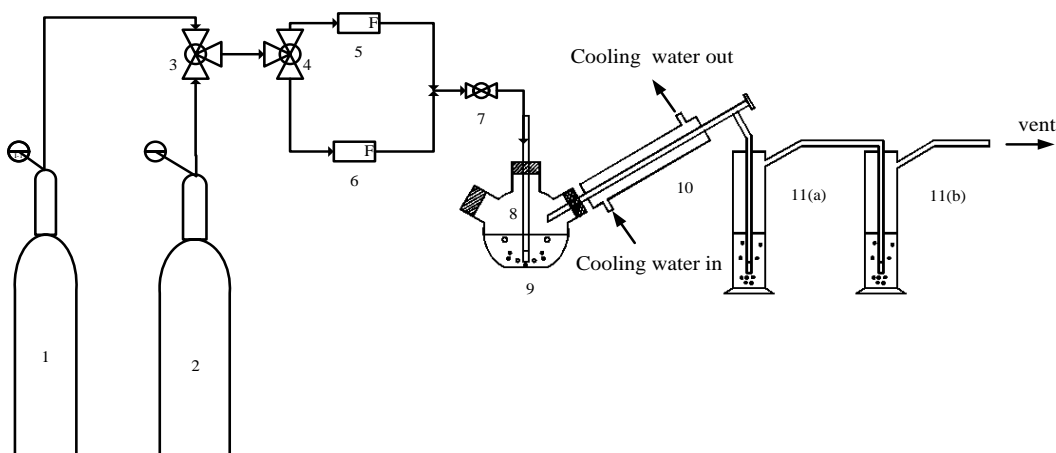
Figure 3.1 Schematic diagram of the semi-batch experimental setup for the Bunsen reaction: (1) SO_2 cylinder; (2) N_2 cylinder; (3), (4) three way plug valve; (5) thermal mass flow meter for SO_2; (6) thermal mass flow meter for N_2; (7) ball valve; (8) gas dispersion tube; (9) reactor; (10) condenser; (11-a) washing bottle filled with toluene; (11-b) washing bottle with methyl orange water solution

3.4 Determination of iodine solubility in hydroiodic acid (HI) solution

The HI solutions with different concentrations ranged from 0 M to 7.6 M were saturated with iodine. For the resulting iodine saturated hydroiodic acid solutions, the iodine concentrations were determined by iodometry method and the proton concentrations were titrated with NaOH solution.

In order to evaluate the effect of H_2SO_4 on the iodine solubility in the hydroiodic acid solution, 5 mL of 0.943 M H_2SO_4 solution was added to 5 mL of 1.9 M hydroiodic acid. Then the HI-H_2SO_4 solutions with different concentrations were prepared by half serial dilution. The iodine solubilities in HI solutions and HI-H_2SO_4 solutions were compared to demonstrate if H_2SO_4 has influence on the iodine solubility in HI solution.

All the experiments were operated at room temperature (23℃ -24℃) unless indicated.

3.5 Determination of the distribution coefficient of iodine between hydroiodic acid (HI) solution and toluene

In order to determine the distribution coefficient of iodine between HI solution and toluene, 5 mL of iodine toluene solution (0.458 M) was mixed with 5 mL of HI solution at different concentrations (0~7.6 M). After mixed thoroughly, the toluene phase and the water phase separated in a separatory funnel. The concentrations of iodine and proton in the water phase were titrated with sodium thiosulfate and sodium hydroxide respectively; the iodine concentration in toluene phase was determined by a UV-Vis spectrometer at 497nm according to Beer-Lambert law (A = εlc). The molar extinction coefficient of iodine in toluene is 1.02×10^3 L mol^{-1} cm^{-1} as reported by Benesi and Hildebrand[24]. The iodine distribution coefficient (D) was

equal to the ratio of the iodine concentration in the HI solution to the iodine concentration in the toluene (Equation 17).

$$D = [I_2]_{\text{HI solution}}/[I_2]_{\text{toluene}} \tag{17}$$

Because the Bunsen reaction product mixture consists of H_2SO_4 and HI, it is necessary to determine if H_2SO_4 affects the iodine distribution coefficient. 5 mL of the mixture of HI solution (0.375 M) and H_2SO_4 solution (0.189 M) was mixed with 5 mL of iodine toluene solution (0.466 M). Then the iodine distribution coefficient was determined as above (Equation 17).

In order to study the influence of volume ratio between toluene phase and HI solution on the distribution coefficient, 5 mL of HI solution (0.506 M) was mixed with 5, 25, 50, 100 mL of 0.257 M iodine toluene solution. Then the iodine distribution coefficient for each of the resulting two-phase mixtures was determined as above (Equation 17).

All above experiments were operated at room temperature (23°C -24°C) unless indicated.

3.6 The rate measurement of the Bunsen reaction in the semi-batch reactor

The semi-batch reactor as illustrated in Figure 3.1 was used to study the rate of the Bunsen reaction. After the reaction was initiated by feeding SO_2 gas, the reaction mixture was sampled by pipette at certain time intervals. The iodine and proton concentrations in toluene phase and water phase were determined as section 3.4. Then the rate of the Bunsen reaction was measured according to the change of the remaining amount of iodine over reaction time.

4. RESULTS AND DISCUSSIONS

4.1 The investigation of the Bunsen reaction in the presence of organic solvents

At first, the idea of the Bunsen reaction in organic solvents was studied in a semi-batch reactor as illustrated in Figure 3.1. Toluene was chosen as the organic solvent. Three reactions were run with varied amount of water for 7 hours. The conditions and results were summarized in Table 4.1. In the Run 1, without water added, 2.3% loss of iodine may be due to the iodine evaporation in nitrogen flow. However, in Run 2, 63.2% conversion of iodine was observed with 30 mL of water used, indicating that the Bunsen reaction can occur readily in the mixture of toluene and excess water. In Run 3, stoichiometric amount of water was used. Only 2.3% loss of iodine was observed. This suggested that the occurrence of the Bunsen reaction is difficult with stoichiometric water in the presence of toluene.

Table 4.1The Bunsen reactions in toluene and water

	Run1 (Blank)	Run2 (Excess of water)	Run3 (Stoichiometric water)
Toluene volume , mL	100	100	100
The mass of iodine, g	1.1257	1.0695	1.1580
Water volume	0	30mL	164 μL
SO_2 (1000ppm) flow rate ,SCCM	150	150	150
Running hours	7	7	7
The loss and conversion of iodine	2.3%	63.2%	2.3%

The observation encouraged us to further explore the problem with HSC software, by which the Gibbs free energy change of the Bunsen reaction was calculated (Table 4.2). The computational result indicated that the Bunsen reaction cannot occur if HI product exists as a gas with stoichiometric water used ($\Delta G > 0$ at 0-125 ^{o}C). Therefore, both the experimental and computational results do not support the validity of the proposal of using stoichiometric water and toluene for the Bunsen reaction.

Furthermore, it is indicated in Table 4.2 that the Bunsen reaction will be driven to the right-hand side if the products HI and H_2SO_4 can be ionized in water ($\Delta G < 0$ at 0-125 ^{o}C). This is to say, the amount of water is the key factor to determine the occurrence of the Bunsen reaction at room temperature. Herein, the water functions as a reactant and a solvent in the Bunsen reaction.

Thus, when toluene and an excess amount of water (relative to iodine in organic solvents) are fed into a reactor, a two-phase reaction mixture is formed. Then the gaseous SO_2 is introduced into water phase directly to start the Bunsen reaction. The reaction will occur in the water phase or at the interface of toluene and water phase, where the amount of water is enough to ionize the products HI and H_2SO_4. During the reaction, the reactant iodine has much higher solubility in toluene than in water and easily moves to water phase to supply the Bunsen reaction; the ionized species HI and H_2SO_4 will stay preferentially in water phase (Figure 4.1).

By this way, the "in organic solvent" method was modified to the "in the presence of organic solvents" method. The water phase is where the Bunsen reaction occurs while the toluene phase is an iodine reservoir.

As described above, the advantages of the Bunsen reaction in the presence of organic solvents are as follows:

1. Organic solvents, by dissolving the solid iodine, help to achieve the close contact between iodine, water, and SO_2 for the Bunsen reaction. Fast Bunsen reaction becomes possible at room temperature instead of 120℃.

2. The excess of iodine can be avoided by dissolving iodine in organic solvents. The organic phase is a reservoir to provide the iodine for the Bunsen reaction in the water phase. In this way, the corrosiveness or deposition due to the volatility of iodine can be reduced substantially.
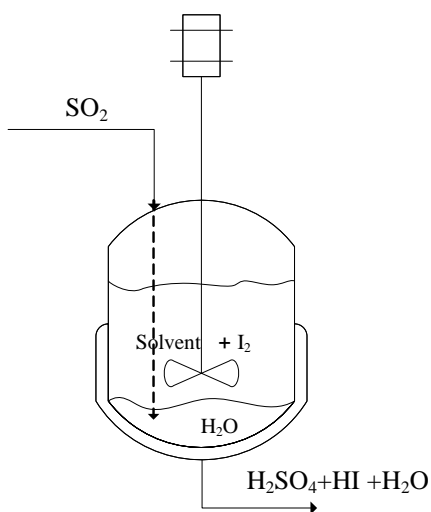
Figure 4.1 Simplified scheme for the Bunsen reaction in the presence of organic solvents

Table 4.2 $\Delta H, \Delta S, \Delta G,$ and K of the Bunsen reaction calculated by HSC,
(a) When stoicheometric water is used, HI is gas and H_2SO_4 is liquid; (b) When excess
amount of water is used, all HI and H_2SO_4 are ionized.

(a)

I_2 (l) + SO_2(g) + $2H_2O \leftrightarrows 2HI$(g) + H_2SO_4(l)					
T, ℃	ΔH , kJ	ΔS, J/K	ΔG, kJ	K	Log(K)
0	119.840	78.933	98.279	1.601E-019	-18.796
25	105.956	28.398	97.489	8.296E-018	-17.081
50	104.178	22.670	96.852	2.204E-016	-15.657
75	102.475	17.591	96.350	3.490E-015	- 14.457
100	100.825	13.014	95.969	3.672E-014	-13.435
125	99.205	8.813	95.697	2.781E-013	-12.556

(b)

I_2(l) + SO_2(g) + $2H_2O \leftrightarrows 4H^+$+ $2I^-$ + SO_4^{2-}					
T, ℃	ΔH, kJ	ΔS, J/K	ΔG, kJ	K	Log(K)
0	-147.253	-299.350	-65.485	3.340E+012	12.524
25	-181.833	-422.599	-55.835	6.067E+009	9.783
50	-199.987	-481.104	-44.519	1.573E+007	7.197
75	-217.367	-532.910	-31.835	5.981E+004	4.777
100	-235.211	-582.391	-17.892	3.197E+002	2.505
125	-254.376	-632.078	-2.714	2.270E+000	0.356

4.2 The selection of organic solvents suitable for the Bunsen reaction

In the efforts to select proper organic solvents for the Bunsen reaction, the screening criteria can be summarized in Table 4.3. The solvents listed in Table 4.4 were the same as Table 2.1 and the solvents' properties such as boiling point, density, solubility in water and fire diamond level were also included. The molar fraction of the iodine solubility in Table 2.1 was converted into g/mL. From Table 4.3 and Table 4.4, the following conclusions can be drawn:

1. Although ethyl ether and ethyl alcohol have higher solubility for iodine, ethyl ether is very volatile and highly flammable and ethyl alcohol is miscible in water.

2. The aromatic solvents such as toluene, xylene, trimethylbenzene, chlorobenzene and bromobenzene may be suitable for the Bunsen reaction. These water-insoluble compounds have low volatility and good chemical inertia.

Initially in our lab, Le Person chose toluene as the solvent for the Bunsen reaction[25]. Toluene is a water-insoluble aromatic solvent with boiling point at 110 ^{o}C and low toxicity, thus suitable for the Bunsen reaction. The NMR result shows no reaction between toluene and iodine (Appendix C).

Table 4.3 Proposed criteria of organic solvents used for the Bunsen reaction

Criteria	Impact
1.High solubility for iodine	Form iodine reservoir to feed the Bunsen reaction
2.No or low solubility for H_2O, HI and H_2SO_4	Keep HI and H_2SO_4 in water phase.
3.High boiling point	High boiling point means low volatility and less hazardous.
4.No reaction with I_2, HI, H_2SO_4, H_2O	Chemical inertia reduces process complexity.
5. Less hazardous	The environment safety and health issues.
6.Less expensive	The process cost.

Table 4.4 Screening of organic solvents for the Bunsen reaction

Organic solvents	Molecular weight	Boiling point°C	H/F/R [*]	Density, g/ml	Solubility in water (g/100ml,20°C)	Iodine[20] solubility, molar fraction,25°C	Iodine solubility, g/mL,25°C
Benzene	78.11	80.1	2/3/0	0.8765	0.08	0.0488	0.146
Toluene	92.14	110.6	2/3/0	0.8669	0.05	0.0639	0.163
o-xylene	106.16	144	2/3/0	0.88	insoluble	0.0786	0.180
p-xylene	106.16	138	2/3/0	0.86	insoluble	0.0760	0.169
m-xylene	106.16	139	2/3/0	0.86	insoluble	0.0825	0.185
1,2,3-trimethylbenzene	120.2	175	0/2/0	0.894	0.005	0.0993	0.208
1,2,4-trimethylbenzene	120.2	169	1/2/0	0.88	very poor	0.0915	0.187
1,3,5-trimethylbenzene	120.2	165	2/2/0	0.864	very poor	0.1058	0.216
1,2,3,4-tetramethylbenzene	134.22	205	1/2/1	0.905	insoluble	0.1167	0.226
ethylbenzene	106.17	136	2/3/0	0.867	0.015	0.0586	0.129
n-propylbenzene	120.19	159	0/2/0	0.862	slightly	0.0589	0.114
cumene	120.19	152	2/3/0	0.864	insoluble	0.0561	0.108
n-butylbenzene	134.22	183	0/2/0	0.86	insoluble	0.0548	0.094
isobutylbenzene	134.22	170	2/2/0	0.853	insoluble	0.0480	0.081
tert-butylbenzene	134.22	169	2/3/2	0.867	insoluble	0.0501	0.086
chlorobenzene	112.56	132	1/3/0	1.106	low	0.0333	0.086
bromobenzene	157.01	156	1/2/0	1.491	insoluble	0.0549	0.140
n-C6H14	86.18	69	1/3/0	0.6548	0.0013	0.00456	0.009
n-C7H16	100.21	98.42	1/3/0	0.684	immiscible	0.00679	0.012
CCL4	153.82	76.72	3/0/0	1.5867	0.08	0.0115	0.030
CHCl3	119.38	61.2	2/0/0	1.483	0.8	0.0228	0.074
CS2	76.139	46.3	3/4/0	1.261	0.29	0.0546	0.243
cyclohexane	84.16	80.74	1/3/0	0.779	immiscible	0.0092	0.022
ethyl alcohol	46.07	78.4	1/3/0	0.789	miscible	0.0471	0.215
ethyl ether	74.12	34.6	2/4/1	0.7134	6.9	0.0896	0.240

[*] H: Level of health hazard; F: level of flammability; R: level of reactivity.

4.3 Iodine solubility in hydroiodic acid solution

As mentioned in the literature review in section 2.4, the iodine solubility in HI solution is substantially higher than in water. For the Bunsen reaction in the presence of toluene, the HI concentration in the water phase will gradually increase as the reaction proceeds. Therefore, iodine solubility in HI solution and the relationship between iodine solubility and HI solution concentrations need to be studied. The experimental results about iodine solubility in HI solution with different concentrations were summarized in Table 4.5. The maximal concentration of commercially available HI solution is 57wt% or 7.60 M.

Table 4.5 Iodine solubility in less than 7.6 M hydroiodic acid

Hydroiodic acid		Hydroiodic acid saturated by iodine				
No.	[HI]	$[H^+]$	±Uncertainty, M	I_2 solubility, M	±Uncertainty M	Molar ratio of I_2 solubility/[HI]
1	7.60	4.42	0.63	8.08	0.53	1.06
2	3.80	3.63	1.74	4.18	0.11	1.10
3	1.90	2.00	0.11	1.81	0.46	0.954
4	0.950	1.061	0.070	0.726	0.066	0.764
5	0.475	0.550	0.070	0.317	0.057	0.668
6	0.238	0.280	0.076	0.1394	0.0001	0.587
7	0.119	0.153	0.012	0.067	0.013	
8	0.0765	0.099	0.016	0.045	0.010	
9	0.0594	0.079	0.031	0.0339	0.0038	
10	0.0380	0.059	0.020	0.0247	0.0087	
11	0.0297	0.048	0.015	0.0181	0.0038	
12	0.0190	0.0439	0.0048	0.0173	0.0037	
13	0.00956	0.028	0.022	0.0115	0.0085	
14	0.00478	0.0160	0.0090	0.0043	0.0017	
15	0.00239	0.0156	0.0060	0.0045	0.0027	
16	0.00120	0.0109	0.0066	0.0030	0.0021	
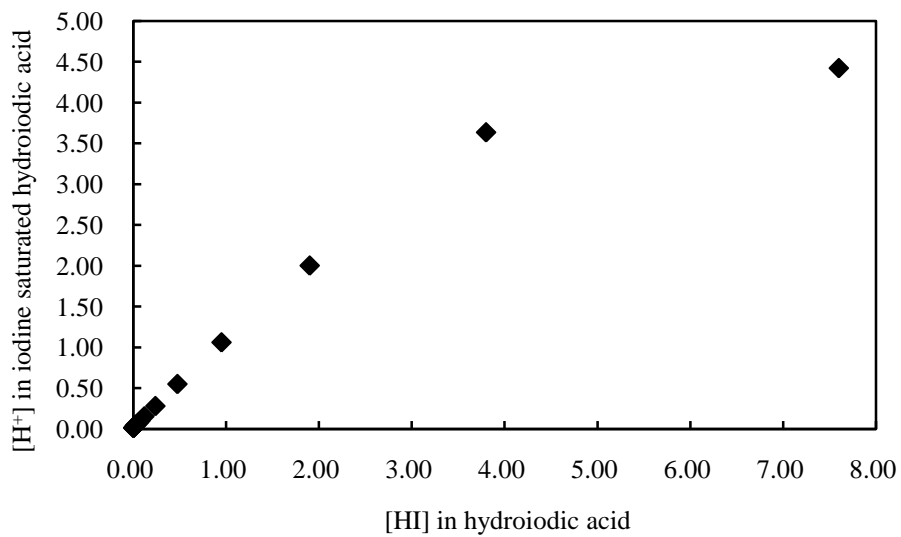
(a)
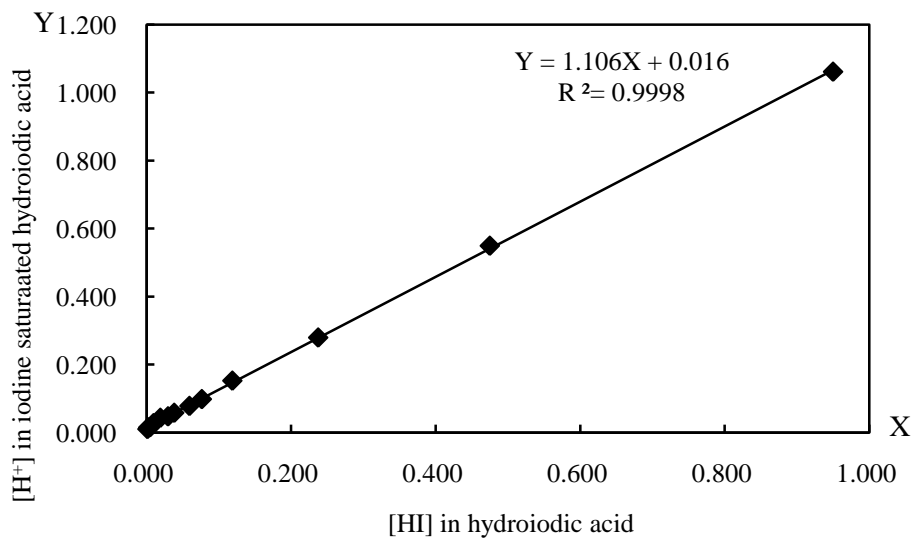
(b)

Figure 4.2 The relationship between [H^+] in iodine saturated hydroiodic acid and [HI] in hydroiodic acid, (a) [HI] range: 0~7.6 M; (b) [HI] range: 0~0.95 M

In Table 4.5, it was found that $[H^+]$ increased when HI solution was saturated by iodine at $[HI] < 1.90$ M, while $[H^+]$ decreased at $[HI] > 1.90$ M. As shown in Figure 4.2a&b, $[H^+]$ shows a linear response to increasing $[HI]$ when $[HI] < 1.90$ M and the plotting of $[H^+]$ against $[HI]$ levels off when $[HI] > 1.90$ M.

The dissolution of iodine in HI solution will be accompanied by the hydrolysis of iodine (Table 4.6) [26, 27]. All the equations in Table 4.6 suggest that the hydrolysis of iodine produces H^+ and the anions such as $I^-, IO^-,$ and IO_3^-. Overall one mole of I_2 produces two moles of H^+. This can explain the increase of $[H^+]$ at $[HI] < 1.90$ M.

Table 4.6 Equilibrium processes of iodine hydrolysis

No.	Reaction
1	$I_2 + H_2O \leftrightharpoons H^+ + I^- + HIO$
2	$I_2 + H_2O \leftrightharpoons H^+ + I_2OH^-$
3	$I_2 + OH^- \leftrightharpoons I_2OH^-$
4	$I_2OH^- \leftrightharpoons HIO + I^-$
5	$I_2 + I^- \leftrightharpoons I_3^-$
6	$H_2OI^+ \leftrightharpoons HIO + H^+$
7	$HOI \leftrightharpoons IO^- + H^+$
8	$I_2 + H_2O \leftrightharpoons H_2OI^+ + I^-$
9	$3I_2 + 3H_2O \leftrightharpoons IO_3^- + 5 I^- + 6H^+$

But it seems to be difficult to explain why $[H^+]$ decreased at $[HI] > 1.90$ M when dissolving iodine in HI solution. In experiments, it was observed that the volume of the resulting solution increased significantly when iodine was dissolved at the saturating concentration in the HI solution with concentration higher than 1.90 M. Therefore, the measured $[H^+]$ in the iodine-

saturated HI solution was lowered. It seems to be reasonable to extrapolate the linear relationship between $[H^+]$ and [HI] even at [HI] > 1.90 M if the volume expansion due to iodine dissolution is taken into consideration. For example, when HI solution (7.6 M) was saturated by iodine, the $[H^+]$ was measured as 4.42 M. According to the linear relationship obtained in Figure 4.2b, if there is no volume expansion, the $[H^+]$ measured should be 8.08 M (Table 4.7). The ratio of the "corrected" $[H^+]$ (8.42 M) to the measured $[H^+]$ (4.42 M) is 1.9, representing 1.9 times of volume expansion due to iodine dissolution. Then the revised iodine solubility is equal to 15.4 M (7.6 M × 1.9). In the same way, the corresponding results for the HI solution (3.8 M, 1.9 M) saturated by iodine were also revised and included in Table 4.7.

Table 4.7 Revised iodine solubility in larger than 1.90 M hydroiodic acid

Hydroiodic acid	Hydroiodic acid saturated by iodine					
[HI]	$[H^+]$		Iodine solubility, M		Molar ratio of I_2 solubility/HI	
	measured	revised	measured	revised	measured	revised
7.60	4.42	8.42	8.08	15.4	1.06	2.02
3.80	3.63	4.22	4.18	4.86	1.10	1.28
1.90	2.00	2.12	1.81	1.93	0.954	1.02

On the basis of the studies on the iodine hydrolysis, the relationship between the iodine solubility and the [HI] in the HI solution was investigated. As shown in Figure 4.3, the iodine solubility was plotted versus [HI]. The iodine solubilities used when [HI] > 1.90 M was the revised values (Table 4.7), while the solubilities used when [HI] < 1.90 M was the measured values directly (Table 4.5).

The plotting of the iodine solubility versus [HI] is a two-phase curve as shown in Figure 4.3. In phase 1, the iodine solubility is linear to [HI] in the concentration range of 0~0.238 M (Figure 4.4); in phase 2, the iodine solubility/[HI] is linear to [HI] in the concentration range of

0.238~7.6 M (Figure 4.5). The equations about the relationship of the iodine solubility versus [HI] were summarized in Table 4.8.

Figure 4.3 The iodine solubility in hydroiodic acid

$$Y = 0.57X + 0.0030$$
$$R^2 = 0.9971$$
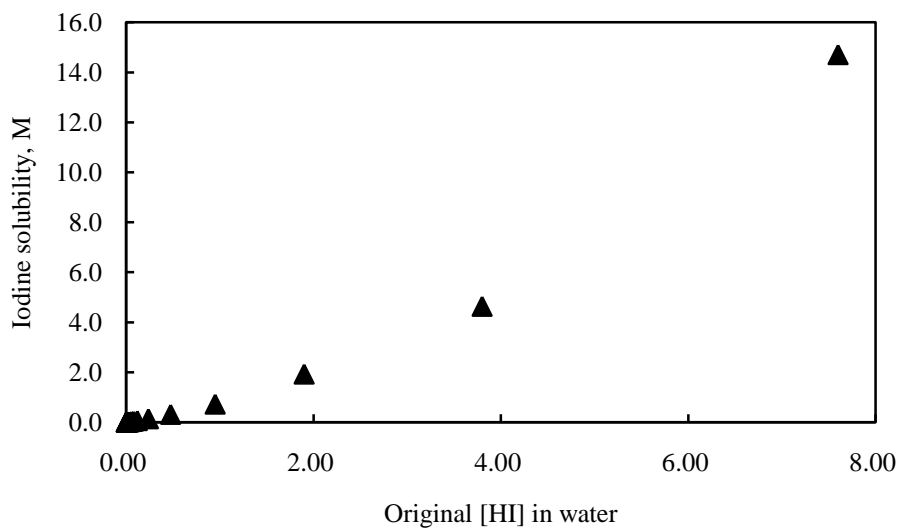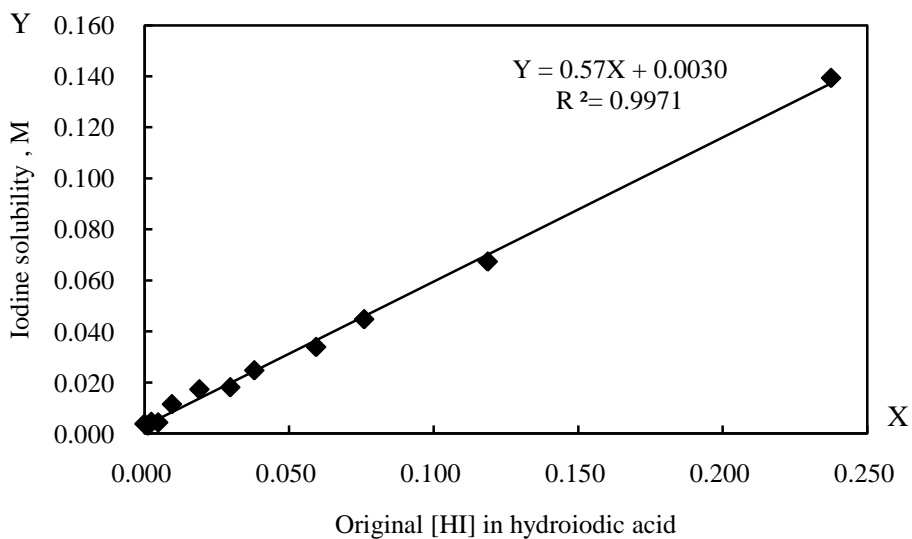
Figure 4.4 The relationship between iodine solubility and [HI] at the [HI] range of 0 to 0.238 M
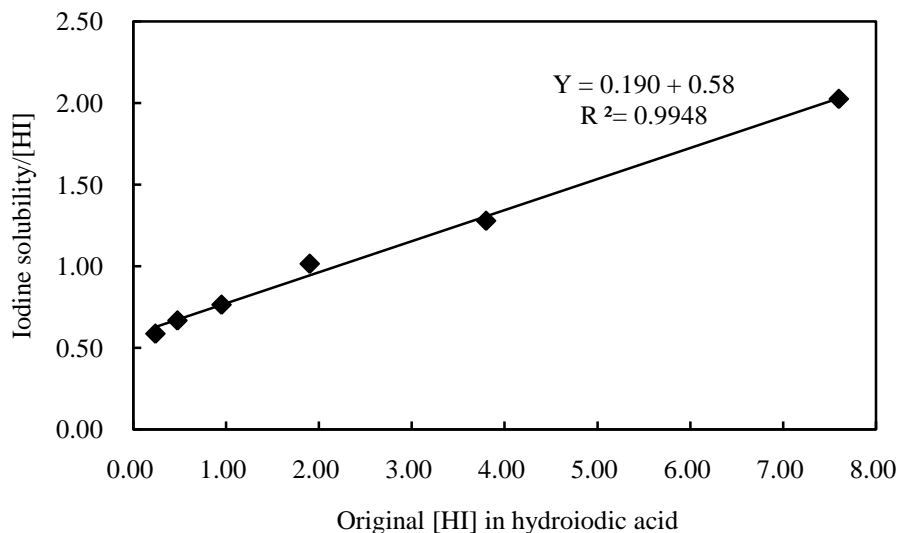
Figure 4.5 The relationship between the molar ratio of iodine solubility/[HI] and [HI] at the [HI] range of 0.238 to 7.6 M

Table 4.8 The relationships between iodine solubility and [HI] in HI solution

	HI concentration range, M	Equation	Coefficient of determination	Sample standard deviation	
				Slope	Intercept M
Phase 1	0~0.238	Y=0.57X+0.0030 Y=[I$_2$],X=[HI]	0.9971	0.01	0.0008
Phase 2	0.238~7.6	Y=0.190X+0.58 Y=[I$_2$]/[HI], X=[HI]	0.9948	0.007	0.02

H_2SO_4 is one of the Bunsen reaction products and stays in the water phase to form a HI-H_2SO_4 solution. So it is necessary to study the iodine solubility in such a solution. In HI-H_2SO_4 aqueous solution which has a molar ratio 2:1 as the stoichiometric ratio of HI to H_2SO_4 in the Bunsen reaction, the iodine solubilities were determined and the results were summarized in Table 4.9.

Table 4.9 The influence of H_2SO_4 on the iodine solubility in HI solution

	HI-H_2SO_4 solution		Solution saturated by iodine
No.	[HI]	[H_2SO_4]	I_2 solubility, M
1	0.950	0.472	0.735
2	0.475	0.236	0.324
3	0.238	0.118	0.137
4	0.119	0.0590	0.0648
5	0.0594	0.0295	0.0363
6	0.0297	0.0147	0.0231
7	0.0148	0.00737	0.0133

In Figure 4.6, it is clearly shown that the iodine solubilities in HI solutions are the same as that in HI-H_2SO_4 solution. Therefore, the relationship between the iodine solubility and [HI] concluded from pure HI solution is still applicable to the HI-H_2SO_4 solution, i.e. the reaction mixture of the Bunsen reaction.
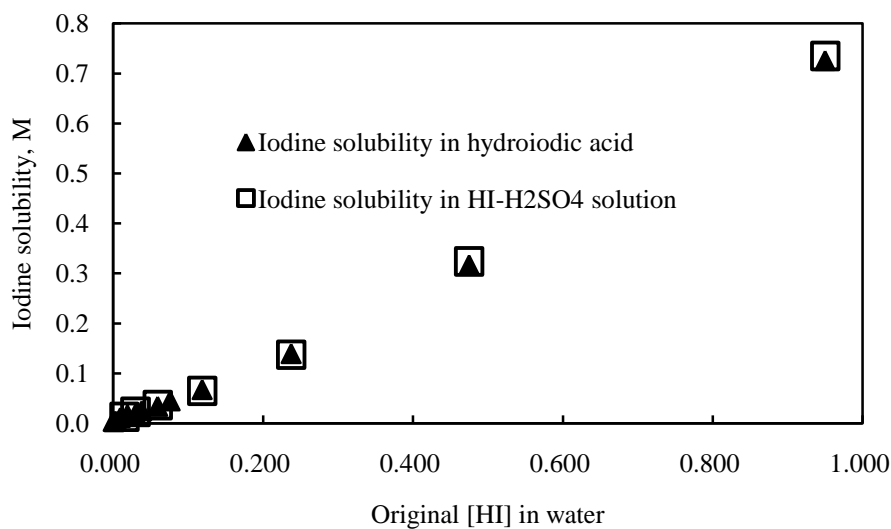
Figure 4.6 The iodine solubility in HI and HI- H_2SO_4 solutions.

In conclusion, the iodine solubility in HI solution was investigated. The linear relationships between the iodine solubility and [HI] were deduced for two different concentration ranges of HI solutions. The existence of H_2SO_4 does not affect iodine solubility in HI solution.

4.4 Distribution coefficient of iodine between hydroiodic acid and toluene

During the process of the Bunsen reaction in the presence of toluene, iodine is consumed and HI is accumulated in the water phase. In such a reaction system, the behavior of the iodine distribution is closely related to the reaction rate because the reaction is very likely to occur at the interface of two phases or in the water phase. In analogy to the reaction mixture, a mixture of toluene and HI solution was used to determine the iodine distribution.

In this experiment, the iodine distribution coefficient (D) between the HI solution and the toluene phase is defined as $[I_2]_{HI\,solution}/[I_2]_{toluene}$, and the volume ratio is defined as $V_{toluene}/V_{HI\,solution}$. In Table 4.9, the concentrations of HI, iodine in HI solution and toluene before and after mixing were presented and distribution coefficients of iodine (D) were calculated under different concentrations of HI solutions.

In Figure 4.7, the distribution coefficients of iodine (D) were plotted versus the concentrations of HI solution. The nonlinear regression analysis indicated the plot is a two-phase curve. At the [HI] range of 0~1.89 M, the relationship of D and [HI] fits in a quadratic equation (inset of Figure 4.8a); at the [HI] range of 1.89~7.54 M, the relationship fits in a linear equation (inset of Figure 4.8b). As shown in Table 4.10, the experimental and calculated D were consistent.

Table 4.9 Distribution coefficient of iodine between HI solution and toluene

(a)

No.	Before distribution			After distribution		
	[HI] in hydroiodic acid	[I$_2$] in toluene phase	Volume ratio	[I$_2$] in water phase	[I$_2$] in toluene phase	D
1	7.54	0.466	1	0.1002	0.00259	38.7
2	3.77	0.466	1	0.2304	0.0132	17.5
3	1.89	0.466	1	0.305	0.0459	6.6
4	0.943	0.466	1	0.275	0.133	2.07
5	0.471	0.466	1	0.178	0.243	0.73
6	0.236	0.466	1	0.0994	0.342	0.291
7	0.118	0.466	1	0.0498	0.382	0.130
8	0.0589	0.466	1	0.0261	0.402	0.0649
9	0.0295	0.466	1	0.0132	0.404	0.0327

(b)

No.	[HI],M	[I$_2$] in water phase	±Uncertainty M	[I$_2$] in toluene phase	±Uncertainty, M
1	7.54	0.100	0.030	0.00259	0.0045
2	3.77	0.230	0.024	0.0132	0.0027
3	1.89	0.305	0.064	0.046	0.030
4	0.943	0.275	0.005	0.133	0.010
5	0.471	0.178	0.021	0.243	0.021
6	0.236	0.099	0.074	0.342	0.015
7	0.118	0.050	0.017	0.382	0.001
8	0.0589	0.0261	0.0012	0.402	0.068
9	0.0295	0.0132	0.0064	0.404	0.058
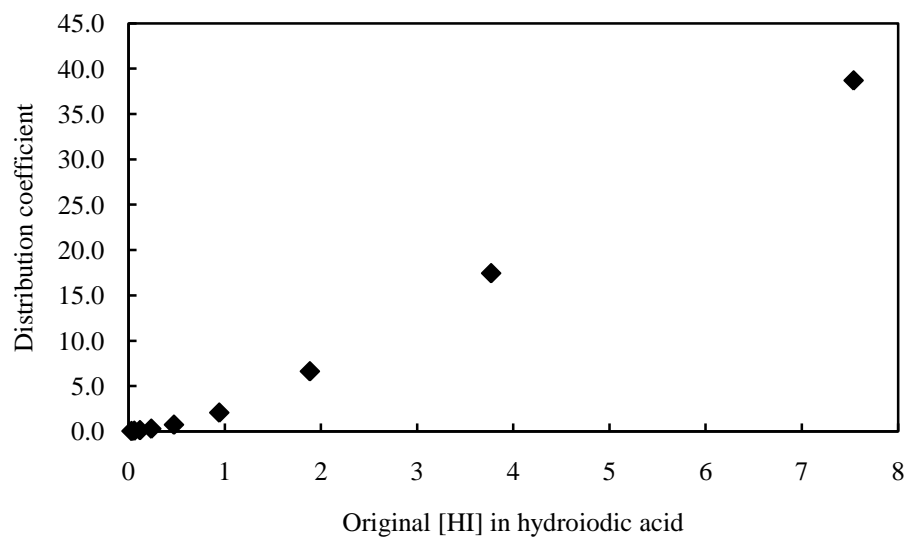
Figure 4.7 Distribution coefficients versus [HI]

$$D = 1.4027[HI]^2 + 0.8638[HI] + 0.0088$$
$$R^2 = 1$$

(a)

33

D = 5.6679[HI] - 4.008
R ^{2}= 1

Distribution coefficient

Original [HI] in hydoiodic acid
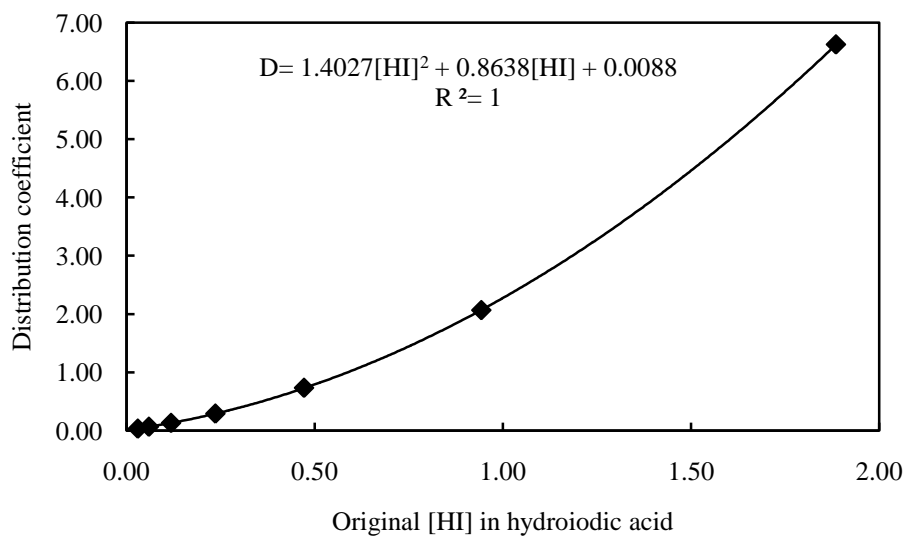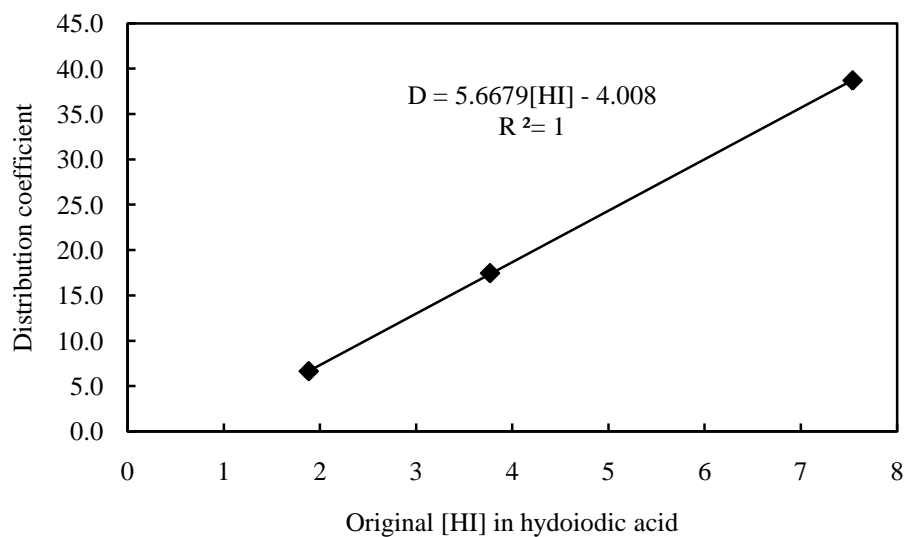
(b)

Figure 4.8 The relationship between D and [HI] in hydroiodic acid (a) [HI] range: 0~1.89 M, (b)
[HI] range: 1.89~7.54 M

Table 4.10 Comparison of experimental and regression D

No.	[HI]	Experimental D	Regression D Calculated	Calculated
1	7.54	38.7	38.7	
2	3.77	17.5	17.5	
3	1.89	6.6	6.67	6.62
4	0.943	2.07		2.07
5	0.471	0.73		0.727
6	0.236	0.291		0.290
7	0.118	0.130		0.130
8	0.0589	0.0649		0.0645
9	0.0295	0.0327		0.0355

4.4.1 Factors that may affect the distribution coefficient of iodine

For the Bunsen reaction in the presence of toluene, the water phase contains H_2SO_4 and HI. It is necessary to study the influence of H_2SO_4 on the iodine distribution. As shown in Table 4.11, the $[I_2]$ in toluene solution was fixed at 0.466 M. When the water phase is 0.375 M of HI solution, the D was determined as 0.490; when the water phase is a mixed HI-H_2SO_4 solution (0.375 M and 0.189 M respectively), the D was determined as 0.482. The two D values agree very well, suggesting that the existence of H_2SO_4 in HI solution does not cause the change of the iodine distribution coefficient.

Table 4.11 Influence of H_2SO_4 on the distribution coefficient

	Before distribution			After distribution		
No.	[HI] in water phase	[H_2SO_4] in water phase	[I_2]in toluene	[I_2] in water phase	[I_2] in toluene phase	D
1	0.375	0.189	0.466	0.148	0.301	0.490
2	0.375	0.00	0.466	0.149	0.308	0.482

Thus far, all the distribution coefficients discussed above were measured from a mixture of toluene and HI solution with a 1:1 volume ratio. Generally speaking, the distribution coefficient is independent of the volume ratio of two phases. Supposedly, this principle is also applicable to the iodine distribution between HI solution and toluene. However, because the dissolution of iodine in HI solution is a complicated process, the volume ratio may be one of the factors that affect the distribution coefficient. In Table 4.12a, as the volume ratios of toluene to HI solution were changed from 1:1 to 20:1, the D values remained constant within experimental errors. This suggests that the volume ratio is not a factor to affect the iodine distribution coefficients.

Furthermore, as shown in Table 4.12b, the $[I_2]$ in HI solution increased as the volume ratio of toluene to HI solution increased. However, the increasing of the $[I_2]$ in HI solution obviously slowed down after the volume ratio > 2:1 (Figure 4.9). Therefore, the 2:1 volume ratio of toluene to HI solution is good enough to maintain almost the maximal $[I_2]$ in HI solution which is helpful to Bunsen reaction.

Table 4.12 Influence of volume ratio on the distribution coefficient

(a)

| No. | Before distribution | | | After distribution | | |
	[HI] in water phase	$[I_2]$ in toluene phase	Volume ratio	$[I_2]$ in water phase	$[I_2]$ in toluene phase	D
1	0.506	0.257	1	0.107	0.121	0.890
2	0.506	0.257	5	0.165	0.220	0.749
3	0.506	0.257	10	0.175	0.237	0.736
4	0.506	0.257	20	0.189	0.246	0.767
					Average value	0.785

(b)

| No. | Before distribution | | | After distribution | | |
	[HI] in water phase	$[I_2]$ in toluene phase	Volume ratio	$[I_2]$ in water phase	$[I_2]$ in toluene phase	D
1	0.506	0.317	1	0.132	0.156	0.850
2	0.506	0.317	2	0.171	0.221	0.774
3	0.506	0.317	3	0.186	0.251	0.743
4	0.506	0.317	4	0.193	0.233	0.827
5	0.506	0.317	5	0.188	0.290	0.649
6	0.506	0.317	6	0.210	0.286	0.734
7	0.506	0.317	7	0.203	0.283	0.715
8	0.506	0.317	8	0.204	0.293	0.756
					Average value	0.756
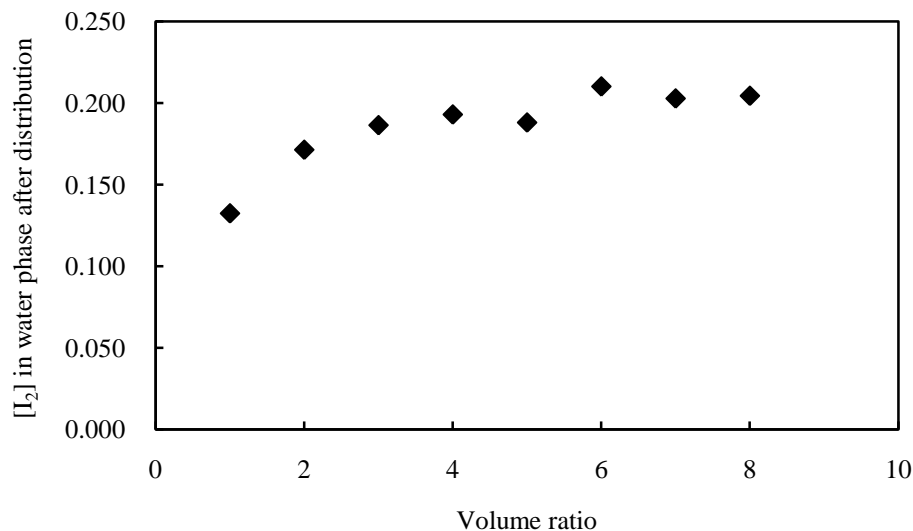
Figure 4.9 The [I_2] in water phase after distribution versus the volume ratio of toluene to HI solution. Volume ratio range: 1:1 ~8:1.

In conclusion, the existence of H_2SO_4 does not affect the iodine distribution coefficient between toluene and HI solution and the volume ratio of toluene to HI solution was optimized as 2:1 for the study of the Bunsen reaction in the presence of toluene.

4.5 Bunsen reaction rate in a semi-batch reactor

4.5.1 Blank experiments

In order to figure out whether there are side reactions accompanying the Bunsen reaction in the presence of toluene, 129.6 SCCM of 1.04% SO_2 gas was introduced into 100 mL of iodine toluene solution (0.105 M). After 60 minutes, the aliquots of reaction mixture were taken out and diluted by 101 times with toluene for analysis by UV-Vis spectrometry. The absorbance at 497

nm was 1.074 and corresponding concentration of iodine in toluene was 0.105 M, which is equal to the original iodine concentration in toluene. This suggested that there is no loss of iodine and no detectable reactions among iodine, toluene and SO_2 unless water is present.

4.5.2 The Bunsen reaction rate in iodine-HI solution

The Bunsen reaction occurs in the water phase or at the interface between toluene and water phases while it cannot take place in toluene phase. Therefore, the rate of Bunsen reaction was first studied in the iodine-HI aqueous solution in the absence of toluene. Then effect of the presence of toluene on the reaction rate was studied.

Iodine-HI solution was prepared by mixing 5.3048 g of iodine with 150 mL of 0.209 M HI solution. The resulting solution stood at room temperature for 1 hour. Then the $[H^+]$ was determined by NaOH solution titration as 0.241 M, and the $[I_2]$ was determined by iodometry titration as 0.0768 M. The solution was put into the reactor as illustrated in Figure 3.1. Then 130.4 SCCM of 1000 ppm SO_2 was introduced. As soon as the SO_2 was fed into the reactor, the Bunsen reaction was started. The $[I_2]$ and the $[H^+]$ in the reaction solution was analyzed at certain interval times. The results were summarized in Table 4.13a. The ratio of $\Delta[H^+]/\Delta[I_2]$ is around 4, consistent with the stoichiometry of the Bunsen reaction. According to the stoichiometry, moles of SO_2 consumed are equal to the moles of iodine consumed or one-fourth of the moles of proton produced. The comparison of the calculated SO_2 consumption and the measured SO_2 by thermal mass flow meter (TMFM) can indicate how much of the feeding SO_2 is consumed in the Bunsen reaction. In Table 4.13a, the ratios of the calculated consumption and the measured feeding of SO_2 (absorbance of SO_2) are approximately 100%. This suggested that

38

the feeding of SO_2 was consumed in the Bunsen reaction completely and rapidly. In experiments, no escape of SO_2 was detected in the washing bottle (11b in Figure 3.1).

Furthermore, the iodine was consumed continually to lower concentration as the feeding of SO_2, but the consumption of SO_2 was still sufficient and efficient. That is to say, the depletion of SO_2 in the Bunsen reaction is independent of the iodine concentration. For example, when 1000 ppm of SO_2 was introduced, the reaction rate ($\Delta[I_2]/\Delta t$) was constant as shown in Figure 4.10 and was equal to the molar flow rate of feeding SO_2 (Table 4.16).

Further work was conducted to investigate the dependence of the Bunsen reaction rate on the feeding of SO_2. When the concentration of SO_2 gas solution introduced was increased from 1000 ppm, 1.04% to 100%, complete consumption of SO_2 was still observed (Table 4.14 and. Therefore, the rate of the Bunsen reaction in HI solution is solely controllable by the introduction of SO_2. The reaction rates ($\Delta[I_2]/\Delta t$) were also found to be equal to the molar flow rate of feeding SO_2 (Table 4.16).

When pure SO_2 was used, the average absorbance of SO_2 was found to be 75%. However, it cannot be concluded that the pure SO_2 did not undertake the reaction completely. It is very likely that the introduced pure SO_2 gas did not disperse thoroughly into the reaction mixture before it escaped from the reaction mixture. This problem can be overcome by increasing the contact interface of the gas phase and solution phase. In conclusion, if SO_2 and iodine can be mixed effectively and sufficiently, the Bunsen reaction in iodine-HI aqueous solution is independent of iodine concentration and the reaction rate is equal to the molar flow rate of SO_2.

Table 4.13 The Bunsen reaction at 130.4 SCCM of 1000 ppm SO_2 with 150 mL iodine-HI
aqueous solution

(a-1)

Volume of water, L	Reaction time(mins)		$[H^+]$	$[I_2]$	$\Delta[H^+]$	$\Delta[I_2]$
	Accumulated	Interval				
0.15	0	0	0.241	0.0768		
0.15	158	158	0.278	0.0670	0.0370	0.00981
0.148	308	150	0.310	0.0588	0.0325	0.00817
0.145	515	207	0.352	0.0456	0.0420	0.01327
0.142	644	129	0.382	0.0378	0.0300	0.00777
0.14	764	120	0.408	0.0305	0.0255	0.00729
0.138	884	120	0.440	0.0229	0.0325	0.00763
0.129	1006	122	0.484	0.0136	0.0440	0.00932
0.126	1126	120	0.507	0.0063	0.0230	0.00723
0.122	1223	97	0.533	0	0.0260	0.00633
Iodine lost , mol		1.69E-04				

(a-2)

$\Delta[H^+]/\Delta[I_2]$	Calculated SO_2 ,mol	SO_2 measured from TMFM, mol	Absorbance of SO_2
3.77	1.39E-03	1.35E-03	102%
3.98	1.20E-03	1.29E-03	94%
3.16	1.52E-03	1.79E-03	85%
3.86	1.07E-03	1.11E-03	96%
3.50	8.92E-04	1.04E-03	86%
4.26	1.05E-03	1.04E-03	102%
4.72	1.20E-03	1.05E-03	114%
3.18	7.25E-04	1.04E-03	88%
4.11	7.72E-04	8.37E-04	92%
Average absorbance of SO_2			95%

(b)

Volume of water, L	Accumulated reaction time, mins	$[I_2]$	Iodine, mol
0.15	0	0.0768	1.15E-02
0.15	157	0.0670	1.01E-02
0.148	308	0.0588	8.71E-03
0.145	515	0.0456	6.61E-03
0.142	644	0.0378	5.37E-03
0.14	764	0.0305	4.27E-03
0.138	884	0.0229	3.16E-03
0.129	1006	0.0136	1.75E-03
0.126	1126	0.0063	7.97E-04
0.122	1223	0.00	0.00E+00

y

$y = -1E-05x + 0.0116$
$R^2 = 0.9995$

Iodine in reaction mixture, mol

Reaction time , minutes

x
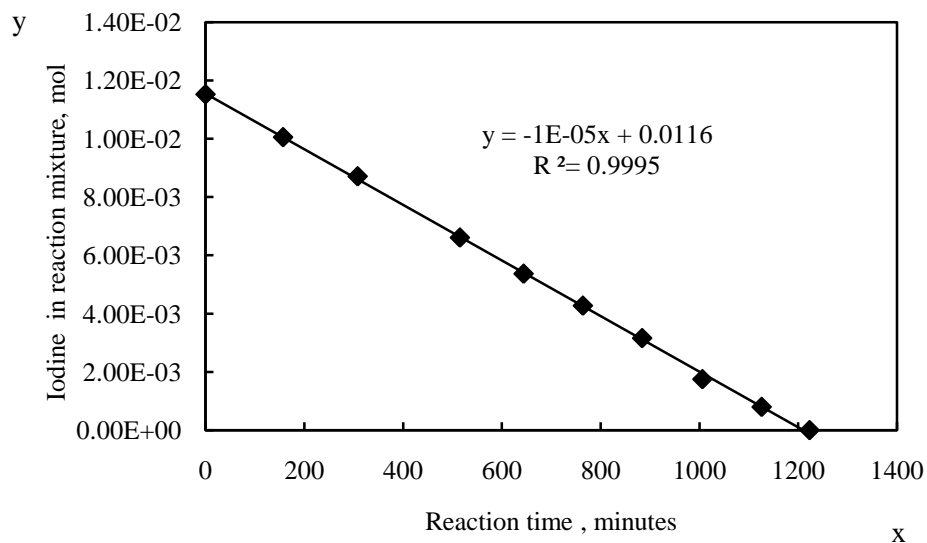
Figure 4.10 Moles of iodine in reaction mixture versus reaction time for the Bunsen reaction at 130.4 SCCM of 1000 ppm SO_2

41

Table 4.14 The Bunsen reaction at 129.6 SCCM of 1.04% SO_2

(1)

Volume of water, L	Reaction time (mins) Accumulated		$[H^+]$	$[I_2]$	$\Delta[H^+]$	$\Delta[I_2]$
		Interval				
0.15	0	0	0.2455	0.0750		
0.15	77	77	0.42	0.0310	0.1745	0.04407
0.147	120	43	0.5065	0.0085	0.0865	0.02249
0.145	133	13	0.538	0.0000	0.0315	0.00848
Iodine lost, mol:		1.69E-05				

(2)

$\Delta[H^+]/\Delta[I_2]$	Calculated SO_2, mol	SO_2 measured from TMFM, mol	Absorbance of SO_2
3.96	0.00654	0.00660	99%
3.85	0.00318	0.00369	86%
3.72	0.00114	0.00111	102%
	Average absorbance of SO_2		96%

Table 4.15 The Bunsen reaction at 40.8 SCCM of pure SO_2

(1)

Volume of water, L	Reaction time (mins)		$[H^+]$	$[I_2]$	$\Delta [H^+]$	$\Delta [I_2]$
	Accumulated	Interval				
0.1	0	0	0.556	0.310		
0.1	5	5	0.807	0.242	0.251	0.0675
0.098	10	5	1.063	0.177	0.256	0.0649
0.096	15	5	1.319	0.113	0.257	0.0646
0.094	22	7	1.770	0.000	0.451	0.1128
Iodine lost, mol		0.00				

(2)

$\Delta [H^+]/ \Delta [I_2]$	Calculated SO_2 ,mol	SO_2 measured from TMFM, mol	Absorbance of SO_2
3.72	0.00628	0.00870	72%
3.94	0.00626	0.00870	72%
3.97	0.00616	0.00870	71%
4.00	0.01060	0.0122	87%
		Average absorbance of SO_2	75%

Table 4.16 Comparison of molar flow rate of SO_2 and reaction rate of iodine for the Bunsen reaction

The volume concentration of SO_2	Flow rate of SO_2		Reaction rate of iodine, mol/min
	SCCM	mol/min	
1000 ppm	130.4	8.63E-06	1.00E-05
1.04%	129.6	8.57E-05	8.00E-05
pure	40.8	1.74E-03	1.40E-03

4.5.3 The Bunsen reaction rate in the presence of toluene

For the Bunsen reaction in the presence of toluene, the reaction rate was studied similarly. As the Bunsen reaction proceeds, more and more HI is produced in the water phase. As the HI concentration in the water phase is increasing, iodine will redistribute between toluene phase and water phase. The influence of toluene on the rate of the Bunsen reaction needs to be explored. An experiment with conditions as shown in Table 4.17 was performed. While SO_2 was introduced into the aqueous phase, the rate of the Bunsen reaction in the presence of toluene changed through 3 stages (Table 4.18):

Stage one (0-38mins): At the initial stage of the Bunsen reaction (0-38mins), most of iodine stayed in the toluene phase due to the low iodine solubility in water and low concentration of HI solution. At this stage, the water phase was observed as colorless solution. During the process of the reaction, complete SO_2 absorbance (determined as 110% absorbance) was observed, indicating that the reaction rate was solely decided by the flow rate of SO_2 at this stage.

Stage two (38-85mins): At this stage, the [HI] in water phase was high enough to compete for iodine with toluene phase. Accordingly, the water phase was observed to change from light yellow to dark red color. According to the conclusions from section 4.5.1, the Bunsen reaction rate in iodine-HI solution at this stage is still equal to the molar flow rate of SO_2.

Stage 3(85-185mins): At this stage, the unreacted iodine was becoming less and less. Therefore, although the HI concentration in water phase continued to increase, it was observed that the water phase turned colorless and most of the iodine stayed in the toluene phase. The iodine concentration in water phase was too low to react with the feeding SO_2 efficiently. The absorbance of SO_2 dropped rapidly from around 100% to 33% (Table 4.18).

In conclusion, for the Bunsen reaction in the presence of toluene, the rate is equal to the molar flow rate of SO_2 unless the iodine concentration is very low. The threshold concentration of iodine was believed to depend on the conditions of the reaction system, such as the interface area, the dispersion efficiency and the flow rate of SO_2.

Table 4.17 Initial conditions of the Bunsen reaction in the presence of toluene

Volume of water phase mL	Volume of toluene mL	Volume ratio	[I$_2$]		[HI] in water	Flow rate of SO$_2$, mol/min
			in water	in toluene		
60	120	2	0	0.106	0	8.63E-05

Table 4.18 The Bunsen reaction in the presence of toluene

(1)

Reaction time, mins Accumulated	Interval	[H$^+$] in water	[I$_2$] in water	Water volume, mL	[I$_2$] in toluene	Toluene volume, mL
0	0	0.000	0	60	0.1056	120.0
38	38	0.240	0.00198	60	0.0732	120.0
85	47	0.500	0.00622	58	0.0293	119.9
132	47	0.760	0	56	0.0123	119.7
183	51	0.878	0	55	0.000213	103.5

(2)

Increased proton, mol	Decreased iodine, mol	Increased proton/Decreased iodine	Calculated SO$_2$, mol	SO$_2$ measured from TMFM, mol	Absorbance of SO$_2$
0.0144	0.00378	3.81	0.00360	0.00328	110%
0.0151	0.00490	3.08	0.00377	0.00406	93%
0.0146	0.00204	7.14	0.00204	0.00406	50%
0.00649	0.00145	4.46	0.00145	0.00440	33%

5. CONCLUSIONS AND FUTURE WORK

In the research of H_2S splitting cycle for hydrogen production, the Bunsen reaction, especially in the presence of organic solvents was explored. The following conclusions were drawn from the work that I have done for this project:

1. Toluene was chosen as a suitable organic solvent used in the Bunsen reaction;

2. The dissolution of iodine in HI solution was discussed. Due to the iodine hydrolysis in HI solution, the $[H^+]$ in I_2-HI aqueous mixture was found to be linear to the original [HI] of the HI solution.

3. On the basis of the study on the dissolution of iodine in HI solution, the iodine solubility in HI solution was investigated. It was found that the iodine solubility is linear to the [HI] in the range of 0~0.238 M and the iodine solubility/[HI] is linear to the [HI] in the range of 0.238~7.6 M. Furthermore, the existence of H_2SO_4 in the HI solution does not change the relationships.

4. The iodine distribution between HI solution and toluene was investigated. Experimental results indicated that the iodine distribution coefficients between the two phases are increasing as the [HI] is increasing. In the [HI] range of 0~1.89 M, the coefficients D are in a quadratic relationship to [HI], while in the [HI] range of 1.89~7.54 M, the coefficients D are in a linear relationship to [HI]. In addition, the existence of H_2SO_4 in the HI solution does not change the relationships and the optimal volume ratio of toluene to HI solution was found to be 2:1.

5. In a semi-batch reactor, the Bunsen reaction rate in iodine-HI aqueous solution was determined. It was found that the reaction rate is independent of the iodine concentration and equal to the molar flow rate of SO_2.

6. In a semi-batch reactor, the Bunsen reaction rate in the presence of toluene was determined. It was found that the reaction rate is also equal to the molar flow rate of feeding SO_2 if the iodine concentration is higher than a certain value. The threshold value of iodine concentration is dependent on experimental conditions.

In the future, the research work on this topic may be carried out on the following aspects:

1. More organic solvents need to be tested to choose the optimal solvent for the Bunsen reaction.

2. The scale-up reactor of the Bunsen reaction in the presence of toluene should be chosen and designed.

3. The development of new method and technology is necessary for the production of hydrogen from the Bunsen reaction mixture. Electrolysis of the HI-H_2SO_4 solution from the Bunsen reaction is one of the candidates.

APPENDIX A
CALIBRATION OF MASS FLOW CONTROLLER

Thermal mass flow meters from SIERRR were used in the experiments:

Port for N_2, serial number: C-26615, range: 0-2000 SCCM;

Port for SO_2, serial number: C-22616, range: 0-200 SCCM.

Mass Flow calibrator was BIOS DryCal DC-2 Dry Primary Flow Calibrator.

For port of N_2, model DC-MC-1was used and for port of SO_2, model DC-LC-1 was used.

STP: 293.15K, 1atm.

Molar volume of gas at STP: 24.055mol/L.

The calibrating results were showed in Table A-1 and A-2.

Table A-1 Calibrating results of flow meter for N_2

MFC reading, SCCM	Calibrator reading, SCCM	Real volume of N_2,SCCM
64	71.05	72.47
120	117.1	119.4
176	156.6	159.7
232	219.9	224.3
280	268.3	273.7
344	329	335.6
400	374.6	382.1
456	427.5	436.1
544	514.3	524.6
632	596.3	608.2
688	659.4	672.6
744	712	726.2
816	770.8	786.2
928	885.7	903.4
1024	989.6	1009
1216	1191	1215
1328	1284	1310
1520	1487	1517
1720	1702	1736
1832	1793	1829

Table A-2 Calibrating data of flow meter for SO_2

MFC Reading, SCCM	Calibrator Reading, SCCM	1000ppm SO_2,SCCM	1000ppm SO_2, mol/min	1.04% SO_2, SCCM	1.04% SO_2, mol/min	Pure SO_2, SCCM	Pure SO_2, mol/min
10.4	6.313	6.437	2.676E-07	6.419	2.775E-06	4.507	1.874E-04
20.8	22.06	22.49	9.351E-07	22.431	9.698E-06	15.75	6.548E-04
40.8	51.61	52.63	2.188E-06	52.478	2.269E-05	36.85	1.532E-03
60.8	83.9	85.55	3.556E-06	85.311	3.688E-05	59.90	2.490E-03
80	114	116.2	4.832E-06	115.917	5.012E-05	81.40	3.384E-03
100	145.3	148.2	6.159E-06	147.744	6.388E-05	103.7	4.313E-03
120	176.1	179.6	7.465E-06	179.062	7.742E-05	125.7	5.227E-03
125.6	185.2	188.8	7.851E-06	188.315	8.142E-05	132.2	5.497E-03
130.4	192.6	196.4	8.164E-06	195.839	8.467E-05	137.5	5.717E-03

Calibrating curve for N_2 were showed in Figure A-1, and calibration curve for 1000ppm, 1.04% and pure SO_2 were respectively showed in Figure A-2, A-3, and A-4.
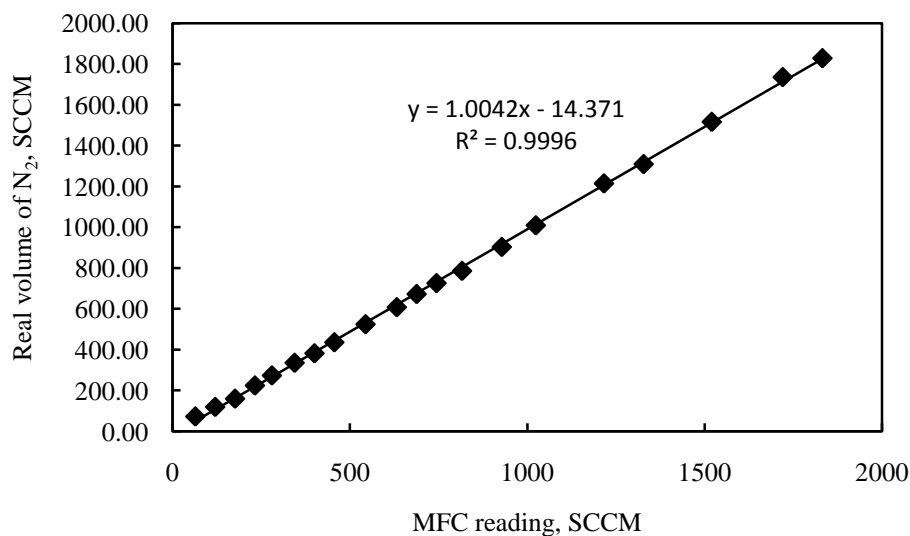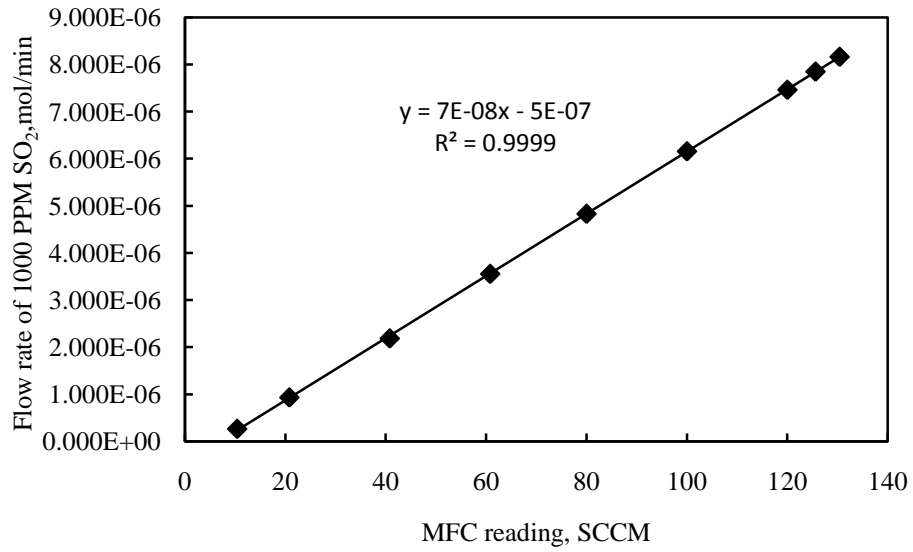

Figure A-1 MFC calibration –N_2 port

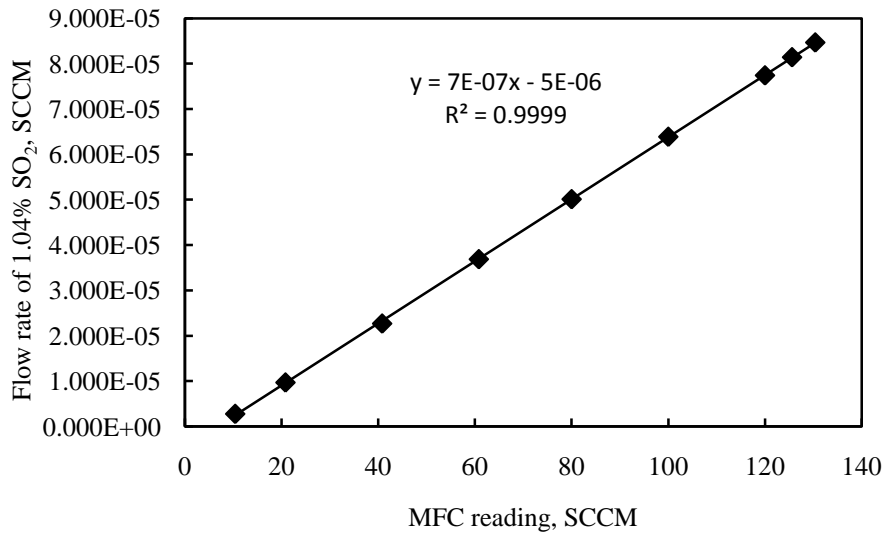Figure A-2 MFC calibration −1000PPM SO_2

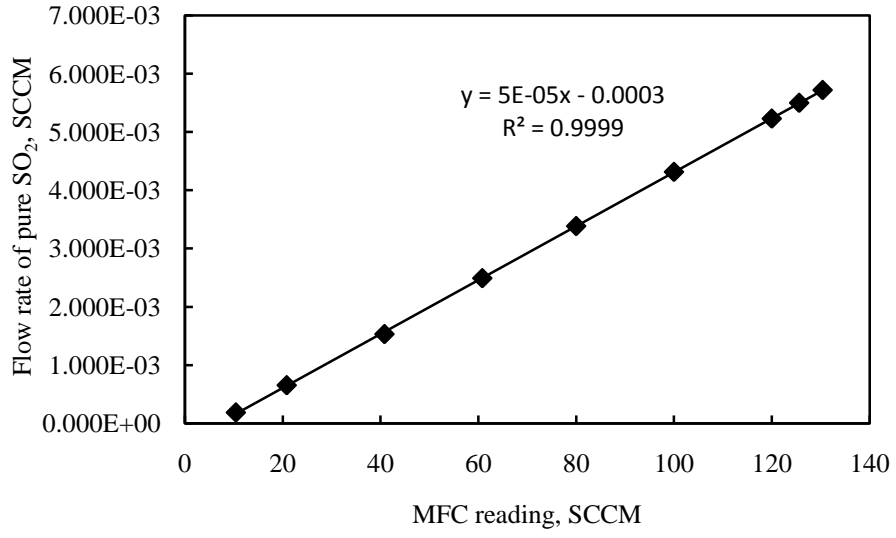Figure A-3 MFC calibration −1.04% SO_2

Figure A-4 MFC calibration –pure SO_2

APPENDIX B
RAW DATA OF EXPERIMENTS

1. Raw data of Iodine solubility in hydroiodic acid

Different concentrations of NaOH and $Na_2S_2O_3$ solution was prepared to satisfy different concentrations of protons and iodine in the iodine saturated hydroiodic. The experimental results are shown in Table B-1(a) and (b), which are the raw data of iodine solubility in hydroiodic acid.

2. Raw data of iodine solubility in HI-H$_2$SO$_4$ solution

Table B-2 listed the raw data of iodine solubility in HI-H$_2$SO$_4$ aqueous mixture.

Table B-1 Raw data for iodine solubility in hydroiodic acid

(a)

	HI Concentration, M	NaOH, M	V_{NaOH} ,mL / 1 mL(V_W)			$Na_2S_2O_3$, M	$V_{Na2S2O3}$, mL / 1 mL (V_W)		
			A	B	C		A	B	C
1	0.0765	0.01231	7.43	8.4	8.25	0.02005	4.00	4.80	4.60
2	0.0383	0.01231	4.23	5.5	4.55	0.00401	11.07	14.34	11.60
3	0.0191	0.01231	3.75	3.5	3.46	0.00401	7.90	9.37	8.60
4	0.00956	0.01231	3.25	2.35	1.8	0.00401	7.30	5.94	3.90
5	0.00478	0.01	1.90	1.2	1.7	0.00103	9.65	6.95	8.50
6	0.00239	0.01	1.47	1.83	1.37	0.00103	9.20	10.70	6.52
7	0.00120	0.01	1.32	0.8	1.15	0.00103	7.73	4.65	5.35
8	0	0.01	1.27	1.27	1.27	0.00103	7.34	7.34	7.34

(b)

	HI concentration, M	NaOH, M	V_{NaOH}, mL / 1 mL(V_W)		$Na_2S_2O_3$ M	$V_{Na2S2O3}$, mL /1 mL (V_W)	
			A	B		A	B
1	7.60	0.4995	8.80	9.00	0.3348	48.00	48.50
2	3.80	0.4995	7.60	7.00	0.3348	25.00	24.90
3	1.90	0.1	19.92	20.10	0.1618	21.95	22.85
4	0.950	0.1	10.55	10.66	0.1618	8.91	9.04
5	0.475	0.1	5.44	5.55	0.1618	3.87	3.98
6	0.238	0.1	2.86	2.74	0.02005	13.90	13.90
7	0.119	0.0123	12.50	12.35	0.02005	6.62	6.83
8	0.0594	0.0123	6.60	6.20	0.02005	3.41	3.35
9	0.0297	0.0123	4.00	3.81	0.02005	1.84	1.78

Table B-2 Raw data for iodine solubility in HI-H_2SO_4 aqueous solution

	HI concentration M	H_2SO_4 concentration M	NaOH, M	V_{NaOH}, mL / 1 mL(V_W)		$Na_2S_2O_3$ M	$V_{Na2S2O3}$, mL /1 mL (V_W)	
				A	B		A	B
1	0.950	0.472	0.4995	3.88	3.90	0.3348	9.05	4.41
2	0.475	0.236	0.1	9.90	10.40	0.1618	3.78	4.23
3	0.238	0.118	0.1	5.05	5.08	0.02005	13.67	13.72
4	0.119	0.0590	0.1	2.59	2.58	0.02005	6.45	6.48
5	0.0594	0.0295	0.0123	12.00	11.45	0.02005	3.85	3.40
6	0.0297	0.0147	0.0123	7.00	6.88	0.02005	2.10	2.50
7	0.0148	0.00737	0.0123	3.85	4.12	0.02005	1.10	1.55

3. Raw data of distribution ratio of iodine between hydroiodic acid and toluene

Table B-3 listed the raw data of iodine distribution between hydroiodic acid and toluene.

Table B-3 Raw data of distribution coefficient of iodine between hydroiodic acid and toluene

	[HI],M	NaOH, M	V_{NaOH} ,mL / 1 mL (V_W)		$Na_2S_2O_3$, M	$V_{Na2S2O3}$, mL /1 mL (V_W)		UV-Vis ABS at 497nm for toluene phase	
			A	B		A	B	A	B
1	7.54	0.5166	16.05	16.08	0.02005	9.76	10.23	0.383×6	0.506×6
2	3.77	0.5166	8.13	8.18	0.02005	23.18	22.79	0.384×36	0.372×36
3	1.89	0.5166	4.15	4.04	0.3348	1.85	1.79	0.468×96	0.518×96
4	0.943	0.5166	2.03	2.06	0.3348	1.65	1.63	0.344×396	0.239×576
5	0.471	0.5166	1.03	1.05	0.3348	1.03	1.10	0.431×576	0.437×576
6	0.236	0.1022	2.60	2.56	0.02005	9.78	10.05	0.893×396	0.887×396
7	0.118	0.1022	1.26	1.26	0.02005	4.98	4.96	0.993×396	0.993×396
8	0.0589	0.1022	0.66	0.70	0.02005	2.65	2.55	0.728×576	0.709×576
9	0.0295	0.1022	0.30	0.35	0.02005	1.30	1.33	1.062×396	1.038×396

where 0.383×6 means the ABS was 0.383 after the iodine toluene solution was diluted by 6 times.

4. Raw data for the Bunsen reaction rate in a semi-batch reactor

Table B-4 Raw data of the Bunsen reaction rate at 130.4 SCCM of 1000 ppm SO_2 with 150 mL volume of iodine–HI solution

Volume of water, L	Interval time, mins	NaOH, M	V_{NaOH} ,mL / 1 mL (V_W)		$Na_2S_2O_3$, M	$V_{Na2S2O3}$, mL /1 mL (V_W)	
			A	B		A	B
0.15	0	0.1	2.41	2.40	0.03269	4.70	4.70
0.15	158	0.1	2.80	2.75	0.03269	4.10	4.10
0.148	150	0.1	3.10	3.10	0.03269	3.60	3.60
0.145	207	0.1	3.52	3.52	0.01130	8.08	8.05
0.142	129	0.1	3.84	3.80	0.01130	6.73	6.65
0.14	120	0.1	4.10	4.05	0.01130	5.40	5.40
0.138	120	0.1	4.40	4.40	0.01130	4.10	4.00
0.129	122	0.1	4.88	4.80	0.01130	2.40	2.40
0.126	120	0.1	5.10	5.04	0.01130	1.12	1.12
0.122	97	0.1	5.34	5.32	0.01130	0.00	0.00

Table B-5 Raw data of the Bunsen reaction rate at 129.6 SCCM of 1.04% SO_2

Volume of water, L	Interval time, mins	NaOH, M	V_{NaOH} ,mL / 1 mL (V_W)		$Na_2S_2O_3$, M	$V_{Na2S2O3}$, mL /1 mL (V_W)	
			A	B		A	B
0.15	0	0.1	2.43	2.48	0.01130	13.30	13.26
0.15	77	0.1	4.20	4.20	0.01130	5.48	5.48
0.147	43	0.1	5.10	5.03	0.01130	1.46	1.54
0.145	13	0.1	5.38	5.38	0.01130	0.00	0.00

Volume of water, L	Interval time, mins	NaOH, M	V_{NaOH} ,mL / 1 mL (V_W)		$Na_2S_2O_3$, M	$V_{Na2S2O3}$, mL /1 mL (V_W)	
			A	B		A	B
0.1	0	0.1	5.57	5.55	0.03296	19.00	18.90
0.1	5	0.1	8.10	8.05	0.03296	14.89	14.75
0.098	5	0.1	10.65	10.6	0.03296	10.90	10.80
0.096	5	0.1	13.18	13.20	0.03296	6.90	6.90
0.094	7	0.1	17.70	17.70	0.03296	0	0

Table B-7 Raw data of the Bunsen reaction rate in presence of toluene

(a)

Interval time, mins	Volume of water, mL	NaOH , M	V_{NaOH}, mL / 1 mL (V_W)		$Na_2S_2O_3$, M	$V_{Na2S2O3}$, mL /1 mL (V_W)		Volume of toluene, mL	UV-Vis ABS at 497nm
			A	B		A	B		
0	60	0.1	0	0	0.01130	0.00	0.00	120	0.980×111
38	60	0.1	2.4	2.4	0.01130	3.50	3.50	120	0.746×101
47	58	0.1	5	5	0.01130	1.10	1.10	119.9	0.592×51
47	56	0.1	7.6		0.01130	0.00		119.7	0.249×51
51	55	0.1	8.8	8.76	0.01130	0.00	0.00	108.5	0.219

(b)

Interval time, mins	Volume of toluene, ml	UV-Vis ABS at 497nm
36	119.8	0.386×51
11	119.7	0.249×51
15	119.6	0.100×51
10	119.5	0.183×6
9	118.5	0.575
7	113.5	0.399
10	108.5	0.219

where, 0.980×111 means the ABS is 0.980 after the toluene phase was diluted by 111times.

APPENDIX C

NMR SPECTRA FOR IODINE TOLUENE SOLUTION

Figure C-1, C-2 and C-3 are respectively NMR spectrum for pure toluene, iodine toluene solution and iodine toluene solution after contacting with 7.6M hydroiodic acid for 24hrs. Three same spectra showed that there was no side reaction between toluene and iodine even in presence of strong acid of 7.6M HI solution.

Integral

ppm

7.80137
7.79873
7.78446
7.77089
7.76848
7.70348
7.68859

4.7595

3.0000

2.87000
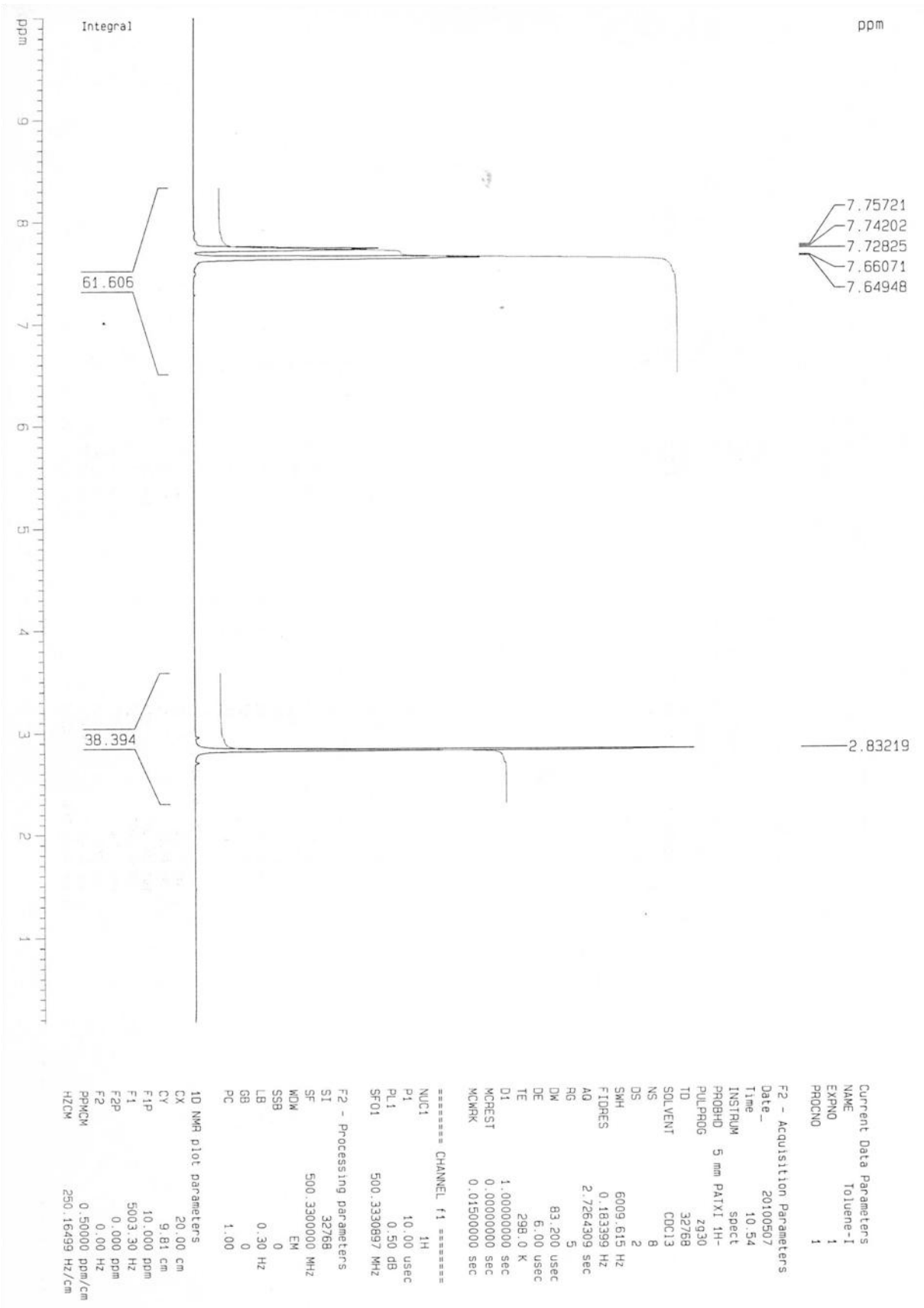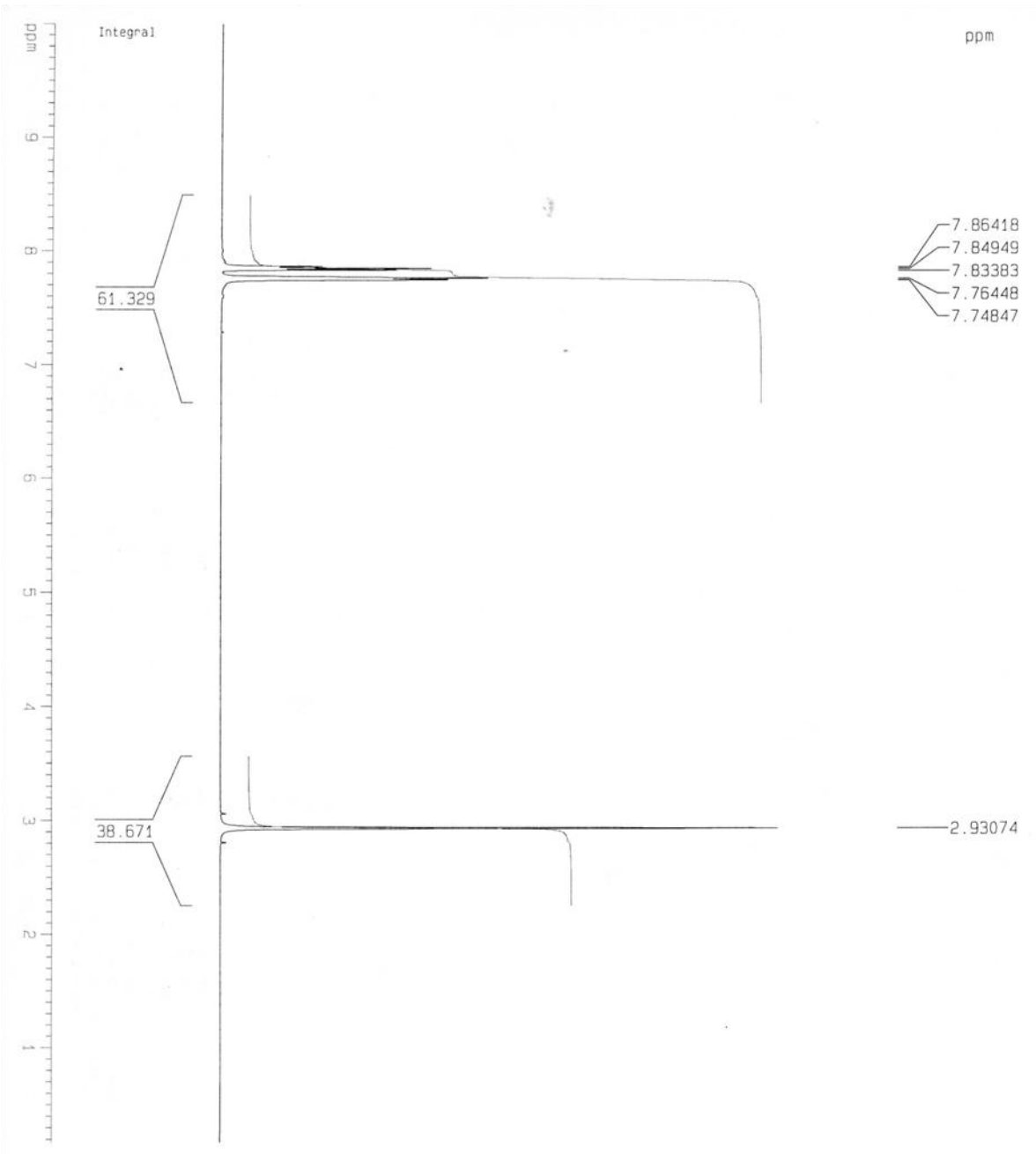
Figure C-1 NMR spectrum of pure toluene
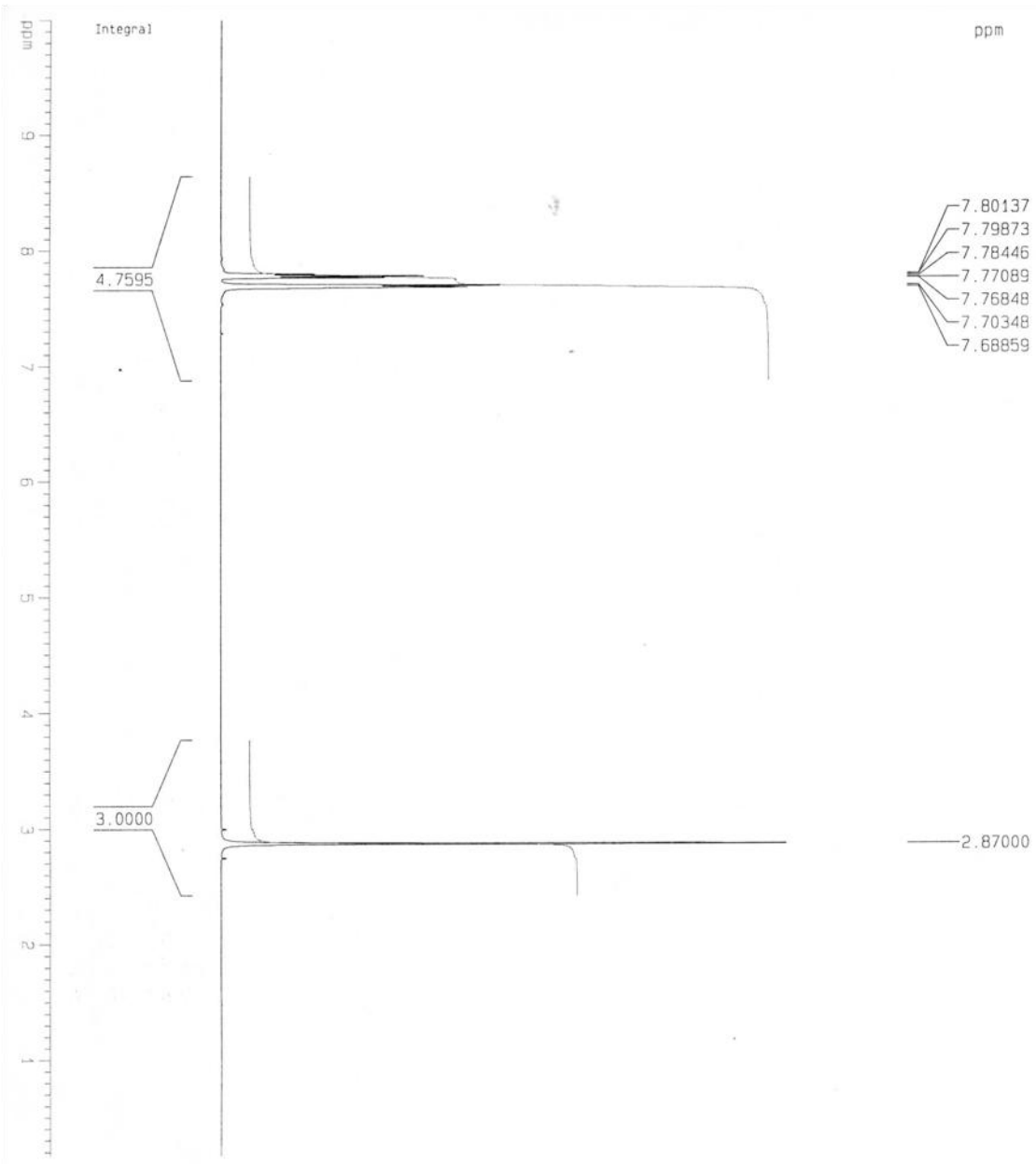
Current Data Parameters
NAME   Toluene
EXPNO   1
PROCNO   1

F2 - Acquisition Parameters
Date_   20100507
Time   10.19
INSTRUM   spect
PROBHD   5 mm PATXI 1H-
PULPROG   zg30
TD   32768
SOLVENT   CDCl3
NS   8
DS   2
SWH   6009.615 Hz
FIDRES   0.183399 Hz
AQ   2.726409 sec
RG   5
DW   83.200 usec
DE   6.00 usec
TE   298.0 K
D1   1.00000000 sec
MCREST   0.00000000 sec
MCWRK   0.01500000 sec

======== CHANNEL f1 ========
NUC1   1H
P1   10.00 usec
PL1   0.50 dB
SFO1   500.3330897 MHz

F2 - Processing parameters
SI   32768
SF   500.3300000 MHz
WDW   EM
SSB   0
LB   0.30 Hz
GB   0
PC   1.00

1D NMR plot parameters
CX   20.00 cm
CY   9.81 cm
F1P   10.000 ppm
F1   5003.30 Hz
F2P   0.000 ppm
F2   0.00 Hz
PPMCM   0.50000 ppm/cm
HZCM   250.16499 Hz/cm

ppm

Integral

61.606

38.394

Figure C-2 NMR spectrum of iodine toluene solution

Figure C-3 NMR spectrum for iodine toluene solution after contacting with 7.6M HI hydroiodic acid for 24 hours

APPENDIX D
ANALYTICAL METHODS

1. Determination of the proton concentration in water phase

The products of the Bunsen reaction are HI and H_2SO_4 with molar ratio 2:1. Both of them are strong acids and tend to be ionized in water phase as soon as they are produced. Therefore, if the proton in water phase is determined, the iodide and sulfate ion can be deduced according to the stoichiometric proportion of the Bunsen reaction. The simplest way to determine the concentration of proton in water phase is acid-base titration. The proton can be titrated by standard solution of sodium hydroxide using phenolphthalein as indicator, and the chemistry is:

$$H^+ + OH^- \rightarrow H_2O$$
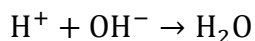
The experimental procedures are followed as below. M_{NaOH} g NaOH was weighed out with electronic balance and then was added into a dry and clean volumetric flask with volume $V_{V.F}$ L. The weighed NaOH was dissolved in less than $V_{V.F}$ L of water and then the flask was filled to the calibration mark by the careful addition of the remaining water. The concentration of NaOH standard solution obtained was in the range of 0.01~0.6M depending on the concentration of protons in titrated sample. The burette was filled to 0 mL mark with NaOH standard solution. V_W mL of water phase was withdrawn by a pipette into 100 mL Erlenmeyer flask. And then five drops of phenolphthalein were added in it. The NaOH standard solution was added slowly from burette to the water phase being titrated. The first last appearance of the pink was taken to the equivalence point of the titration. The volume of NaOH standard solution was recorded as V_{NaOH} mL. Finally, the proton concentration in water phase can be calculated by the following equation:

$$[H^+] = \frac{M_{NaOH} \ V_{NaOH}}{40 \times V_{V.F.} \times V_W}$$

where

[H^+]: Concentration of proton in water phase, mol L^{-1}

M_{NaOH}: The mass of NaOH, g

V_{NaOH}: Volume of NaOH standard solution, mL

$V_{V.F.}$: Volume of volumetric flask, L

V_W: Volume of water phase being titrated, mL

2. Determination of the concentration of iodine in water phase

As discussed in section 2.4, HI can increase the iodine solubility in water phase. Therefore, the water phase will dissolve more amount of iodine with more HI produced by the Bunsen reaction. The classic analytical method to determine the iodine concentration in water is iodometry using thyodene (Fisher) as indicator. The chemistry is:

$2 \ S_2O_3{}^{2-} \ (aq) + I_2 \ (aq) \rightarrow S_4O_6{}^{2-} \ (aq) + 2 \ I^- \ (aq)$
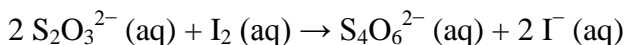
The experimental procedures are followed as below. $M_{Na_2S_2O_3}$ g $Na_2S_2O_3$ was weighed out by electronic balance and then was added into a dry and clean volumetric flask with volume $V_{V.F}$ L. The weighed $Na_2S_2O_3$ was dissolved in less than $V_{V.F}$ L of water and then the flask was filled to the calibration mark by the careful addition of the remaining water. The concentration of $Na_2S_2O_3$ standard solution was in the range of 0.01~0.4M depending on the concentration of iodine in titrated sample. The burette was filled to 0 mL mark with $Na_2S_2O_3$ standard solution. A pipette was used to withdraw V_W mL of water phase into 100 mL Erlenmeyer flask. Then a small amount of thyodene (indicator) was added into it. The $Na_2S_2O_3$ standard solution was added

slowly from burette to the water phase being titrated. The end point was reached when the water phase in the Erlenmeyer flask turns to colorless from blue. The volume of $Na_2S_2O_3$ standard solution $V_{Na_2S_2O_3}$ mL was recorded. Finally, the iodine concentration in water phase can be calculated by the following equation:

$$[I_2] = \frac{M_{Na_2S_2O_3} V_{Na_2S_2O_3}}{158.11 \times V_{V.F.} \times V_W}$$

where

$[I_2]$: Concentration of iodine in water phase, mol L^{-1}

$M_{Na_2S_2O_3}$: The mass of $Na_2S_2O_3$, g

$V_{Na_2S_2O_3}$: Volume of $Na_2S_2O_3$ standard solution, mL

$V_{V.F.}$: Volume of volumetric flask, L

V_W: Volume of water phase being titrated, mL

3. Determination of the molar extinction coefficient of iodine in toluene phase and iodide in water phase

A UV-Vis spectrophotometer is used to determine the concentration of iodide in the water phase and iodine in the toluene phase according to the Beer-Lambert law.

$$A = -\log_{10} \frac{I}{I_0} = \varepsilon \cdot l \cdot c$$

where

A: Absorbance

I_0 and I: Intensity of incident light and that of transmitted light, respectively

ε: Molar extinction coefficient, L mol^{-1} cm^{-1}

l: Path length, cm

c : Concentration of the absorbing species in materials

3.1 Molar extinction coefficient of iodine in toluene

Figure D-1 is the UV-Vis absorbance spectrum of iodine toluene solution $(2.1 \times 10^{-4}$ M). Two absorbance peaks for iodine in toluene within 200-700 nm are at 315 nm and 497 nm. The peak at 275 nm belongs to toluene. The peak at 497 nm is used to determine the concentration of iodine because the absorbance of iodine at 315 nm is too strong and close to the absorbance peak of toluene at 275 nm. A calibration curve of iodine in toluene was determined from 7 deferent concentrations of iodine toluene solutions as shown in Figure . Excellent linearity was observed for the plotting of absorbance over concentration. According to Beer-Lambert law ($A = \varepsilon lc$), the slope of linear calibration curve can give the molar extinction coefficient (ε) of iodine in toluene. The experiment was repeated for four times and the average molar extinction of iodine in toluene is $(1.03 \pm 0.09) \times 10^{3}$ L mol^{-1} cm^{-1} at 497 nm (Table D-1).
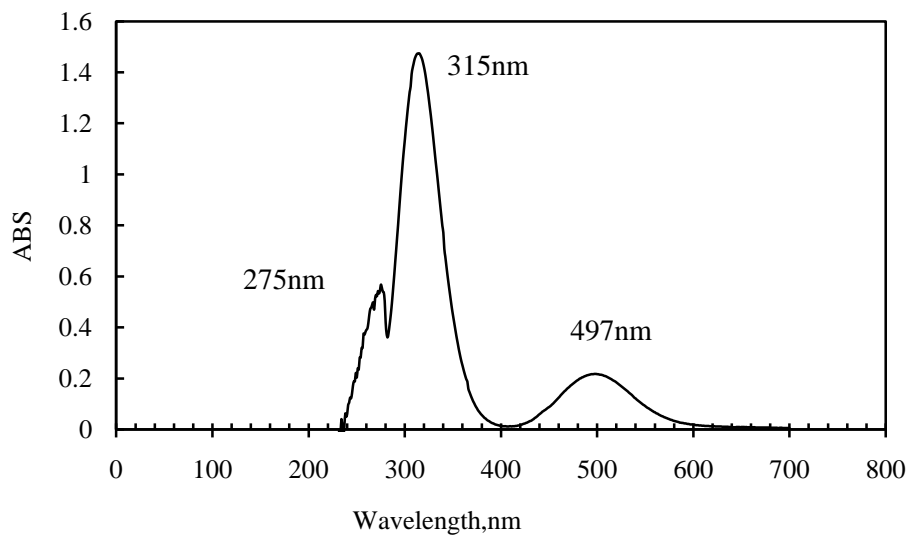
Figure D-1 Absorption spectrum of 2.1×10^{-4} M iodine toluene solution
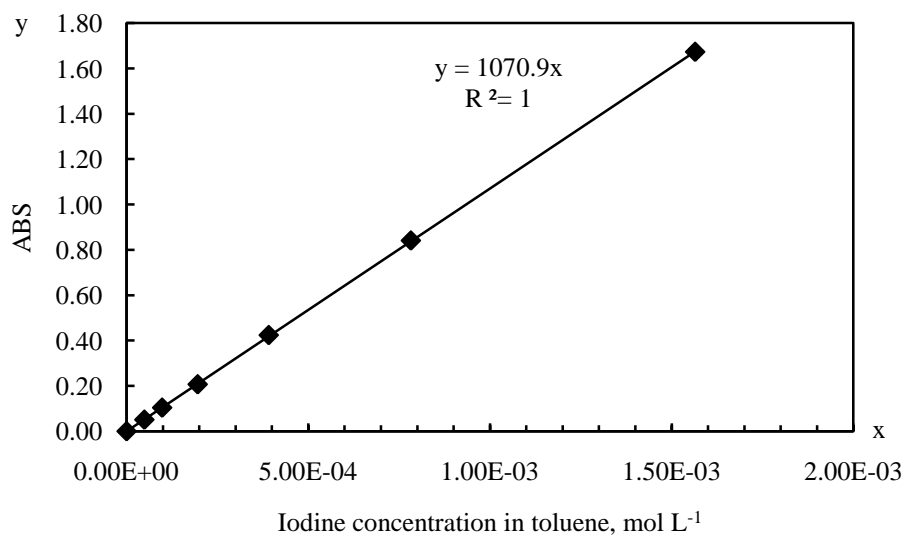

Figure D-2 UV-Vis calibration curve of iodine in toluene

Table D-1 Molar extinction coefficient of iodine in toluene

No.	Wavelength nm	Extinction coefficient (ε, L mol^{-1} cm^{-1})	Coefficient of determination	Uncertainty (L mol^{-1} cm^{-1})
1	497	1071	1	2
2	497	1036	1	1
3	497	1070	1	2
4	497	942	1	1
Average	497	1.03×10^3		0.09×10^3

3.2 Molar extinction coefficient of iodide in water

In the same way, the molar extinction coefficient of iodide in water was determined. Figure D-3 is the UV-Vis absorbance spectrum of iodide solution (1.6×10^{-5} M).There is one maximum absorbance peak for iodide in water at wavelength 226nm. One of calibration curves is shown in Figure D-4. The average molar extinction coefficient is 1.34×10^4 L mol^{-1} cm^{-1} (Table D-2).
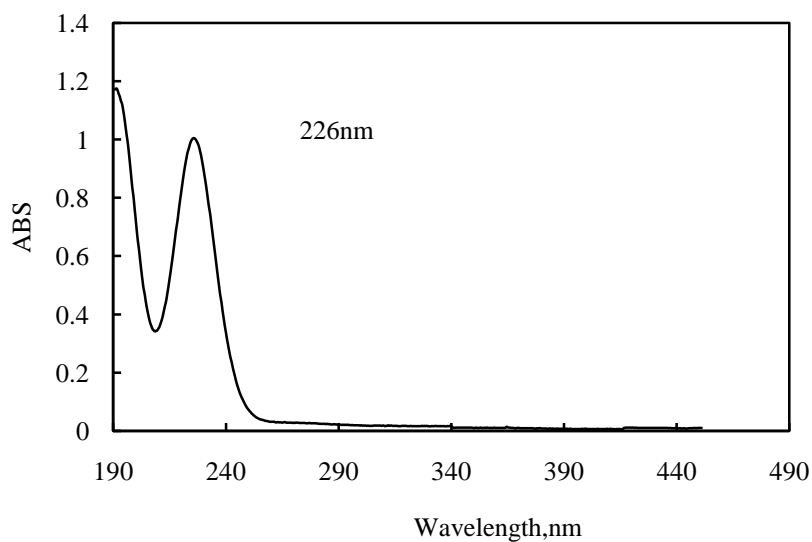

Figure D-3 Absorption spectrum of 1.6×10^{-5} M iodide aqueous solution

$y = 13474x$
$R^2 = 0.9994$
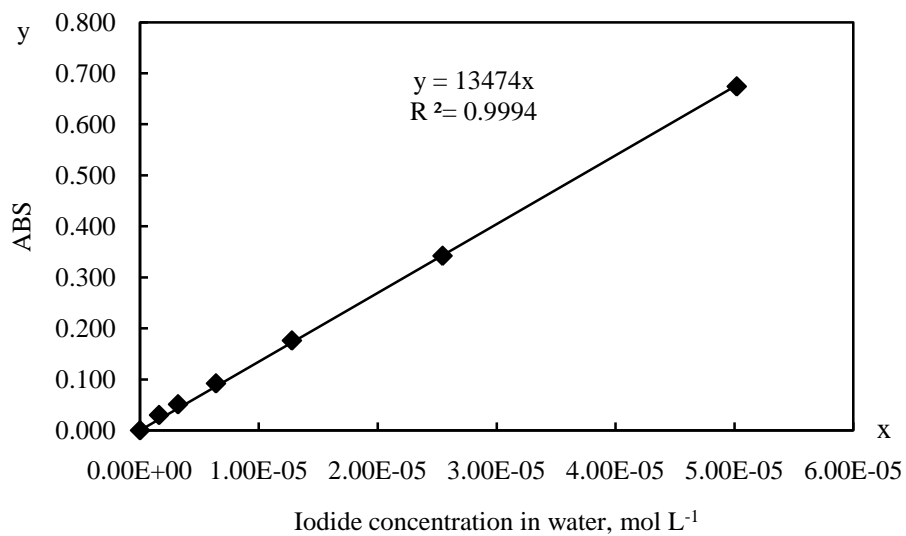
Iodide concentration in water, mol L^{-1}

Figure D-4 UV-Vis calibration curve of iodide in water

Table D-2 Molar extinction coefficient of iodide in water

No.	Wavelength (nm)	Extinction coefficient (ε, L mol^{-1} cm^{-1})	Coefficient of determination	Uncertainty (L mol^{-1} cm^{-1})
1	226	13455	0.9981	299
2	226	13474	0.9994	120
3	226	13447	0.9998	79
4	226	13215	0.9999	76
5	226	12974	0.9999	76
Average	226	1.34×10^4		0.03×10^4

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