5-2010

LIQUID-LIQUID EQUILIBRIUM FOR IODINE-HYDROIODIC ACID-WATER MIXTURES AT ELEVATED TEMPERATURES AND PRESSURES FOR THE SULFUR-IODINE CYCLE

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Recommended Citation

Mena, Sarah, "LIQUID-LIQUID EQUILIBRIUM FOR IODINE-HYDROIODIC ACID-WATER MIXTURES AT ELEVATED TEMPERATURES AND PRESSURES FOR THE SULFUR-IODINE CYCLE" (2010). *All Theses*. 760.
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LIQUID-LIQUID EQUILIBRIUM FOR IODINE-HYDROIODIC ACID-WATER MIXTURES AT ELEVATED TEMPERATURES AND PRESSURES FOR THE SULFUR-IODINE CYCLE

A Thesis
Presented to
the Graduate School of
Clemson University

In Partial Fulfillment
of the Requirements for the Degree
Master of Science
Chemical Engineering

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by
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May 2010

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ABSTRACT

An alternative scenario to the overdependence on fossil fuels is the use of thermochemical cycles to split water into hydrogen and oxygen. The Sulfur-Iodine (SI) cycle, developed at General Atomics in the mid 1970s, is a leading candidate of international interest for the centralized production of hydrogen from nuclear and/or solar power. For a comprehensive assessment of the SI cycle, thermodynamic data for I_2-HI-H_2O mixtures at elevated temperatures and pressures have been identified as a basic research need.

The focus of this study was liquid-liquid equilibrium (LLE) measurements for the above system. To carry out the measurements, a continuous-flow apparatus (CFA) with corrosion-resistant wetted surfaces rated for 350°C and 150 bar was designed and constructed. In the course of the development of this apparatus, tantalum and its tungsten alloys were found to be capable of withstanding the aggressive chemicals and conditions.

Using our CFA, the first observations for the LLE for the binary I_2-H_2O above 225°C are presented, with measurements being made to 300°C and 70 bar. Based on these results, we estimate the upper critical solution temperature for this binary to be 310-315°C. For the ternary I_2-HI-H_2O, phase boundaries for the LLE in the HI-lean region of the ternary diagram were mapped at 160 and 200°C. In addition, equilibrium-tie lines were determined at 160°C. Phase compositions for the water-rich side were accurately determined by titration, but for the I_2-rich side, they were estimated from the overall mass balance. Our results indicate that current models are still inadequate for prediction of the LLE phase behavior for this highly nonideal system.

DEDICATION

To my father, Carlos Alfredo Mena and to the memory of his father, Leonardo Mena.

ACKNOWLEDGMENTS

I would like to express my appreciation to the following people for their contribution to this research:

My advisor, Dr. Mark Thies, for his bravery in initiating a research project with so many technical difficulties, from which I've learned tremendously.

Dr. David Bruce, for his mentorship, constant guidance and advice. His sharp and accurate ideas were the solutions for many problems.

Dr. John O'Connell, Dr. Maximilian Gorensek and James Murphy for their valuable modeling effort and their help finding the relevant literature for the project.

Eduardo Gallas Cervo, for showing me what a real researcher is. For teaching me the manual skills I needed for the project and for his insight during the development of the experiments, and, in the end, for patiently reviewing this document. Without his input, I would not have accomplished as much.

The rest of the Thies research group, Ward, Sourabh, Halil, David and Julian, for their help, the heavy-lifting work, the meals shared, the rich conversations and their continuous support; and to Rebecca Alway-Cooper for her friendship during my time at Clemson. They have influenced my life far beyond my academic education.

Dr. Douglas Hirt and the Department of Chemical Engineering, Jane Jacobi and the SEAGEP fellowship for their financial support.

Phil Landreth and Jeff Holliday, for their amazing work building the tantalum parts and all the other gadgets that allowed the correct operation of the apparatus.

And finally, to my family, for their moral and economic support and for being my greatest blessing.

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CHAPTER I

INTRODUCTION

The shortage of fossil fuels, as well as the negative impact of their burning on the environment, has motivated the scientific community to look for other technologies to satisfy the world's increasing energy demands. Hydrogen is a strong candidate to become the energy carrier of a sustainable economy that will reduce dependence on liquid hydrocarbons. However, before hydrogen can be incorporated as a fuel, several technological problems need to be resolved in the areas of production, storage, transportation, delivery and conversion. The research discussed here deals with the methods for hydrogen production.

Hydrogen can be produced using a variety of methods, including steam reforming [1] [2], electrolysis [3], biological processes [4], and thermochemical cycles. Feed-stocks vary from traditional fuels like coal and methane to biomass and water. Thermochemical water-splitting is a promising technology for obtaining hydrogen, which is currently under research. Early work suggests thermochemical processes have the potential to be highly energy-efficient, and they produce oxygen as the only byproduct. Moreover, the hydrogen produced is free of trace contaminants, which are known to degrade fuel-cell performance.

THERMOCHEMICAL WATER-SPLITTING CYCLES

The direct thermolysis of water occurs at temperatures exceeding 1720°C [5], as shown in equation 1.1:

$$H_2O \rightarrow H_2 + \tfrac{1}{2}O_2 \quad (2220\ ^\circ C) \qquad 1.1$$

At 2220 °C and atmospheric pressure, the reaction will reach slightly over 4% completion [5]. A thermochemical water-splitting cycle will accomplish reaction 1.1 at much lower temperatures, which leads to a more efficient process.

Thermochemical water-splitting is the process of converting water into hydrogen and oxygen through a series of chemical reactions, where heat and water are the only overall inputs to the system as shown in Figure 1.1.

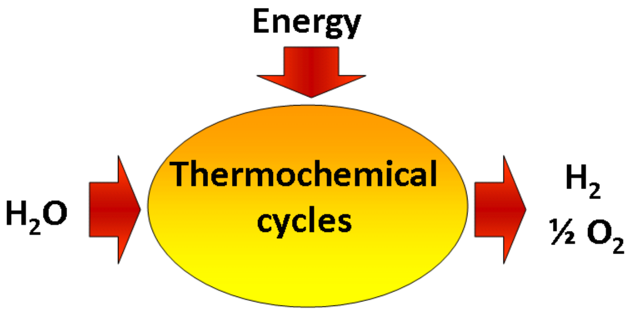

Figure 1.1 Simplified representation of a thermochemical cycle

Thermochemical cycles operate similar to a heat engine: Heat is input into the cycle via one or more endothermic reactions occurring at high temperatures while low heat is rejected from the cycle via one or more low temperature exothermic reactions [6].

There are many groups of reactions that could accomplish the process depicted in Figure 1.1. A study funded by the Department of Energy (DOE) [7] evaluated the feasibility of 115 cycles. Two pure thermochemical cycles were rated far above the others: The adiabatic UT-3 and the sulfur-iodine (SI) cycle. Along with them a hybrid cycle, the hybrid-sulfur (HS) [8] cycle (or Westinghouse cycle) was also found to be of interest. A short description of these three cycles is given below.

ADIABATIC UT-3 THERMOCHEMICAL CYCLE

The adiabatic UT-3 cycle was developed at University of Tokyo in the late 1970s. It is based on four reaction steps [9]:

$$CaBr_2(s)+H_2O(g)\xrightarrow{760^\circ C}CaO(s)+2HBr(g) \qquad 1.2$$

$$CaO(s)+Br_2(g)\xrightarrow{572^\circ C}CaBr_2(s)+\tfrac{1}{2}O_2(g) \qquad 1.3$$

$$Fe_3O_4(s)+8HBr(g)\xrightarrow{220^\circ C}3FeBr_2(s)+4H_2O(g)+Br_2(g) \qquad 1.4$$

$$3FeBr_2(s)+4H_2O(g)\xrightarrow{560^\circ C}Fe_3O_4(s)+6HBr(g)+H_2(g) \qquad 1.5$$

If the cycle is operated without the condensation of water, all reactants and products involved are solid or gases at the conditions of operation [9]. The reactions take place in packed bed reactors that contains the solid species where the gases flow and react [6]. The efficiency of hydrogen generation for this process is predicted to be 35%-40%. Higher efficiencies of 45%-49% are predicted when operated in co-generation with electricity [6].

SULFUR-IODINE CYCLE

The SI cycle was developed at General Atomics in the mid 1970s and consists of three reactions [10]:

$$2H_2O + I_2 + SO_2 \xrightarrow{120°C} H_2SO_4 + 2HI \qquad 1.6$$

$$2HI \xrightarrow{320°C} H_2 + I_2 \qquad 1.7$$

$$H_2SO_4 \xrightarrow{830°C} H_2O + SO_2 + \tfrac{1}{2}O_2 \qquad 1.8$$

Although the cycle has been extensively studied and the overall process is generally well-defined, there is still ambiguity about the best method for performing reaction 1.7, because of the purification needed for the HI coming from reaction 1.6. The flow sheet for the process proposed in 1980 indicated that the production of hydrogen can be accomplished at 52% efficiency [6], which is the highest efficiency reported for any water-splitting process.

HYBRID CYCLES

Hybrid cycles are water-splitting processes that involve one electrolytic step in addition to one or more thermochemical reactions. The most extensively studied hybrid cycle is the hybrid-sulfur (HS) [8] cycle also known as the Westinghouse cycle, that consists of two reactions:

$$H_2SO_4 \xrightarrow{850°C} SO_2 + H_2O + \frac{1}{2}O_2 \tag{1.9}$$

$$SO_2 + 2H_2O \xrightarrow{77°C} H_2SO_4 + H_2 \tag{1.10}$$

Note that equation 1.9 of the HS cycle is the same 1.8 for the SI cycle. The difference is that the HS process closes the cycle with the 1.10 electrolytic step where hydrogen is produced. The drawback of hybrid cycles is that they are uneconomical on a large scale. Energy-efficient electrochemical processes require thin membranes between the anode and cathode, which are limited to small electrode areas [6].

COMPARISON AMONG UT-3, SI AND HS PROCESSES

A table comparing the main advantages and disadvantages of the three processes UT-3, SI, and HS, prepared from the comments used to score each cycle in the DOE study [6], is presented in Table 1.1

Table 1.1 Comparison the UT-3, SI and HS cycles [7]

	Advantages	Disadvantages
UT-3	▪ Solids remain in fixed beds, with only gases being transported ▪ Fully flow-sheeted ▪ Reported efficiency of 40% ▪ Cycle operated on pilot-plant scale	▪ Cannot be operated in steady-state without moving solids ▪ Beds of solids must be periodically shifted from one temperature to another ▪ High-temperature reaction has a positive free energy value at the operating conditions ▪ Operated at temperatures close to the melting point of bromides, which could cause blockage of the beds
	Comments: Only cycle that has been studied on large scale. Information for some parts of the cycle is not available in the open literature. $CaBr_2$ is a liquid at 750°C, which is the temperature of the reaction in the one it is consumed.	
SI	▪ All fluid phases ▪ High-temperature step can be coupled to a nuclear reactor ▪ Minimal side reactions ▪ Fully flow-sheeted ▪ Cycle operated at bench scale ▪ Highest reported efficiency 52% ▪ H_2SO_4 decomposition demonstrated using solar energy ▪ H_2 generated at high pressure, so its compression is not needed	▪ The concentration of H_2SO_4 and HI from the Bunsen reaction are both capital- and energy-intensive processes [11] ▪ No agreement about the most efficient alternative for the HI decomposition or its energy requirements [12]
	Comments: Extensive work was and is being carried out in other countries (Germany, France, Japan, Korea, India, and Italy)	
HS	▪ All fluid phases ▪ Two reactions ▪ Thermodynamic properties well-known ▪ Fully flow-sheeted ▪ High-temperature step can be coupled to a nuclear reactor ▪ Cycle operated at Bench and pilot plant scale ▪ H_2SO_4 decomposition demonstrated using solar energy	▪ Scale-up problems inherent to electrochemical processes
	Comments: There is probably little room for improvement	

In 2005, the Nuclear Hydrogen Initiative chose the SI cycle as the primary thermochemical cycle for demonstration, when coupled to an advanced, high-temperature nuclear reactor for the centralized production of hydrogen. In addition, it is the focus of this thesis. Therefore it is explained in more detail below.

SI CYCLE FOR THE PRODUCTION OF HYDROGEN

The SI cycle has been extensively studied in the past four decades. Early researchers rejected it because of the problems encountered with the separation of H_2SO_4 from HI in reaction 1.6, which is called the Bunsen reaction. However, the discovery of a fortuitous separation of the acidic products into two phases in the presence of excess water and iodine, as shown in Figure 1.2, spurred further research. This mechanical separation of the acids without the consumption of energy was a key factor of the original process design [10].

Further issues were revealed by Engels et al. [11], who performed an analysis of the original process in 1986 and showed that capital and energy-intensive procedures were needed for the separation and decomposition of the HI from the unreacted water and iodine present in the lower liquid phase from the Bunsen reaction.

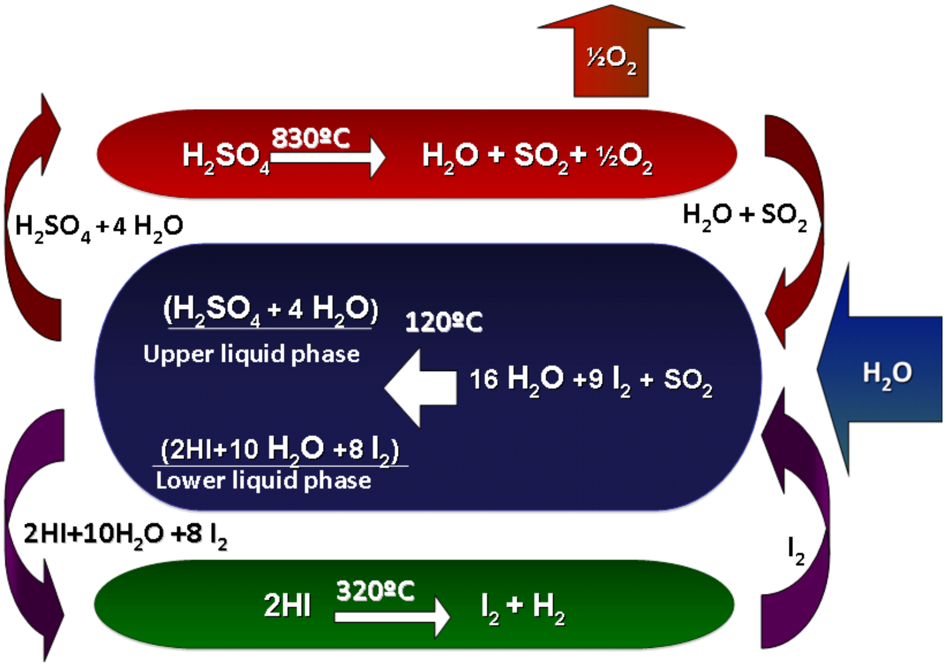

Figure 1.2 SI cycle, with true molar quantities being shown. Excess water and iodine in the Bunsen reaction (middle) result in the natural separation of the acidic products.

The main challenges regarding the separation and decomposition steps are (1) the slow and incomplete reaction of decomposition from HI into hydrogen [13] that is limited by the chemical equilibrium and does not exceed 22.4% at 450°C [14]; (2) the large amounts of water and iodine present in the lower liquid phase coming from the Bunsen reaction, which introduce a high calorific demand to the mixture [13]; and (3) the formation of an HI-H_2O azeotrope at ~15% mol HI, which prevents one from obtaining high concentrations of HI [13], because high hydrogen production rates could only be obtained from a mixture with concentrations of HI above the azeotrope [15].

In an effort to increase the efficiency of the cycle, several options to perform the HI separation have been proposed, including an extractive distillation column using phosphoric acid [10], a reactive distillation column [16], the use of membrane reactors using hydrogen ceramic permselective membranes [17], and the use of ion-exchange membranes to increase HI molality [18]. The reactive distillation column is one of the leading candidates.

Reactive distillation, which was proposed by researchers at RWTH-Aachen [19], is a process that separates HI from excess water and iodine while simultaneously decomposing the HI. Hydrogen is obtained as the overhead product, while iodine is separated as a bottom product. A schematic of the column is shown in Figure 1.3. The concentrations presented are a rough estimate of a possible set of operating conditions for the column, as reported in the Final Project report by Summers at NERI [20]. An interesting behavior expected in the column [13] is the change from the thermodynamic non-favored reaction 1.11 to the thermodynamically favored reaction 1.12, where iodine is in the liquid phase.

$$2HI_{(g)} \rightleftharpoons H_{2(g)} + I_{2(g)} \qquad \Delta G = 11 \,{}^{kJ}\!/_{mol} \qquad 1.11$$

$$2HI_{(g)} \rightleftharpoons H_{2(g)} + I_{2(l)} \qquad \Delta G = -29 \,{}^{kJ}\!/_{mol} \qquad 1.12$$

The flow sheet analysis for the HI decomposition was found to be challenging [21], and additional thermodynamic data for the I_2-HI-H_2O system were identified as a basic need for the complete assessment of the column.

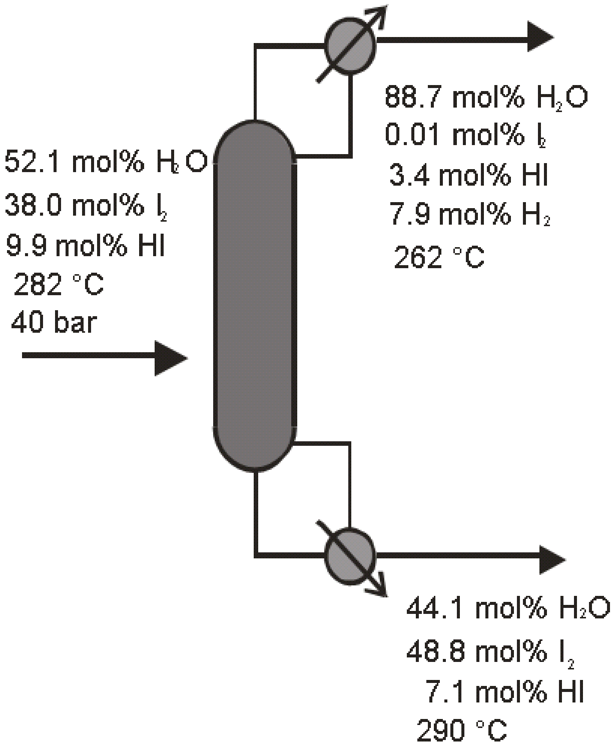

Figure 1.3 Schematic of the reactive distillation column. Data are estimates from Summers [20].

The chemical systems involved in the column exhibit highly non-ideal thermodynamic behavior that is poorly understood. For instance, the binary I_2-H_2O is a highly immiscible system, the binary HI-H_2O is strongly electrolytic and forms a maximum boiling point azeotrope, and the ternary I_2-HI-H_2O has two separate regions of immiscibility [22]. Data for these systems is either limited or nonexistent, as shown in Table 1.2. For the liquid-liquid equilibrium (LLE) of the binary I_2-H_2O, for example, eleven points in the range of 127-225°C were measured by Kracek [23] in 1931, and the only other measurements since then were 4 points in the range of 120 to 150°C performed by Parsly [24] in 1970. For the vapor-liquid equilibrium (VLE) of the ternary I_2-HI-H_2O system, measurements by Engels [16] in 1985 were done in a static phase-equilibrium apparatus. This led to the undesired decomposition of HI into hydrogen and iodine, which prevented the determination of thermodynamic equilibrium. A recent study by Larousse et al. [25] was also carried out in a closed system at temperatures ranging from 120 to 270°C and pressures up to 30 bar (~435 psi), where the decomposition of HI was also observed. The only liquid-liquid equilibrium (LLE) data for the ternary system consist of 23 composition estimates by O'Keefe [10] in 1984, using a nonsampling synthetic method, at temperatures from 24 to 152°C.

The lack of measurements for these systems is because of the technical difficulties related to the corrosive nature of the chemicals involved at high temperatures and pressures. This added challenge also explains the choice of

Table 1.2 Published Experimental Data for the I_2-HI-H_2O System. Reprinted with permission from ref [12]. Copyright 2009 Elsevier.

System	Data Type	Author Year Source	Data Points	Temperature Range (°C)	Composition Range
HI-H_2O	VLE	Bates 1919	8[a]	$T=25$	$0.10 < x_{HI} < 0.15$
		Hasse 1963	21	$T=25$	$0.08 < x_{HI} < 0.35$
		Wüster 1979	75	$78<T<281$	$0.02 < x_{HI} < 0.19$
		CRC 1976	1	$T=127$	$x_{HI} = 0.16$
		Sako 1981	30	$100<T<127$	$0.01 < x_{HI} < 0.17$
		Doizi 2007	8	$25<T<113$	$0.16 < x_{HI} < 0.222$
		Hodotsuka 2008	31[a]	$102<T<183$	$0.04 < x_{HI} < 0.16$
		Liberatore 2008	34	$101<T<144$	$0.04 < x_{HI} < 0.22$
		Engels 1986	[b]	$120 < T < 300$	$0.02 < x_{HI} < 0.08$
	VLLE	Haase 1963	1	$T=25$	-
	LLE	O'Keefe 1984	2	$24 < T < 70$	-
		Besenbruch 1982	5	$70 < T < 149$	-
	CAL	Vanderzee 1974	65	$T=25$	$2E-06 < x_{HI} < 0.25$
I_2-H_2O[c]	LLE	Kracek 1931	11	$127 < T < 225$	$7E-04 < x_{I2} < 5E-03$
		Parsley 1970	4	$120 < T < 150$	$1E-05 < x_{I2} < 1E-03$
	SLE	Kracek 1931	3	$77 < T < 106$	$1E-05 < x_{I2} < 4E-04$
		Ramette 1965	9	$2 < T < 50$	$1E-05 < x_{I2} < 5E-05$
		Parsley 1970	14	$0 < T < 112$	$1E-05 < x_{I2} < 5E-04$
		Sanemasa 1984	5	$15 < T < 50$	$2E-05 < x_{I2} < 5E-05$
HI-I_2	VLE	O'Keefe 1982	4	$25 < T < 90$	$0.42 < x_{I2} < 0.92$
	SLE	O'Keefe 1982	4	$25 < T < 90$	$0.42 < x_{I2} < 0.92$
HI-I_2-H_2O	VLE	Engels 1985	281	$100<T<285$	$0.02 < x_{HI} < 0.16$ $0.00 < x_{I2} < 0.86$
		Doizi 2007	9	$101<T<131$	$0.10 < x_{HI} < 0.13$ $x_{I2}=0.39$
		Hodotsuka 2008	29[a]	$123<T<134$	$0.11 < x_{HI} < 0.16$ $1E-03 < x_{I2} < 0.42$
		Liberatore 2008	34	$123<T<134$	$0.04 < x_{HI} < 0.22$ $4E-04 < x_{I2} < 0.65$
		Doizi 2009	96	$26<T<135$	$0.03 < x_{HI} < 0.20$ $0.04 < x_{I2} < 0.85$
		Larousse 2009	51	$96<T<264$	$0.10 < x_{HI} < 0.18$ $0.12 < x_{I2} < 0.39$
		Engels 1986	[d]	$120<T<300$	$0.02 < x_{HI} < 0.16$ $3E-3 < x_{I2} < 0.86$
	LLE	O'Keefe 1984	23	$24<T<152$	-

a Apparently inconsistent with other data in the same range of conditions.

b Correlation of data measured and correlated by Wüster ; some values also reported by Neumann.

c Note that no VLE data exist for the I_2–H_2O binary.

d Correlation of data measured by Neumann .

batch systems over flow apparatuses that are more complicated and expensive to build, maintain, and operate. Unfortunately, the use of a batch system results in decomposition of the HI, affecting the thermodynamic measurements for the system.

The work presented in this thesis deals with the design, construction, and operation of a Continuous-Flow Apparatus (CFA) for measuring phase equilibria, with corrosion-resistant wetted surfaces capable of operating at the conditions expected for the reactive distillation column. Using this apparatus, liquid-liquid equilibrium (LLE) data for the I_2-H_2O and I_2-HI-H_2O systems at elevated temperatures and pressures, as required for the operation of the reactive distillation column, were obtained and are presented. These data are expected to be of assistance both for the validation of system models currently under development [12] and for the final evaluation of the SI cycle for commercial use.

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CHAPTER II

A CONTINUOUS-FLOW APPARATUS FOR THE MEASUREMENT OF THE LIQUID-LIQUID EQUILIBRIUM FOR THE I_2-HI-H_2O AND THE I_2-H_2O SYSTEMS

ABSTRACT

Vapor-liquid (VLE) and liquid-liquid (LLE) equilibrium were studied for the binary iodine-water system at temperatures and pressures to 300 °C and 104 bar, and for the ternary iodine-hydroiodic acid-water system at temperatures and pressures to 160 °C and 56 bar. For iodine-water, LLE was discovered to exist at temperatures over 300 °C, contradicting the predictions of previous workers. For iodine-hydroiodic acid-water, the first accurate measurements of the LL phase boundaries for this system were obtained. A new, tantalum-alloy, continuous-flow apparatus (CFA) incorporating a view cell has been designed and constructed for measuring complex phase equilibria for highly corrosive systems at temperatures and pressures to 350 °C and pressures to 150 bar, and is described herein. A key advantage of our CFA is the elimination of the HI dissociation reaction because of the short residence times at elevated temperatures, allowing the measurement of true equilibrium data.

INTRODUCTION

Combustion of fossil fuels supplies 85% of the primary energy consumed in the United States [1], which produces over 5900 million metric tons of carbon dioxide and accounts for more than 80 percent of U.S. greenhouse gas emissions [2]. An alternative scenario to this overdependence on fossil fuels is the use of thermochemical hydrogen cycles to split water into hydrogen and oxygen, with the required heat coming from a hydrocarbon-free energy source, such as nuclear and/or solar. A study evaluating over 100 cycles [3], funded by the Department of Energy, concluded that the Sulfur-Iodine (SI) cycle has the highest reported efficiency and was the most suitable for coupling to a nuclear reactor [4].

The SI cycle [4], originally developed by General Atomics (GA), generates hydrogen and oxygen from water through three main chemical reactions:

$$2H_2O + SO_2 + I_2 \xrightarrow{120°C} H_2SO_4 + 2HI$$

Bunsen reaction

(Exothermic, ~120°C) 2. 1

$$2HI \xrightarrow{320°C} H_2 + I_2$$

Hydriodic acid decomposition

(Endothermic, 300-450°C) 2. 2

$$H_2SO_4 \xrightarrow{830°C} H_2O + SO_2 + \tfrac{1}{2}O_2$$

Sulfuric acid decomposition

(Endothermic 830-900°C) 2. 3

The Bunsen reaction [5] is operated with an excess of water and iodine in order to induce the appearance of two immiscible acidic liquid phases that can be separated mechanically without the consumption of energy, as shown below:

$$16H_2O + SO_2 + 9I_2 \rightarrow \underbrace{H_2SO_4 + 4H_2O}_{\text{upper liquid product phase}} + \underbrace{2HI + 10H_2O + 8I_2}_{\text{lower liquid product phase}} \qquad 2.\,4$$

The process flowsheet for the SI cycle is divided into three sections [6], with each being associated with the three reactions shown above: Section I: Recycle and acid generation; Section II: Sulfuric acid concentration and decomposition; Section III: Hydroiodic acid concentration and decomposition.

An exergoeconomic analysis of the cycle [7] has shown that the HI separation step of the original GA process, using extractive distillation, was both expensive and energy-intensive. Since then, several alternatives have been proposed for improving the efficiency of the process in Section III, including an electro-electrodialysis concentration process [8], the use of membrane reactors [9], and a reactive distillation (RD) column [10]. Up to now, there is no consensus on the most efficient process for Section III. However, reactive distillation, which allows for the simultaneous distillation of the I_2-HI-H_2O mixture and HI decomposition, is a strong candidate.

Process modeling of the RD column represents major challenges because of the complex chemistry of the I_2-HI-H_2O system, including diverse phase behavior (e.g., vapor-liquid (VL), liquid-liquid (LL), and liquid-liquid-vapor (LLV) equilibrium), and chemical reaction/ionization equilibria that are essentially unknown at column operating conditions. For example, the binary I_2-H_2O exhibits liquid-liquid equilibria (LLE) [11], the binary HI-H_2O is an azeotropic, strongly electrolytic system [6], and two regions of immiscibility have been identified for the ternary system I_2-HI-H_2O [12]. Thermodynamic measurements for the SI cycle, and in particular Section III, have been identified by the international community as a basic research need for the hydrogen economy [13-15]. Thus, there have been several studies of the I_2-HI-H_2O system in recent years. In particular, groups in France, Japan, and Italy [16-21] have investigated VLE for the ternary I_2-HI-H_2O at temperatures and pressures to 264 °C and 30 bar.

The goal of this research project was to investigate the region of LLE that exists for this system. Because the I_2-H_2O binary exhibits LLE at elevated temperatures, the ternary I_2-HI-H_2O also exhibits LLE until the concentration of HI becomes high enough to induce complete liquid miscibility. An experimental apparatus was designed and constructed for the measurement of VLE, LLE, and LLVE at temperatures and pressures corresponding to the expected operating conditions of the RD column in Section III. In this chapter, LLE results are presented for the binary I_2-H_2O system at temperatures to 300°C. In addition, phase-boundary measurements for the ternary I_2-HI-H_2O are presented at temperatures to 200°C. Kracek [11] measured LLE for the I_2-H_2O binary at temperatures to 225°C and estimated an upper critical solution temperature of 300 °C, while Mathias and Brown [6], using Kracek data and an ASPEN model, estimated it to be ~280 °C. The only LLE work previously reported for the ternary is from an internal GA report [12], and the LLE region of interest was in the high HI/low iodine region, and thus are not of particular interest for the RD column. Furthermore, these measurements were made only at relatively low temperatures (i.e., up to 150 °C). Finally, the reported compositions were estimated by the synthetic method and were not directly obtained.

EXPERIMENTAL SETUP

MATERIALS

Prilled Iodine (I_2) with a stated purity of 99.8% was obtained from SQM North America Corp. and used without further modification. A 55 wt/wt % solution of hydroiodic acid (HI) in water (Cat. NC949806), unstabilized (ACS reagent), was obtained from Fisher Scientific and diluted with deionized water in order to obtain the desired concentration for our experiments. Deionized reagent-grade water (CAS 7732-18-5) was obtained from Fisher Scientific.

EXPERIMENTAL APPARATUS AND PROCEDURE

A continuous-flow apparatus (CFA) was designed and constructed for obtaining phase-equilibrium data for both binary I_2-H_2O and ternary I_2-HI-H_2O mixtures at temperatures and pressures to 350 °C and 150 bar, respectively.

At elevated temperatures, the dissociation of HI into hydrogen and iodine can occur, making it impractical to obtain true equilibrium data for the I_2-HI-H_2O system with a static phase equilibrium apparatus [5]. With our CFA, residence times are on the order of minutes, so the extent of HI dissociation is negligible, enabling us to directly obtain the desired equilibrium data without simplifying assumptions. An additional advantage of the CFA is that more than one set of equilibrium conditions can be investigated in a single day, as approximately one hour is required in order to first reach steady-state and then achieve equilibrium again at another set of conditions.

Although the CFA concept has been previously used by Thies and co-workers [22-24] to measure phase behavior for a variety of aqueous mixtures, a new apparatus had to be designed and constructed for this work for withstanding the highly corrosive nature of the components of interest. In addition, because iodine is a solid at ambient temperatures (mp = 113.5°C), a method for pumping molten iodine had to be devised. A schematic of the CFA is given in Figure 2.1. Unless otherwise noted herein, all tubing was 97.5% Tantalum- 2.5% Tungsten alloy (Ta-2.5W) with an o.d. of 1.59 mm (1/16 in) and an i.d. of 0.508 mm (0.020 in).

In brief, our CFA is operated by delivering two streams, one of molten I_2 and the other an H_2O-HI solution, to an isothermal bath (oven), where the streams are preheated to the desired temperature and then mixed together in an impingement mixing tee. The resulting phases are then allowed to further equilibrate in a long section of tubing prior to entering the view cell, where they separate gravimetrically and are then collected after being reduced to ambient pressure. A detailed description of the experimental procedure is presented below.

In preparation for an experimental run, solid iodine prills are charged to the iodine (I_2) reservoir from the top after removing the tantalum tee (Figure 2.2). The reservoir is filled no more than ¾ full, as solid iodine expands by 25% upon

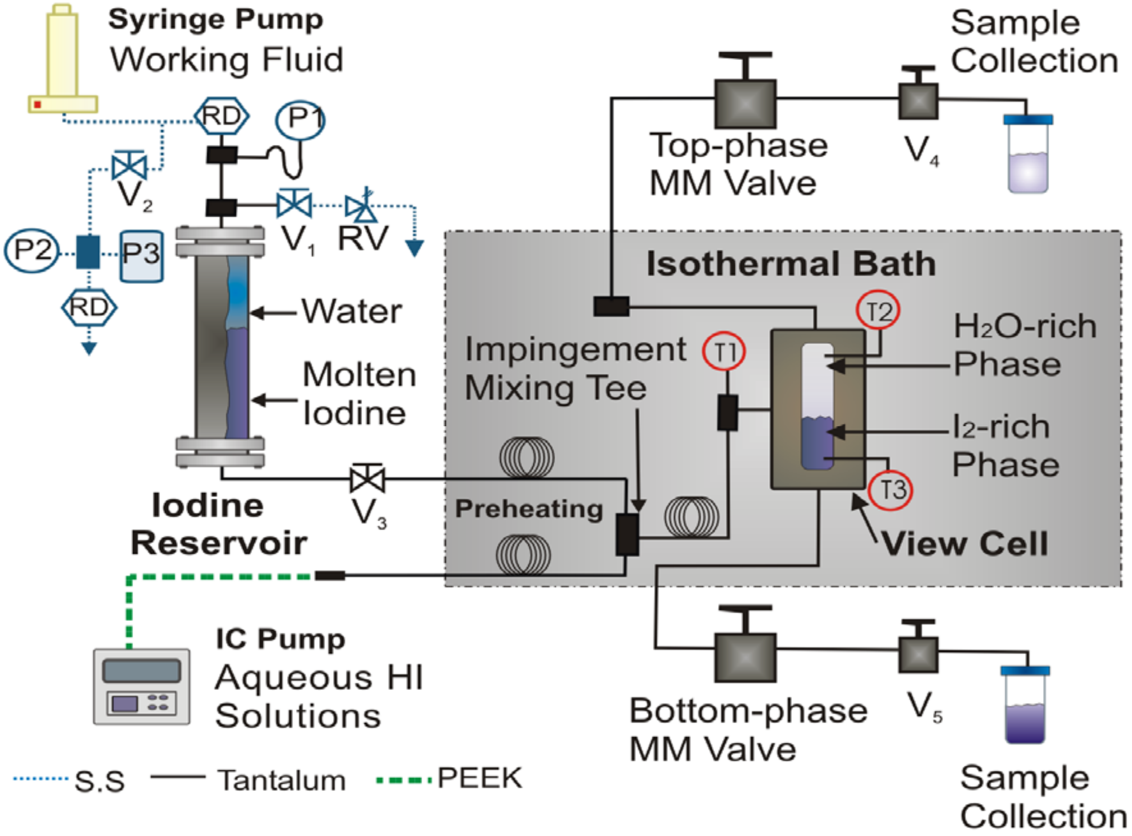

Figure 2.1 Schematic of continuous-flow apparatus for measuring LLE, VLE, and VLLE for highly corrosive mixtures at elevated temperatures and pressures. Components shown are constructed of tantalum alloy (——), PEEK (- - - -), or stainless steel (⋯⋯)

melting (solid iodine density is 4.93 g/cc [25] liquid iodine density is 3.98 g/cc at 386.65 K [26]). The reservoir is then pressure-tested to 100 bar by closing valves V_1, V_2, and V_3 and pumping water (the working fluid) into the reservoir with a syringe pump (Isco, model 500D). Finally, the rest of the system, including the view cell, is pressure-tested to 100 bar by closing valves V_3 and V_5 and feeding compressed nitrogen through valve V_4. Here, the pressure of the system is monitored with an external pressure gauge (not shown). The isothermal bath (See Figure 2.1) is turned on and set to the desired set point, and enough time (typically 6-8 hr) is allowed for the oven and its contents to come to temperature.

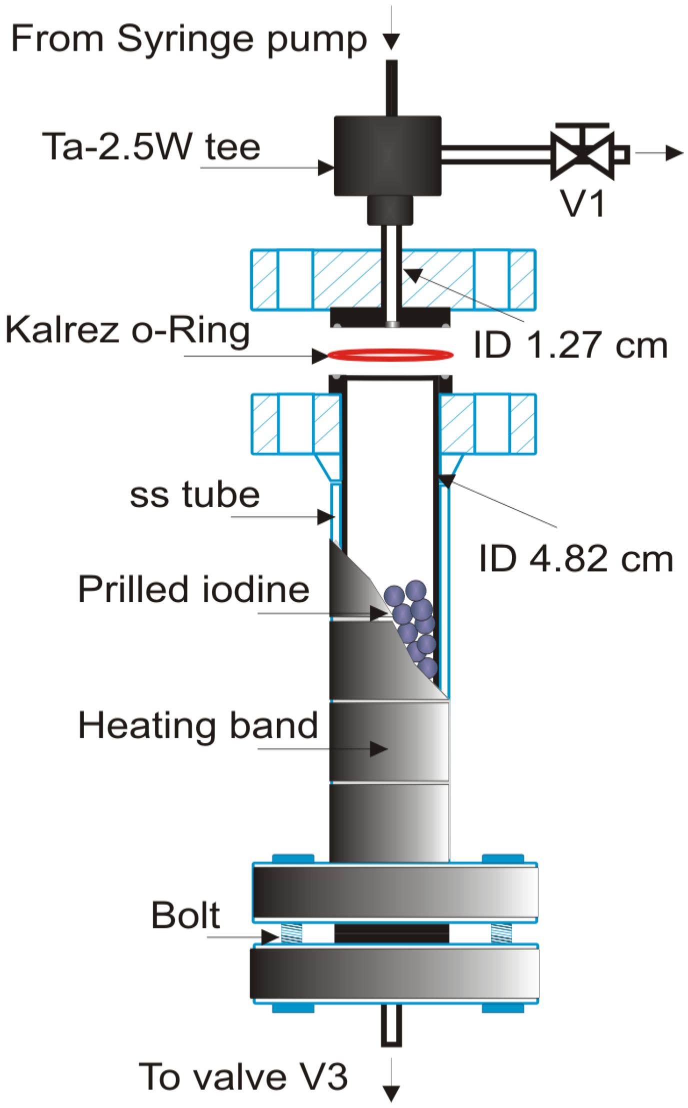

Figure 2.2 Detailed schematic of the I_2 reservoir, illustrating the Ta-2.5W tee at the top of the reservoir, the flange connections used to seal both ends of the reservoir, and the location of the heating bands. Here (—) correspond to SS, (—) to tantalum alloy.

To begin an experimental run, all valves shown in Figure 2.1 are initially closed. V_1 is then opened and water is pumped with the syringe pump at a flow rate of 1.0 mL/min into the I_2 reservoir. The pressure of the system is maintained at 8 bar by relief valve RV. Thus, a constant flow rate of water passes through the tubing and fittings that lead to the I_2 reservoir. After filling the reservoir, the water exits through RV and is collected as waste in a glass jar, where it is observed to have a light orange color, due to the presence of iodine. This constant flow of water has been observed to be crucial for the successful operation of the I_2 reservoir, as it prevents the diffusion of iodine into the stainless steel (ss) lines that precede the reservoir. Without such a water "purge", the diffusing iodine can precipitate out as a solid and plug the lines connected to pressures gauges P_1-P_3, the rupture disk (RD), and the syringe pump. An equally important role of the water purge is to prevent corrosion of the ss components described above. Before the water purge was installed, the products of such corrosion would end up inside the I_2 reservoir and, as a result, would frequently plug the lines entering and exiting the view cell.

While maintaining the water purge across the top of the I_2 reservoir, I_2 prills inside the reservoir are melted by heating to 135 °C. Such heating is carried out from the top to the bottom of the reservoir, in order to prevent the possibility of melting, expanding iodine that is trapped between solid plugs of iodine from rupturing the reservoir. To accomplish this stepwise heating, six heating bands (Watlow, part nos. Q071205L1-H1 and STB7A1J1-C72) are distributed along the bottom ¾ of the reservoir, with a six-channel controller (Omega, part no. CN616TC1) being used to sequentially heat the reservoir up to temperature. Note that even at 155 °C, iodine and water form two essentially immiscible liquid phases, with the solubility of iodine in water being 0.13 mol% (1.83 w/w%) and of water in iodine being 3.91 mol% (.288 w/w %) [11]. Thus, hot compressed liquid water (ϱ~ 1 g/mL) can be used as the working fluid to indirectly pump molten iodine from the reservoir into the view cell.

Once the iodine in the reservoir has been liquefied, the Ta-2.5W line (3.05 mm (1/8 in) o.d. x 1.4 mm (0.055 in)) i.d. that connects the bottom of the reservoir to the contents of the oven, including valve V_3, is also heated in a stepwise manner (i.e., from reservoir to oven) to 140°C for the same reason as described before. The Ta lines that exit the oven, including valves V_4 and V_5, are also heated to 140°C.

Once all parts of the system are heated to temperature, flow of the feed streams is initiated. First, the water purge flow rate from the syringe pump is increased from 1 ml/min to the desired I_2 flow rate; then valve V_1 is closed and valves V_2 and V_3 are opened to initiate the flow of molten iodine into the system. An ion chromatograph (IC) pump (Dionex, model IP25) is used to deliver either pure water, when the binary I_2-H_2O system is of interest, or HI-H_2O mixtures, when the ternary I_2-HI-H_2O system is of interest. For example, to deliver a ternary I_2-HI-H_2O mixture with an overall composition of 90.6 mol % H_2O, 2.3 mol % HI, and 7.1 mol % I_2, the IC pump is used to deliver a 2.5 mol% (15.5 wt%) mixture of HI-H_2O at 1.58 ml/min and the syringe pump an I_2 flow rate of 0.42 ml/min. For the syringe pump, recall that water is used as the working fluid to push the molten iodine out the bottom of the reservoir.

As shown in Figure 2.1, both feed streams are preheated to temperature in coiled tubing before being mixed. The aqueous HI solution is preheated in a 6.4 m- and the iodine in a 4.7-m long section of tubing. After preheating, the streams are mixed in an impingement mixing tee. Optimum mixing is achieved by connecting the feed lines at opposing sides of the tee and by reducing the diameter of the tubing 25 cm prior to entering the tee to an i.d. of 0.25 mm (0.001 inches) in order to increase the momentum of the iodine and HI-H_2O streams [27]. Furthermore, the opposing feed stream lines are brought as close as possible to each other inside the tee (as the line stops in the tee are bored out). After exiting the impingement mixer, the resultant, two-phase stream flows through an additional 2.7 m-long section of tubing, in order to allow the phases to equilibrate and come to their final temperature. The mixture then enters through a port in the middle of the view cell, where the two phases are observed to gravimetrically separate into a lighter H_2O-rich phase, and a heavier I_2-rich phase.

The phases are then drawn off through exit ports located at the top and bottom of the view cell. The I_2-rich phase exits through the bottom of the view cell through 3.175 mm o.d. x 1.397 mm i.d. (1/8 in o.d x 0.055 in i.d.) Ta-2.5W tubing, while the H_2O-rich phase exits through the top of the view cell through a 1.59 mm o.d., 0.508 mm i.d. Ta-2.5W tubing. After exiting the isothermal bath, each phase is expanded to atmospheric pressure through micrometering (MM) valves, modified from their ss counterpart (Autoclave Engineers, part no. 60VRMM4882) so that all wetted surfaces are either of Ta-2.5W or Ta-10W alloy. The MM valves are used to control both the system pressure and the location of the LL interface in the view cell. After exiting the valves, the phases are collected separately in 250 mL sealed glass jars (Fisher, Part No. 05719450) placed in a water-propylene glycol bath at 0 °C in order to avoid the loss of volatile species.

The I_2 reservoir (See Figure 2.2) was designed and constructed by General Atomics (GA) in collaboration with Clemson University researchers. Although there is no code for Ta alloy vessels, the reservoir was designed, fabricated, and inspected to the intent of ASME boiler and pressure vessel code, Section VIII, Division I. It consists of a 90% Ta – 10% W alloy tube with an o.d. of 4.82 cm (1.9 in), a wall thickness of 8.9 mm (0.035 in), and a total volume of approximately 700 mL. A 7.32 cm (2.88 in) o.d. x 4.84 cm (1.905 in) i.d. x 0.56 cm (0.22 in) thick Ta alloy plate serves as the tube flange and is welded to each end of the tube. This flange is grooved to hold a Kalrez No. 227 O-ring (DuPont AS-568A). Another Ta alloy plate, 7.29 cm (2.87 in) o.d. x 1.28 cm (0.502 in) i.d. x 0.56 cm (0.22 in) thick, serves as the top connection flange and has a 1.27 cm (0.5 in) o.d. x 8.89 mm (0.035 in) wall x 15.24 cm (6 in) long Ta alloy tube welded to the central hole of the plate. This plate is also grooved for the Kalrez O-ring. An identical plate serves as the bottom connection flange, except that the i.d. dimension is 0.64 cm (0.252 in), and a 0.635 cm (0.25 in) o.d. tube (same wall and length) is welded to the central hole of the plate. The O-ring is sealed to the end and connection flanges with 1 ½ ", 900#, ss pipe flanges. The pipe-flange nuts are torqued to 325 N-m (240 ft-lb). Finally, for additional pressure support, the 4.82 cm o.d. Ta alloy tube is enclosed by a 5.72 cm (2.25 in) o.d. x 0.48 cm (0.188") wall ss tube.

The reservoir was designed for routine operation at 140 °C and 104.4 bar (1500 psig) and was hydrostatically tested at 156.6 bar (2250 psig) after assembly. Overpressure protection is provided by two rupture disks, one rated for 138.9 and the other for 207.9 bar (High Pressure Equipment, part Nos. RD 2000 and RD 3000). The 207.9 bar rupture disk is used as an extra safety feature for protection of the Heise gauge.

The view cell assembly, shown in Figure 2.3, follows the design of Roebers [28], but has been modified to withstand the corrosiveness of the components of interest. In particular, the centerpiece of 450 ss was replaced with one of Ta-2.5W. It has one inlet port in the center, outlet ports in the top and bottom, and thermocouple (T/C) ports near the outlet ports. The borosilicate windows (Power Plus International, part number A1 high pressure flat glass) are sealed against the inner chamber and cover plates using graphite gaskets (UCAR, Grafoil). The two cover plates, made of 450 ss, are bolted together using eight high temperature service 0.5 in x 7.5 in B7 studs and 2H heavy hex nuts, tightened to 108 N-m (80 ft-lbf). The loss of the required load on the window gaskets due to differential thermal expansion is minimized by placing 4 Belleville washers (Key Bellevilles, part number AFB 1-60) on each stud, with the washers arranged as 2 series of 2 in parallel. The overall volume of the view cell is ~14 mL. Finally, an insulating jacket of boron nitride is fitted around the view cell in order to minimize temperature gradients in the cell block.

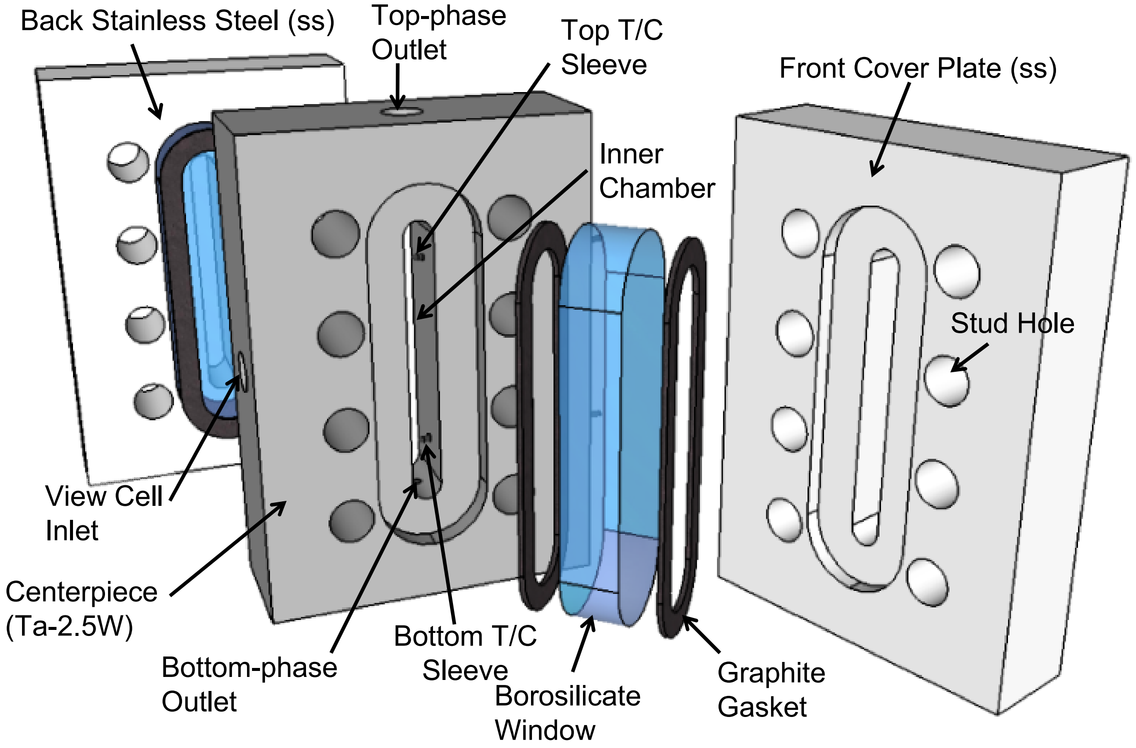

Figure 2.3 Components of the view cell. Wetted parts were designed to withstand HI and I_2 at up to 350°C, 150 bar.

Depending in the concentration of iodine and HI, both the H_2O-rich and I_2-rich phases (and the interface) in the cell can be opaque to the naked eye. In their previous work, GA [29] found that IR could be used for phase observation. Thus, we used an infrared electro-viewer (Electrophysics, model 7215-SAC) to observe the contents of the cell. The source of IR light is a 300 W halogen lamp placed opposite the IR viewer, with the cell and its windows between. Thus, the IR light is transmitted through one window of the view cell, passes through the contents of the cell chamber, and exits the through the other cell window to be received by the IR electro-viewer. This infrared setup has been used to observe VLE, LLE, and even LLVE over a wide range of temperatures, pressures, and compositions.

As previously described, all wetted surfaces of the MM valves (See Figure 2.1) had to be fabricated of Ta-2.5 W or Ta-10W. However, changes to the valve design itself were also required in order to obtain better pressure control. Initially, the valve stem and tip were machined out of Ta-10W, albeit with dimensions identical to the original Autoclave design. However, because of the high density of the I_2-containing solutions and the low flow rates used in our experiments, control of the system pressure was difficult. Therefore, as shown in Figure 2.4, the angle of the stem and the original i.d. of the seat were reduced in order to reduce the valve flow coefficient (Cv) and better pressure control was then obtained (the stem angle was increased to 3° so that we could use the old stems, even though a 1° angle would be better).

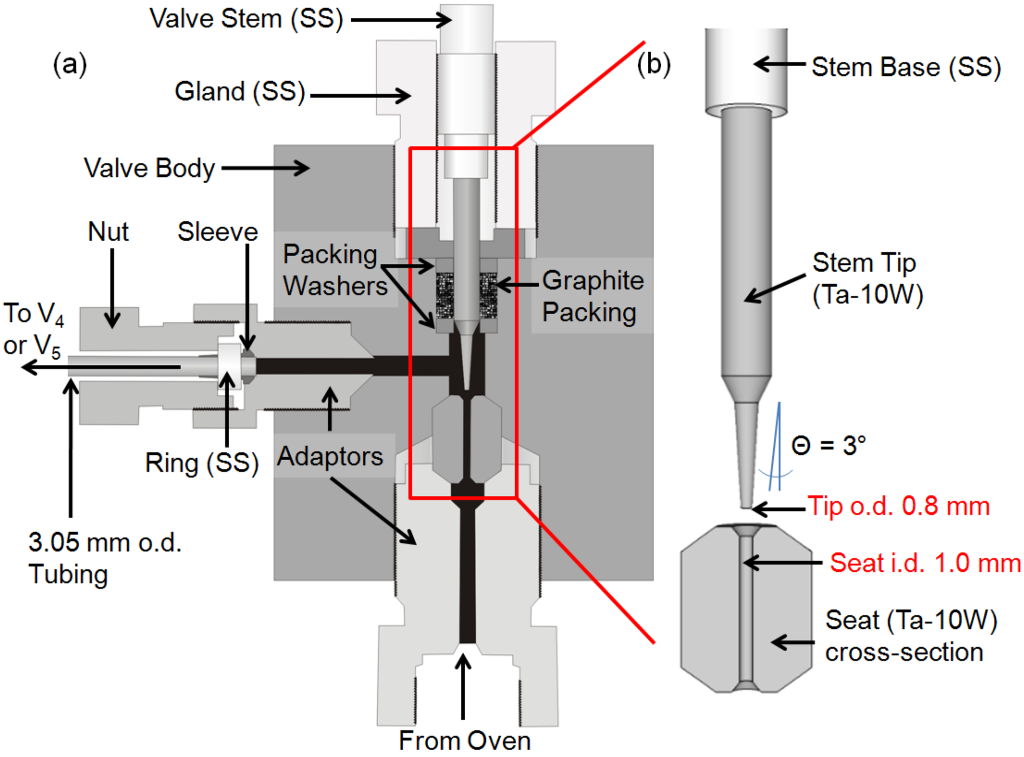

Figure 2.4 (a) Cross-sectional view of MM valve constructed to withstand I_2 and HI at elevated temperatures and pressures. Unless otherwise specified, parts are made of Ta-2.5W alloy. (b) Re-designed stem and seat used in the MM valves. Original design from Autoclave Eng. has a pitch angle (θ) of approximately 1° (part no. 101B-5897), a tip i.d. of 1.3 mm, and a seat i.d. of 1.52 mm (part no. 101C-5405).

The isothermal bath shown in Figure 2.1 consists of a forced-convention, high-temperature oven with a nitrogen purge in order to establish an inert atmosphere and prevent oxidation of the Ta components at temperatures over 300°C [30]. The oven is capable of controlling the temperature of the view cell to within ± 0.1°C [31], and also provides heating for the preheating section of tubing, the impingement mixing tee, and the lines exiting the view cell. Key safety features of the bath include (1) a polycarbonate shield mounted over the viewing window in case of a cell window rupture and (2) an independent, high temperature shutoff.

In addition to the oven, several additional features were incorporated into the apparatus in order to keep iodine in the liquid state. To prevent iodine from solidifying inside the top and bottom cell lines as they exit the isothermal bath, electrical heating tape is wrapped around the tubing, which is maintained at temperatures between 135 and 150 °C. 3.175 mm (1/8 in) o.d. lines are heated using Thermo Scientific heating tapes BWH051-040 and BWH051-080, while 1.59 mm (1/16 in) o.d. lines are heated using Glas-Col heating tapes, part no 103A DET0.254. The preheating lines entering the oven and the top and bottom lines exiting the oven were found to frequently become plugged with solid iodine in the region where they passed through the port hole in the insulated bath wall (See Figure 2.1). To solve this problem, the lines were clad with a heated copper block, which was maintained at ~140 °C with a 125W cartridge heater (McMaster-Carr, 3618K293). Valves V_3, V_4, V_5, and the two MM valves, were heated by clamping heated 0.95 cm-thick aluminum (Al) blocks to the valve bodies. The Al blocks themselves were heated with the 125W cartridge heaters described above inserted into holes drilled into the blocks.

EXPERIMENTAL MEASUREMENTS

The temperature of the feed mixture (T_1) and of each phase in the cell (T_2 and T_3) are measured with type K differential thermocouples referenced to an aluminum block located inside the isothermal bath. This differential thermocouple-RTD setup is described elsewhere [27]. The thermocouples T_1, T_2 and T_3 (Figure 2.1) are made of ss with an o.d. of 0.8 mm (Omega, part no. SCASS-032G-6-SHX) and are enclosed in a tantalum sheath (Omega, part no. EI1203104/XTA-116-4-CL). The absolute temperature of the aluminum block is measured with a secondary standard platinum resistance temperature detector (RTD) (Burns Engineering, model 200G05B035/LY360/LM99, serial no. 533184). The temperature-measuring capability of this setup is accurate to within 0.1 °C [27]. However, the temperatures reported below in our results are believed to be no more accurate than ± 3 °C, as some temperature variation is a normal consequence of operating a flow apparatus. Both fluctuations in the bath temperature and adjustment of the MM valves to control pressure and liquid level in the view cell are responsible for this variation. Finally, we note that thermocouple T_1 could be used only on an intermittent basis, because of leakage at the feed tee just prior to entering the view cell.

Operating pressures are measured using two gauges: a Bourdon-tube type, Heise gauge (P_2), (model CM, 0-206.8 bar range), and a Heise pressure transducer (P_3), (model HPO, 0-344.7 bar range). Both gauges were calibrated against a Budenberg deadweight tester (model 380H) to an accuracy of ± 0.14 bar. Even though the pressure gauges were calibrated to a high level of accuracy, pressure fluctuations are inevitable when working with essentially incompressible fluids in a flow apparatus. Thus, the experimental pressures reported for the binary I_2-H_2O system are believed to be accurate to ± 0.69 bar (± 10 psi) and for the ternary I_2-HI-H_2O to ±1.03 bar (±15 psi). The pressure gauge P_2 and the pressure transducer P_3 are connected to the top of the I_2 reservoir through valve V_2. In addition, a third gauge P_1 (Ashcroft, ss 0-206.8 bar, 1008 gauge) is used to monitor the pressure of the I_2 reservoir while heating and cooling down the reservoir.

When the CFA was first constructed, the pressure of the system was measured from a line connected directly to the top of the view cell. However, we found this line to constantly clog during experiments because of the flow of iodine from the view cell towards the pressure gauges, caused both by diffusion and by pressure fluctuations. Because the pressure gauges are located outside the oven at room temperature, the iodine precipitated inside the line soon after it exited the oven. To overcome this problem, the pressure gauges were re-located to the top of the iodine reservoir, as shown in Figure 2.1, where the diffusion of iodine is prevented by keeping a constant flow of pure water in the line leading to the I_2 reservoir, as described earlier. Tests were conducted comparing the pressure readings obtained directly from the top of the view cell and the readings obtained from the top of the iodine reservoir. Results indicated a negligible difference (i.e., ± 0.3 bar) between the two methods.

To assist in the collection of data, the differential thermocouples T_1, T_2, and T_3 and pressure transducer P_3 are connected to a data acquisition unit (Agilent, model 34970A). The software BenchLink Data Logger, provided by Agilent, enables the computer to interface with the data acquisition unit (DAU) and record system data at set time intervals, normally 5 s, during an experimental run. Readings from the secondary RTD located inside the isothermal bath are obtained using a digital multimeter (HP, model 34401A) and are also recorded every 5 s into an Excel spreadsheet using Agilent software (BenchLink Data Logger).

CORROSION FEATURES

Prior to constructing the CFA, special attention was given to the selection of materials that could withstand the highly corrosive HI and iodine. Several versions of the CFA incorporating different materials, including polymers such as Teflon and PEEK, and alloys such as Hastelloy C and tantalum-tungsten (Ta-W), were made. Of these, only Ta-W, graphite (Grafoil) and borosilicate were found to successfully withstand the highly corrosive environment at the temperatures and pressures of interest. However, PEEK and Teflon were found to be suitable for applications at ambient temperatures. For example, the IC pump that is used to pump HI-H_2O mixtures uses sapphire pistons, and all other wetted parts are made out of PEEK. Also made of PEEK is the 1/16 in tubing that connects the IC pump to the Ta-2.5W 1/16 tubing that enters the oven (See Figure 2.1). All other components, such as valves, fittings, and the equilibrium view cell, were made from Ta-W alloys and were fabricated by Machine and Technical Services at Clemson University. Ta-10W was used for the stems and seats because of the higher mechanical strength compared to pure tantalum, Ta-2.5W was used for parts that were too expensive to buy in Ta-10W, and pure tantalum was only used for parts that needed to be built in a short period of time (delivery times for pure tantalum could be as little as one week, compared to 5-6 for Ta-W alloys).

RESULTS AND DISCUSSION

BINARY I_2-H_2O

For the binary I_2-H_2O system, an experimental run at a given temperature is initiated by filling the view cell with water at a rate of 2 mL/min (using the IC pump). At this point, both top- and bottom-phase 3-way valves (V_4 and V_5) are kept closed in order to allow liquid water to accumulate inside the view cell. Once the view cell becomes filled with water and the pressure starts to build up, V_4 is opened and the top-phase MM valve is used to control the system pressure. At this point, the flow of water into the system is reduced to approximately 1.0 mL/min, while the flow of molten iodine is initiated at 1.0 mL/min, resulting in a total feed flow rate of 2.0 mL/min. Once the I_2-rich phase is seen to accumulate in the bottom of the view cell, V_5 is opened and the system pressure, as well as the liquid level of the I_2-rich phase, is maintained by controlling both the top- and bottom-phase MM valves.

Bubble-point pressures are obtained by slowly raising the pressure (at constant temperature), from the three-phase VLLE region until the last trace of vapor phase disappears in the view cell. The pressure is then slowly lowered until the vapor phase reappears. The process is repeated. Table 2.1 summarizes the bubble-point pressures obtained at temperatures ranging from 150 to 300°C, as well as observations of the system behavior at each temperature.

Table 2.1 LLE for the I_2–water system at temperatures from 150-300 °C

Temperature, °C	VLLE Press. psig	Comments re Experimental Runs
150	< 100	LLE interface observable with visible light
200	300	LLE interface opaque with visible light, and for all higher temperature runs, but easily detectable with IR
246	600	LLE interface easily detectable with IR detector/light source
276	1000	LLE interface easily detectable with IR detector/light source
277	1020	LLE interface easily detectable with IR detector/light source
300	1500	LLE interface still easily detectable, but light transmission significantly decreased

Photographs of selected events during these measurements are shown in Figure 2.5. Figure 2.5a shows the startup of an experiment, when the view cell is initially filled with pure water and the flow of iodine has just started. The brown-colored stream coming into the middle left port of the view cell at 200°C and 19.7 bar (300 psig) is the H_2O-rich liquid phase (containing a small amount of iodine) and is seen to flow downwards, as it is denser than the pure water initially contained in the cell. The I_2-rich liquid phase is also entering the cell from the middle left port with the H_2O-rich phase, but it cannot be easily seen because it is flowing straight down the inner wall of the view cell because of its high density.

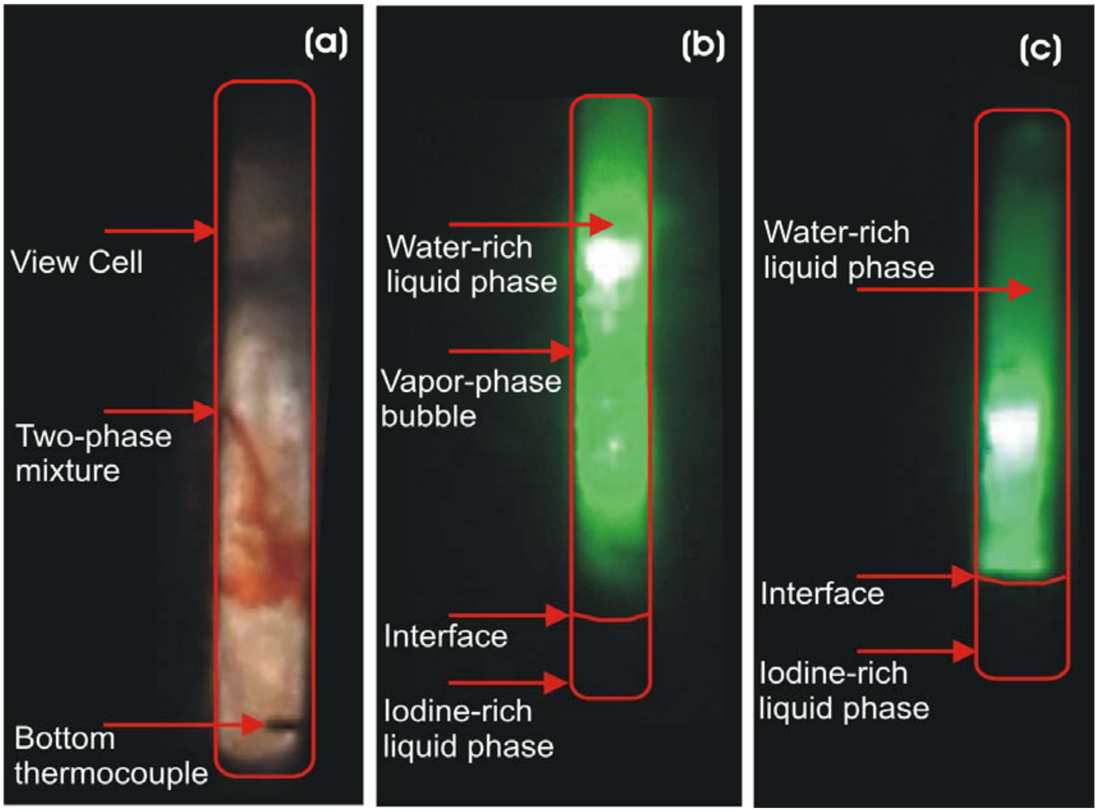

Figure 2.5 Contents of the view cell, as seen through its windows, at (a) 200, (b) 276, and (c) 300 °C. The feed port is in the middle left of the cell; entering phases include the two-phase LLE mixture and for (b) a vapor-phase bubble. Photograph (a) was taken with the naked eye, and (b) and (c) with the IR viewer.

As more water and iodine flow into the view cell, two phases become apparent to the naked eye: a dark and opaque liquid phase that steadily accumulates in the bottom of the view cell and a clear vapor phase that steadily decreases in volume as it is removed out the top of the view cell through MM valve V_4. (Recall that during startup V_4 is kept open, while V_5 is closed). At this point, the IR viewer is turned on, and the dark liquid phase becomes clearer and is actually seen to consist of two distinct liquid phases: a lighter and a darker one. The darker liquid phase is the I_2-rich phase and is seen to accumulate in the bottom of the view cell as it is much denser. The lighter liquid phase is the H_2O-rich phase. As noted in Table 2.1, for the binary I_2-H_2O system the IR viewer is required to detect the LLE interface only at temperatures higher than 200°C. At lower temperatures, the amount of iodine present in the H_2O-rich phase is not enough to turn that phase opaque.

Photographs illustrating VLLE and LLE for the I_2-H_2O binary system are shown in Figures 2.5b and 2.5c, respectively. The VLLE shown in Figure 2.5b was obtained at 276 °C and the bubble-point pressure recorded at approximately 70 bar (1000 psig). The LLE shown in Figure 2.5c was obtained at 300°C and 102.4 bar (1500 psig). These results are the first reported observation of LLE for this system at temperatures above 225 °C [11]. Thus, we have shown that, in contrast to literature estimates [6,11] that place the upper critical solution temperature for this system at 280-300 °C, the I_2–H_2O system exhibits LLE at temperatures above 300 °C. Based on our observations and experience observing LLE critical points for other systems {22,28], we estimate an UCST for this system of 310-315 °C.

TERNARY I_2-HI-H_2O

For the ternary I_2-HI-H_2O system, a typical experimental run is initiated exactly as for the binary I_2-H_2O as previously described. However, for the ternary system, instead of pure water an aqueous solution of HI of specified concentration is pumped into the view cell until it is full and the pressure starts to build. At this point, V_4 is opened and the top-phase MM valve is used to control the system pressure. The flow rate of aqueous HI solution is reduced to approximately 1.0 mL/min as the flow of iodine is initiated at 1.0 mL/min, resulting in a total feed flow rate of 2.0 mL/min. Once the I_2-rich phase is seen to accumulate in the bottom of the view cell, V_5 is opened and the system pressure, as well as the liquid level of the I_2-rich phase, is maintained by controlling both the top- and bottom-phase MM valves.

Our goal for the ternary system of interest was to locate the phase boundaries for the water rich-side of the region of LLE that exists at low HI concentrations. For a given feed flow rate of molten I_2 and aqueous HI solution, the overall system composition is fixed. To determine whether LLE exists for this specified overall composition at a given temperature and pressure, the bottom valve V_5 is closed, and the system pressure is controlled with only the top-phase MM valve. The I_2-rich phase is then allowed to accumulate until the entire view cell is filled with it. At this point, V_4 is closed, V_5 is opened, and the pressure of the system is controlled using only the bottom-phase MM valve. The level of I_2-rich liquid phase inside the view cell is then seen to slowly decrease as it is drained out, while the level of the H_2O-rich liquid phase increases. Once the I_2-rich liquid phase is drained, the bottom valve V_5 is closed once again. The I_2-rich phase is then allowed to accumulate once again up to ¾ of the total volume of the view cell. At this point, the bottom phase is drained one more time. If, after this second drainage, an I_2-rich phase was seen to accumulate, then it was concluded that at the given overall feed composition, temperature, and pressure, the ternary I_2-HI-H_2O system exhibits LLE. If, on the other hand, no accumulation of an I_2-rich liquid phase occurred, then it was concluded that only one phase exists. Clearly, the most desirable situation was to operate at a composition such that the accumulation of the bottom I_2-rich liquid phase was very low, thus establishing a two-phase point close to the desired phase boundary.

Note that with a CFA, these experimental observations are carried out most conveniently within a single experiment by changing the feed flow rate of the aqueous HI-H_2O mixture, the concentration of the aqueous HI mixture, and/or the I_2 flow rate. Changes to the temperature of the isothermal bath generally require a day to complete, and the effect of pressure on the phase behavior of this LLE system is negligible within the pressure range of interest.

Figure 2.6 and Table 2.2 show our experimental observations for the ternary I_2-HI-H_2O system at 160 and 200 °C. Also plotted are the LLE predictions for this system from a model recently developed by Murphy and O'Connell [32]. For all of these observations, the system pressure was kept ~14 bar (200 psi) above the bubble point of the mixture so that only LLE would be observed. Thus, for the compositions shown in Fig. 2.6, the operating pressure ranged from 35.5 to 49.3 bar (500-700 psig), with the pressure variation being ±1 bar (15 psia) for a given experimental run.

The predictions of the model are in reasonable agreement with our work. For example, at 160 °C the model correctly predicts the increase in I_2 content in the H_2O-rich liquid as the amount of HI in aqueous the feed increases from 2.5 to 5 mol%. Also, for an aqueous feed composition of 2.5 mol% HI, the model agrees with our experimentally observed observation that a change in temperature from 160 to 200 °C results in an increase in iodine in the H_2O-rich phase. Note, however that our phase-boundary measurements do not give us any tie-line information, so we are not able to evaluate the slopes, and thus the predicted component selectivities, in the Murphy-O'Connell model.

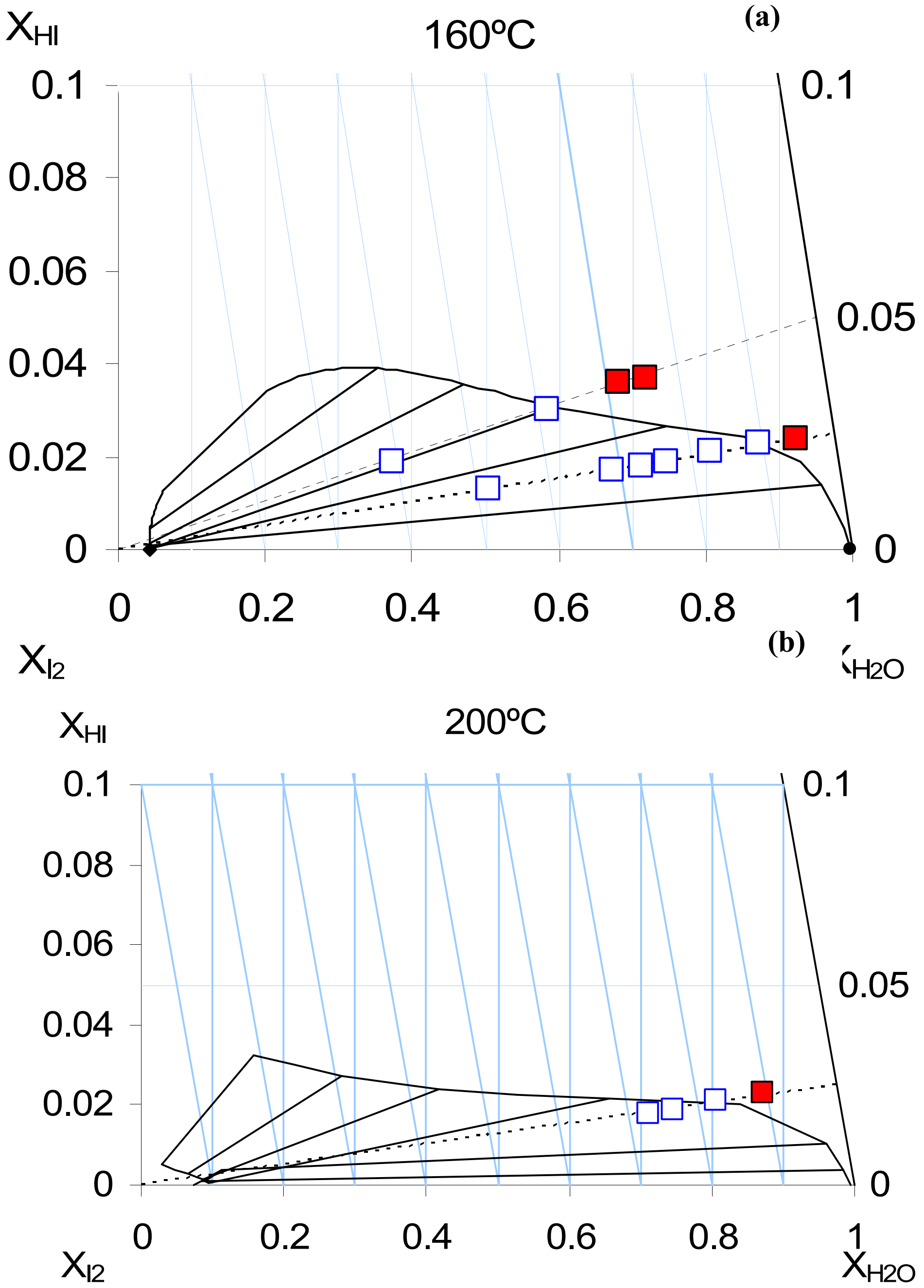

Figure 2.6 Ternary diagram at (a) 160 and (b) 200˚C for I_2-HI-H_2O. The continuous lines represent the phase envelope and equilibrium tie-lines predicted by the model of Murphy and O'Connell [32]. The open squares (□) denote an overall feed composition where two phases were observed in the view cell; solid squares (■) where one phase was observed. The dotted lines represents the feed line for (a) 5.0 and (b) 2.5 mol% HI in water with molten iodine.

Table 2.2 Flow rates and compositions for experiments of the ternary I_2-HI-H_2O system, conducted at 160 and 200 °C

Temperature 160 C°						
	Flows (mL/min)		Feed Molar Composition			Observed
HI Feed	$HI\text{-}H_2O$	I_2	H_2O	HI	I_2	Liquid Phases
0.025 mol fraction HI	0.65	1.355	0.50	0.01	0.48	2
	1.0	1.0	0.67	0.02	0.31	2
	1.1	0.9	0.71	0.02	0.27	2
	1.19	0.813	0.75	0.02	0.24	2
	1.37	0.633	0.81	0.02	0.17	2
	1.78	0.224	0.92	0.02	0.05	1
	1.58	0.416	0.87	0.02	0.11	2
0.05 mol fraction HI	1.254	0.746	0.72	0.04	0.25	1
	1.16	0.835	0.68	0.04	0.28	1
	0.93	1.066	0.58	0.03	0.39	2
	0.52	1.476	0.37	0.02	0.61	2
Temperature 200 C°						
	Flows (mL/min)		Feed Molar Composition			Observed
HI Feed	$HI\text{-}H_2O$	I_2	H_2O	HI	I_2	Liquid Phases
0.025 mol fraction HI	1.10	0.9	0.71	0.02	0.27	2
	1.19	0.81	0.75	0.02	0.24	2
	1.37	0.63	0.81	0.02	0.17	2
	1.58	0.42	0.87	0.02	0.11	1

Selected photographs of the contents of the view cell, illustrating both one and two-phase equilibrium via the IR viewer, are shown in Figure 2.7.

Finally, to confirm that the preheating section, impingement mixing tee, and mixing equilibrium sections were working properly such that the resulting phases in the view cell were in equilibrium, feed flow rates were varied by ±50%, in order to determine whether any mass transfer limitations were present.

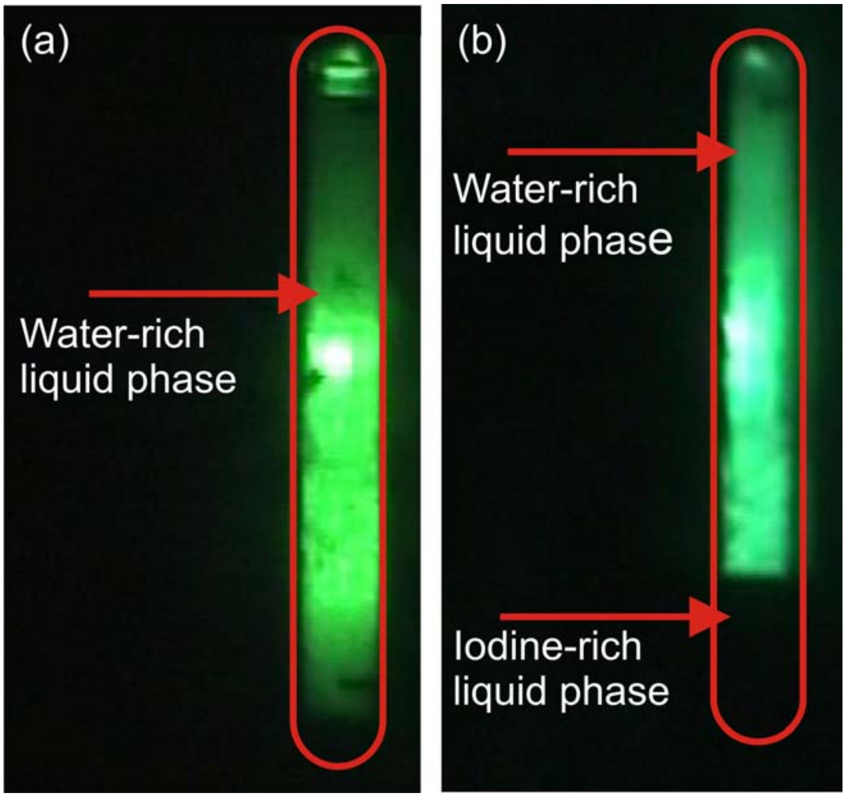

Figure 2.7 Contents of the view cell as seen through its windows at 160°C and 35.5 bar, showing (a) one phase at 0.923 mol fraction water, 0.024 mol fraction HI and 0.054 I_2 and (b) two phases at 0.872 mol fraction water, 0.023 mol fraction HI and 0.106 I_2. Photographs taken with the IR viewer.

Thus, as shown in Table 2.3, two feed compositions close to the LL phase boundary were evaluated: one where one phase was originally observed and another where two phases existed. For both situations, no deviation from the original phase behavior was observed.

Table 2.3 Test for equilibrium. Large changes in feed flow rates had no impact on the observed phase boundaries

Overall feed compositions (mol fraction)			Original flows (mL/min)		Original flows – 50% (mL/min)		Original flows + 50% (mL/min)		Observed liquid phases
H_2O	HI	I_2	HI-H_2O	I_2	HI-H_2O	I_2	HI-H_2O	I_2	
0.923	0.024	0.054	1.78	0.224	0.89	0.112	2.67	0.336	1
0.872	0.023	0.106	1.58	0.416	0.79	0.208	2.37	0.624	2

CONCLUSIONS AND RECOMMENDATIONS

We have constructed a new, unique, continuous-flow apparatus, designed for the measurement of complex phase-behavior data for highly corrosive systems at elevated temperatures and pressures. In the course of the development of this apparatus, Ta and its W alloys were found to be capable of withstanding the aggressive chemicals and conditions that exist for the I_2-HI-H_2O reactive distillation process. For low-temperature, high-pressure applications with these chemical species, PEEK polymers were found to work well. Ta valves and fittings fabricated at Clemson University were found to perform as well as their analogous ss counterparts. We have also demonstrated the reliable indirect pumping of molten I_2 via a custom-built syringe pump, using water as the working fluid. Using our apparatus, we have observed two-phase behavior for mixtures of the binary I_2-H_2O system at temperatures to 300°C, in contradiction to the predictions of previous workers. For the ternary system, we have located the LLE region for mixtures of I_2, HI, and water, and have shown that it decreases with increasing temperature.

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CHAPTER III

DIRECT PHASE COMPOSITION MEASUREMENTS FOR THE TERNARY I_2-HI-H_2O SYSTEM

Although locating phase boundaries, as described in Chapter II, provides useful information for the development of thermodynamic models, equilibrium tie-lines are still required for accurate model development and, as a result, for process simulation. Thus, this chapter deals with the development of methods for analyzing the samples of the phases collected from our equilibrium view cell using the CFA.

MATERIALS

Prilled Iodine (I_2) with a purity of 99.8% was obtained from SQM North America Corp. and used without modification. A 55% wt/wt solution of hydroiodic acid (HI) and water, unstabilized (ACS reagent), was obtained from Fisher Scientific and diluted with deionized water to the feed concentrations used in our experiments. Deionized reagent-grade water, CAS 7732-18-5, was obtained from Fisher Scientific. A 0.2N volumetric standard solution of sodium hydroxide (cat. no. SS274-4), titrated at 25°C to pH 8.6 (phenolphthalein endpoint) against NIST potassium acid phthalate was obtained from Fisher

Scientific. A 0.025N sodium thiosulphate solutions, standardized at 25°C against NIST potassium dichromate was also obtained from Fisher Scientific (cat. no. SS370-1). The starch indicator was prepared from soluble starch ACS reagent obtained from Aldrich Chemical Company (Cat No 9005-84-9). The granular potassium iodide (KI) was manufactured by JT Baker (CAS 7681-11-0).

EXPERIMENTAL APPARATUS AND PROCEDURE

A continuous-flow apparatus (CFA), shown in Figure 3.1, was used to obtain liquid-liquid equilibrium (LLE) data for the ternary I_2-HI-H_2O system. The apparatus is rated to 350°C and 150 bar, and has been designed to withstand the highly corrosive nature of the system of interest. Details of the design and construction of the apparatus, as well as a thorough description of most aspects of the experimental procedure, are given in Chapter 2. Thus, only a brief a description of the CFA is given here. However, there were a few changes that had to be made in order to incorporate sample collection, and these are described in detail below.

In brief, our CFA is operated by delivering two streams, one of molten iodine and the other an H_2O-HI solution, to an isothermal bath (oven), where the streams are preheated to the desired temperature and then mixed together in order to achieve phase equilibrium.

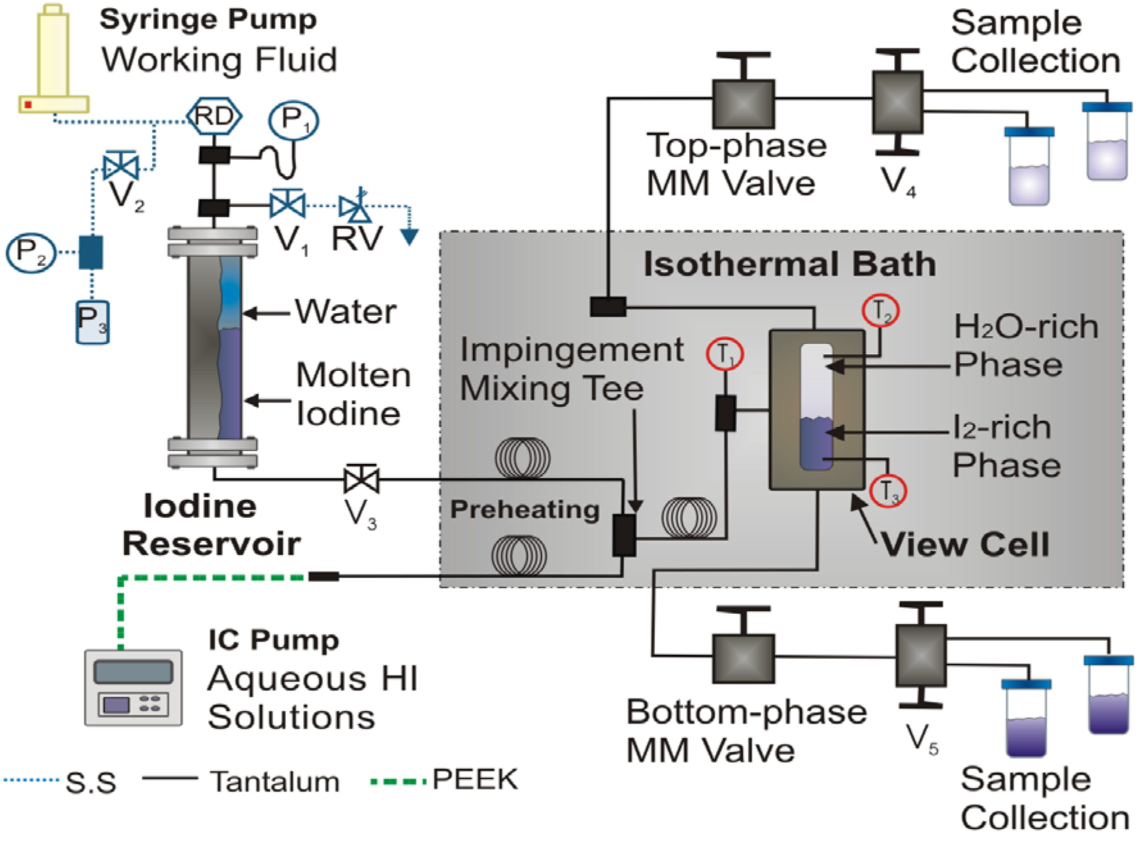

Figure 3.1 Schematic of continuous-flow apparatus for measuring LLE and VLE for highly corrosive mixtures of I_2, HI, and water at elevated temperatures and pressures.

The combined flow rates of the two streams are 2.00 mL/min. The resulting phases are then allowed to equilibrate in a 2.7-m section of tubing prior to entering the view cell, where the two phases are seen to separate gravimetrically. The heavier I_2-rich phase accumulates in the lower part of the view cell and the lighter H_2O-rich phase in the upper part. The separated top and bottom phases then exit through ports located in the top and bottom of the view cell and are reduced to ambient pressure after passing through micrometering (MM) valves. The phases are then collected for further analysis in septa-sealed jars partially immersed in a cold bath of 0 to -5 °C. After collection, both top- and bottom-phase samples are kept in a refrigerator to prevent the loss of any volatiles and minimize any possible decomposition reactions.

Each phase then enters a sealed sample collection jar that creates a slight positive pressure buildup in the jar when a proper seal around the sampling tubing is obtained. The jar is cooled using a recirculating cold bath with a propylene glycol-water mixture to prevent the loss of volatile species, in particular HI. To create the seal between the Ta tubing exiting the 3-way on/off valves V_4 and V_5 (they were 2-way valves in Chapter 2) and the septum caps, a short segment (1/2-inch long) of PFA tubing (McMaster Carr Cat. No 5773K12, od: 3/16" (4.763mm), id: 1/8: (3.175 mm) is tightly placed on the tip of the Ta tubing. To do this, a hot Phillips screwdriver is carefully inserted into the tubing to slightly increase its i.d. Immediately afterwards, the PFA tubing is placed around the Ta tubing. When it cools down, the PFA is tight onto the metal so that the seal is between the PFA tubing and the septa.

Photographs of the top- and bottom-phase sample collection jars are shown in Figure 3.2. As shown in Figure 3.2a, the top phase consists of a dark-colored brown liquid and some I_2 crystals accumulated on the inner walls of the jar.

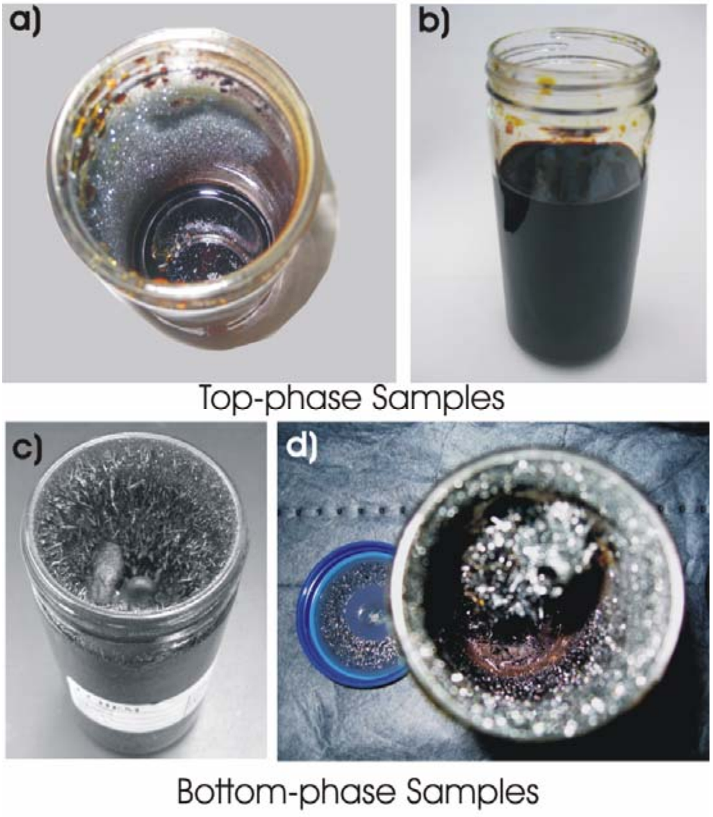

Figure 3.2 Photographs of typical samples collected during a CFA run. a) shows the top phase before its homogenization; the sample is a liquid with some solid iodine crystals on the walls of the glass jar. b) is a top sample after homogenization with KI; it is a dark liquid and care must be taken to assure the total dissolution of the solid iodine. c) and d) are pictures of the bottom phase; the sample is mostly a solid phase (the liquid is not noticeable from these pictures).

Figure 3.2b shows a sample of the top phase after being homogenized with a 10 w/w % solution of KI. On the other hand, as shown in Figs. 3.2c and d, samples of the bottom phase consist primarily of solid I_2 and a barely noticeable liquid phase that can be seen only when the jar is tilted.

Typically, triplicate samples of the top and bottom phases are collected for 30-40 minutes each, resulting in top- and bottom-phase samples weighing 40 to 150 g each, respectively. In previous work in Thies's lab, Crosthwaite [1] showed how relatively large samples of each phase need to be collected to ensure that a representative sample is obtained, as the samples become inhomogeneous and split into two or more phases as they cool upon exiting the isothermal bath. Note that samples of both top and bottom phases are continuously collected in our CFA by interchanging the collection jars using the 3-way valves V_4 and V_5.

SAMPLE ANALYSIS

Top-phase, water-rich samples obtained from the CFA were first weighed, homogenized with a KI solution, re-weighed, and then titrated for HI and I_2 content. In this phase, water was estimated by difference because it was the major component. Bottom-phase samples, on the other hand, have not been successfully analyzed thus far; however, two methods have been tested and are presented later in this chapter.

SAMPLE HOMOGENIZATION

A range of solvents, including ethanol, hydrochloric acid (HCl), water, and aqueous solutions of potassium iodide (KI), were tested for the homogenization of the top- and bottom-phase samples obtained from the CFA for the ternary I_2-HI-H_2O system. Ethanol is an excellent solvent for iodine, but was found to react with HI. For this same reason, other common organic solvents (e.g., toluene) cannot be used with HI-containing systems. Water and HCl solutions are also inappropriate because they are poor solvents for iodine. However, solutions of potassium iodide (KI) were found to readily dissolve the solid iodine because of the formation of triiodide ions (I_3^-)[2]. KI also has the advantage that it does not react with HI or iodine.

Consequently, from the solvents tested, a solution of 10 w/w % KI in water was prepared to homogenize the top-phase samples. For each top sample weighing 40 g, approximately 160 g of 10 w/w % KI solution was added until all solid I_2 had been dissolved. As discussed below, homogenization of the bottom-phase samples with KI solution is also possible, but requires a much greater amount of KI, as these samples are mainly composed of I_2.

From each homogenized top-phase sample, three subsamples of approximately 5 grams each are taken for titration with NaOH in order to determine the HI content, following reaction 3.1:

$$HI + NaOH \rightarrow NaI + H_2O \tag{3.1}$$

The pH of the solution is monitored using a pH meter (Accumet basic AB15, with electrode Accumet cat. no. 13-620-285), while a 0.2 N standardized NaOH solution is added to the sample using a burette. As shown in Figure 3.3, the first point after the steep rise in pH is taken as the point at which all HI has reacted.

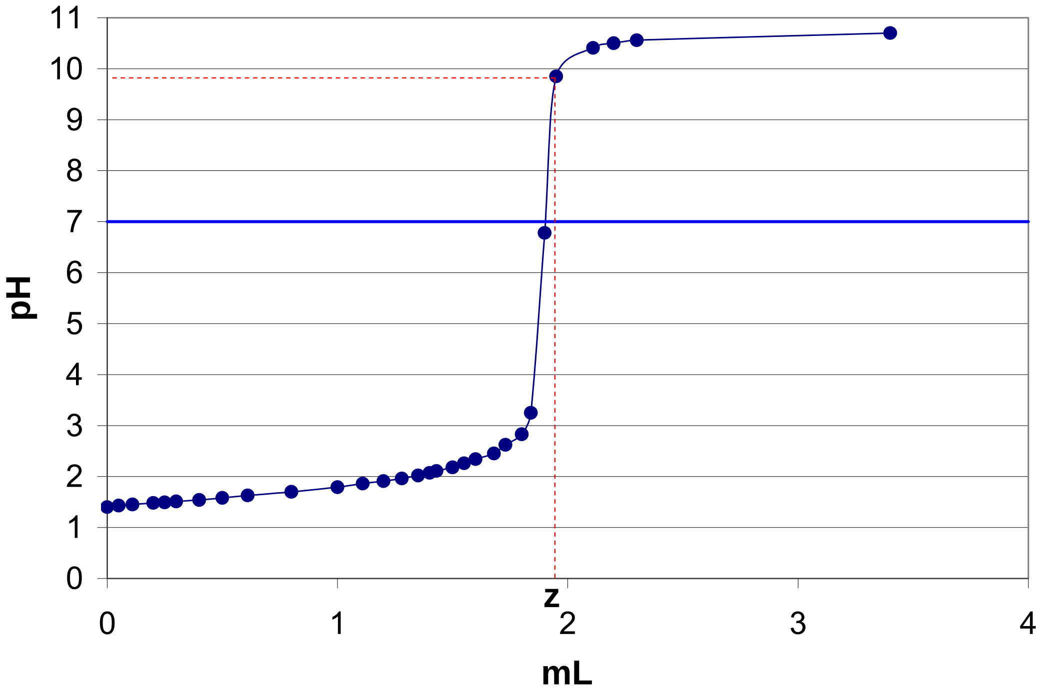

Figure 3.3 Titration of a ternary sample containing I_2-HI-H_2O. The value Z represents the mL needed for the reaction of all the HI in the sample with NaOH (for this particular titration NaOH=0.5M).

Three other subsamples of approximately 0.2 grams each are also taken from each homogenized top-phase sample for analyzing its iodine content by titration with sodium thiosulfate, per reaction 3.2:

$$2Na_2S_2O_3 + I_2 \rightarrow 2NaI + Na_2S_4O_6 \qquad 3.2$$

The standardized solution of sodium thiosulfate (0.025N) is added to the subsamples by means of a burette up to the point where the solution turns from dark purple into a light yellow color. The addition of approximately 0.5 mL of a starch indicator solution (0.01 g/mL) turns the solution from light yellow into a dark blue color characteristic of complex known as amylase iodine (or starch-iodine) that is formed when I_2 is present. Titration with sodium thiosulfate continues until all iodine has reacted and the solution becomes transparent. Recent studies [2] indicate that the iodide ions, formed after the addition of the KI in the aqueous solution, are not consumed in the amylase-iodine complex formation and hence do not interfere with the iodine titration.

To validate our methodology, standard samples containing known amounts of I_2, HI, and H_2O were prepared and titrated as described above. To prepare these samples, known amounts of the analytes were weighed using an analytical balance (Denver Instruments, M-310) and then homogenized with a 10 wt% KI solution. Table 3.1 shows the results from the titrations of HI and I_2 for the four

Table 3.1 Percent deviation error in titration methods for the analysis of the top phase. All compositions are in mol fraction. Note that water is found by difference.

Standard 1 (mol fraction)			
Prepared Compound	**Compositions**	**Titrated compositions**	**% deviation error**
I_2	0.019	0.019	0.60
H_2O	0.969	0.969	0.00
HI	0.012	0.012	0.98

Standard 2 (mol fraction)			
Prepared Compound	**Compositions**	**Titrated compositions**	**% deviation error**
I_2	0.038	0.037	0.47
H_2O	0.945	0.946	0.06
HI	0.017	0.017	2.14

Standard 3 (mol fraction)			
Prepared Compound	**Compositions**	**Titrated compositions**	**% deviation error**
I_2	0.008	0.008	0.49
H_2O	0.986	0.987	0.05
HI	0.006	0.006	6.98

Standard 4 (mol fraction)			
Prepared Compound	**Compositions**	**Titrated compositions**	**% deviation error**
I_2	0.058	0.059	1.55
H_2O	0.922	0.921	0.14
HI	0.020	0.020	2.10

*where % deviation error is defined as $\frac{(composition - titrated\ composition)}{composition} \times 100$

standards prepared. Note that the compositions of the prepared standards are intended to simulate the compositions of the top-phase samples obtained from the CFA at typical operating conditions. Overall, the titration results presented in Table 3.1 indicate that I_2 can be estimated with an average error of less than 1.5 % deviation when present in concentrations ranging from 3.8 to 0.8 mol% (10 to 44 wt%). For HI, the results indicate an average error of approximately 2% deviation for solutions containing between 1.2 to 2 mol% (6 to 8 wt%) HI. However, for solutions with lower HI content, the error is seen to increase up to 7 % deviation. In this case, a less concentrated NaOH solution could be used to increase the accuracy of the titration.

BOTTOM-PHASE COMPOSITIONS

Bottom-phase samples obtained from the CFA for the I_2-HI-H_2O system contain approximately 90 to 95 wt% iodine (see also Figure 3.2 (c) and (d)). Therefore, iodine in the bottom-phase samples can be readily estimated from a component mass balance, as both feed and top-phase compositions are accurately known. However, because water and HI are minor components in the bottom phase, they cannot be accurately estimated simply by mass balance, but must be quantified by an analytical method in order to validate our results. Thus such methods that were evaluated for this purpose are discussed below.

Homogenization with KI

Just as is done for the top-phase samples, the bottom-phase samples can also be homogenized with KI solution, and the HI content determined by titration with NaOH. For example, a bottom-phase sample obtained from experiment CFA 22 and weighing 108 grams required 2014 g (~ 2L) of 10 w/w% KI for homogenization. Sub-samples were then taken and titrated with a standard solution of NaOH. The results are shown in Table 3.2. Note that for each sub-sample, less than 1 mL of NaOH solution was used for the complete titration of the HI content.

Table 3.2 Titration of the Bottom phase (Bottom 1, CFA 22)

Bottom-phase sample (g)		108.92	
10 wt% KI (g)		2014.29	
NaOH (M)		0.2164	
Sub-sample	Weight (g)	Added NaOH (mL)	w/w fraction HI
S1	4.7146	0.14	0.016
S2	5.0574	0.10	0.011
S3	4.1751	0.05	0.006
Average w/w fraction HI		0.0111	
Std deviation		0.0048	

As shown in Table 3.2, the HI content in the bottom-phase sample was calculated to be approximately 1.1 ± 0.5 wt%. Such a large deviation is not surprising if one takes into account that approximately 2 L were required to homogenize the 109 g of bottom-phase sample. To improve the accuracy of this method, a more concentrated solution of KI could be used, as well as a less concentrated solution of NaOH to perform the titration.

Gas Chromatography

Both HI and water content in homogenized bottom-phase samples can be estimated using gas chromatography (GC) coupled with a thermal conductivity detector (TCD). Preliminary results indicate that GC-TCD can used to separate mixtures of I_2-HI-H_2O using a GasPro Column (Agilent, PLOT column, 30m, part no. 113-4332). However, the ternary mixtures tested thus far have had a low I_2 content, limited by the I_2 solubility in HI-H_2O solutions. To obtain accurate results for HI and H_2O content, aqueous solutions cannot be used as a solvent to homogenize the bottom-phase samples, as water is a minor component present in the analyte. Thus, KI solutions cannot be used. Organic solvents are also inappropriate because, as discussed previously, they react with HI. With that in mind, a distillation method was employed to separate HI and water from the solid iodine present in a bottom-phase sample so that the distillate could be directly analyzed by GC-TCD.

Distillation

As shown in Figure 3.4, the distillation setup consisted of a heated reaction kettle (Corning, part no. 6947-500) fitted with a total condenser and a distillate collection flask. A sample jar containing approximately 93 g of iodine and 7 g of a 1 wt% HI-H_2O solution (expected calculated composition for a bottom-phase sample) was then prepared and placed inside the reaction kettle. Note that in Figure 3.4, for clarity, only a small section of the actual heating tape is shown. (During a distillation experiment, the tape is wrapped all around the exterior of the kettle.) lso, note that all wetted parts are glass and the reaction kettle O-ring is made out of Teflon, materials known to withstand the corrosiveness of HI and I_2. The cap of the kettle is held to the kettle using a spring-loaded clamp (not shown in Figure 3.4) that allows for the cap to open in case of pressure buildup. Air was the contact fluid between the sample and the vessel; a better conductor was not used to avoid reaction with the evaporated HI.

Before the distillation started, the weight of the round distillate collection flask was accurately measured and recorded. The basic idea was to separate the HI-H_2O phase (the boiling point of this azeotrope is 127°C [3]) from the iodine crystals (boiling point 184.3°C [3]) and to conduct a titration of the liquid obtained. After 2 hours of distillation at 180°C, a few drops of liquid were observed on the inner walls of the condenser, but unfortunately, not enough had condensed to be collected in the distillate flask. After this preliminary test, it was concluded that the HI-H_2O content in a typical bottom-phase sample was too small to be completely distilled without losing some of the distillate in the setup, which would significantly affect the accuracy of subsequent GC analyses.

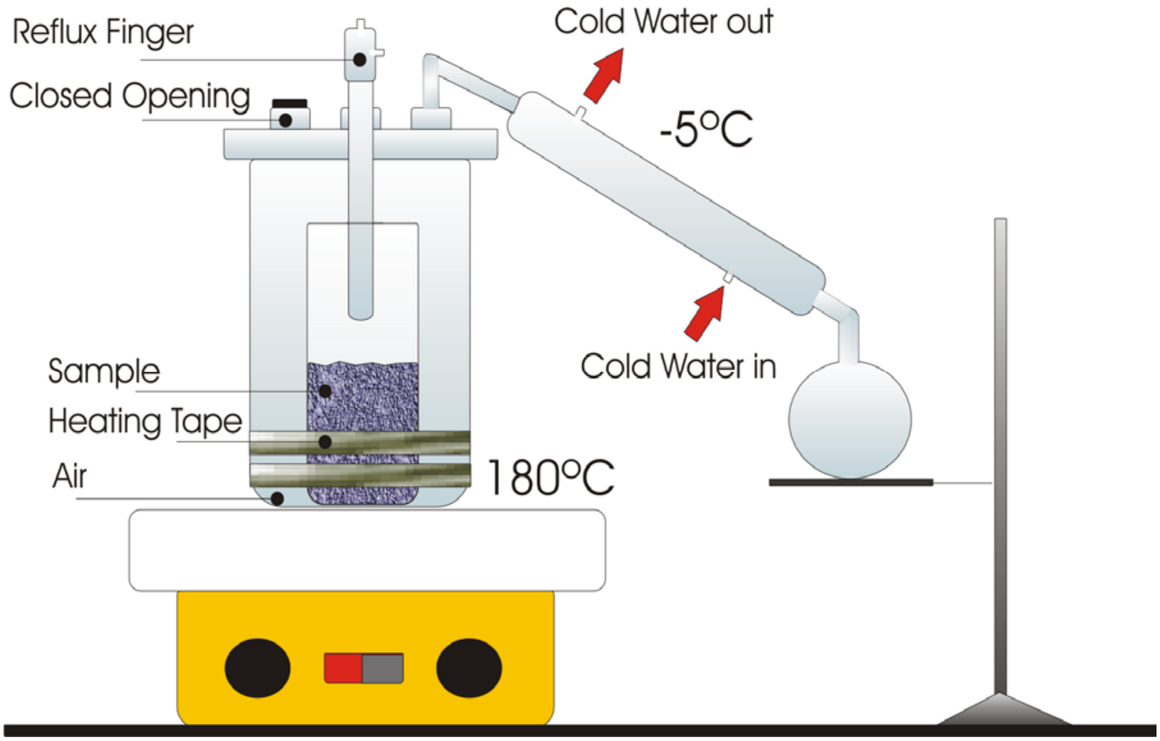

Figure 3.4 Schematic of the distillation equipment tested for the analysis of the bottom phase.

RESULTS AND DISCUSSION

PHASE EQUILIBRIUM MEASUREMENTS AT 160°C

Using the CFA, measurements for the ternary I_2-HI-H_2O system were carried out at 160 °C at three different feed compositions. As shown in Table 3.3, the concentrations of HI-H_2O solutions used were 0.9, 2.4, and 4.9 mol% HI, labeled CFA 21 to 23, respectively. Also shown are the flow rates of molten iodine and HI-H_2O solutions delivered to the impingement mixing tee shown in Figure 3.1, and the resulting overall feed compositions being delivered to the view cell.

Table 3.3 Summary of conditions for experimental runs CFA 21-23 at 160 °C

	CFA 21	**CFA 22**	**CFA 23**
System Pressure (psig)	700	500	600
HI-H_2O (mol fraction2 HI)	0.024	0.009	0.049
HI-H_2O flow rate (mL/min)	1.00	1.00	0.70
I_2 flow rate (mL/min)	1.00	1.00	1.30
Overall Feed compositions (mol%)			
HI	1.84	0.71	3.17
H_2O	75.94	77.31	61.73
I_2	22.22	21.98	35.10

Table 3.4 Top-phase sample titration results for I_2 and HI content. Samples obtained from run CFA 21 at 160 °C. Good reproducibility between samples (Top 1 to 3) and subsamples 1 to 3 was obtained.

	Iodine mol fraction		
	Top 1	Top 2	Top 3
Subsample 1	0.027	0.026	0.028
Subsample 2	0.027	0.027	0.027
Subsample 3	0.026	0.026	0.027
Average	0.027	0.026	0.027

	HI mol fraction		
	Top 1	Top 2	Top 3
Subsample 1	0.017	0.016	0.016
Subsample 2	0.016	0.017	0.016
Subsample 3	0.016	0.016	0.016
Average	0.017	0.016	0.016

For each experiment (CFA 21 to 23), three samples each were collected for the top (water-rich) and bottom (iodine-rich) phases. Top-phase samples were titrated for I2 and HI content. The titration results for CFA 21 are shown in Table 3.4. As can be seen, good reproducibility is obtained between the samples and subsamples. Average titration results for experimental runs CFA 21 to 23 are summarized in Table 3.5.

Table 3.5 Top-phase compositions for runs CFA 21 to 23 at 160 °C. Compositions and standard deviations are given in mol fraction.

Run	**Average compositions of the top samples**		
	I_2	HI	H_2O
CFA 21	0.027±0.001	0.017±0.0002	0.957
CFA 22	0.011±0.001	0.008±0.0002	0.981
CFA 23	0.049±0.001	0.025±0.0008	0.926

To obtain the composition of the bottom-phase samples, an overall mass balance was performed on the system. That is, because the HI, H_2O, and I_2 content are all known for the feed and top phase, component mass balances can be carried out in order to estimate the compositions of the bottom phase. The results are presented in Table 3.6 and the details of the overall mass-balance calculations are given in Appendix F. As expected, there is a higher degree of scatter in the bottom-phase compositions, showing the importance of developing an analytical technique for the bottom-phase samples.

Table 3.6 Compositions of the bottom phase for run CFA 21-23 at 160 °C, as obtained by overall mass balance. All compositions are given in mol fraction.

	CFA 21			
Compound	**mol fraction**			
	Sample 1	Sample 2	Sample 3	Average
HI	0.023	0.022	0.022	0.022±0.001
H_2O	0.293	0.388	0.462	0.381±0.085
I_2	0.684	0.590	0.516	0.597±0.084
	CFA 22			
Compound	**mol fraction**			
	Sample 1*	Sample 2	Sample 3*	Average
HI		0.006		0.006
H_2O		0.137		0.137
I_2		0.857		0.857
	CFA 23			
Compound	**mol fraction**			
	Sample 1	Sample 2	Sample 3	Average
HI	0.036	0.038	0.039	0.038±0.002
H_2O	0.424	0.344	0.304	0.357±0.061
I_2	0.541	0.618	0.657	0.605±0.059

*Mass balances for this samples did not close.

Table 3.7 Comparison between measured and pump setting flow rates

Run	Sample No	Sample weight measured by sample collection	Sample weights from ISCO and IC pump settings	%Error*
CFA 21	1	188.13	191.178	1.62
CFA 21	2	211.24	211.302	0.03
CFA 22	2	163.58	148.77	-9.05
CFA 22	3	143.67	148.77	3.55
CFA 23	1	166.43	166.86	0.26
CFA 23	2	212.42	208.58	-1.81

*where % error is defined as $\frac{(estimated - measured)}{estimated} \times 100$

Table 3.7 shows the difference between the weights of a total sample collected (sum of top, water-rich and bottom, iodine-rich phases) and the weight of the combined streams delivered as feed by both the ISCO and the IC pumps during the sample collection time (usually 30 min).

The water-rich top-phase and the iodine-rich bottom-phase compositions obtained from CFA Runs 21-23 are plotted below as equilibrium tie lines in Figure 3.5. To our knowledge, these are the first LLE phase compositions ever obtained for the ternary I_2-HI-H_2O system.

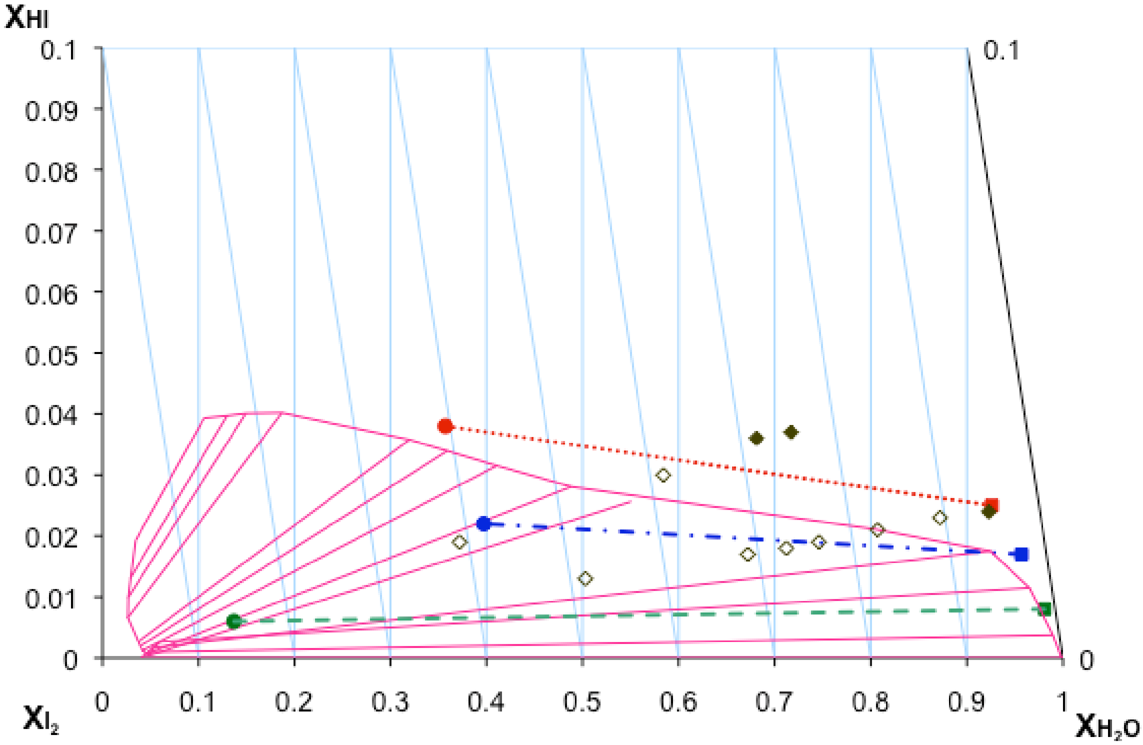

Figure 3.5 Ternary diagram for the system I_2-HI-H_2O at 160°C. Pink, solid (——) lines are the model predictions [4]; (---) is the tie line for run CFA 22 (0.9% HI in feed) (-·-·-) is for run CFA 21 (2.4% HI in feed) and (····) is for run CFA 23 (4.9% HI in feed). Squares (■) denote the titrated compositions for the top phase while circles (●) denote the calculated compositions for the bottom phase. Solid diamonds (♦) represent overall feed compositions for when one phase was observed in the view cell. Open diamonds (◊) represent overall feed compositions for when two phases were observed.

Also shown on Figure 3.5 are the modeling predictions by Murphy and O'Connell [4]. Clearly, there is a discrepancy between the modeling predictions and our LLE measurements for the ternary I_2-HI-H_2O system. At this time we do not have a good explanation for the differences observed.

The top-phase compositions used to generate the tie lines presented in Figure 3.5 are the average of the titrations for the three subsamples collected during each experiment; the bottom-phase compositions are the average of the mass balances performed for each subsample (See Appendix F). The variation among each subsample is shown in Figure 3.6.

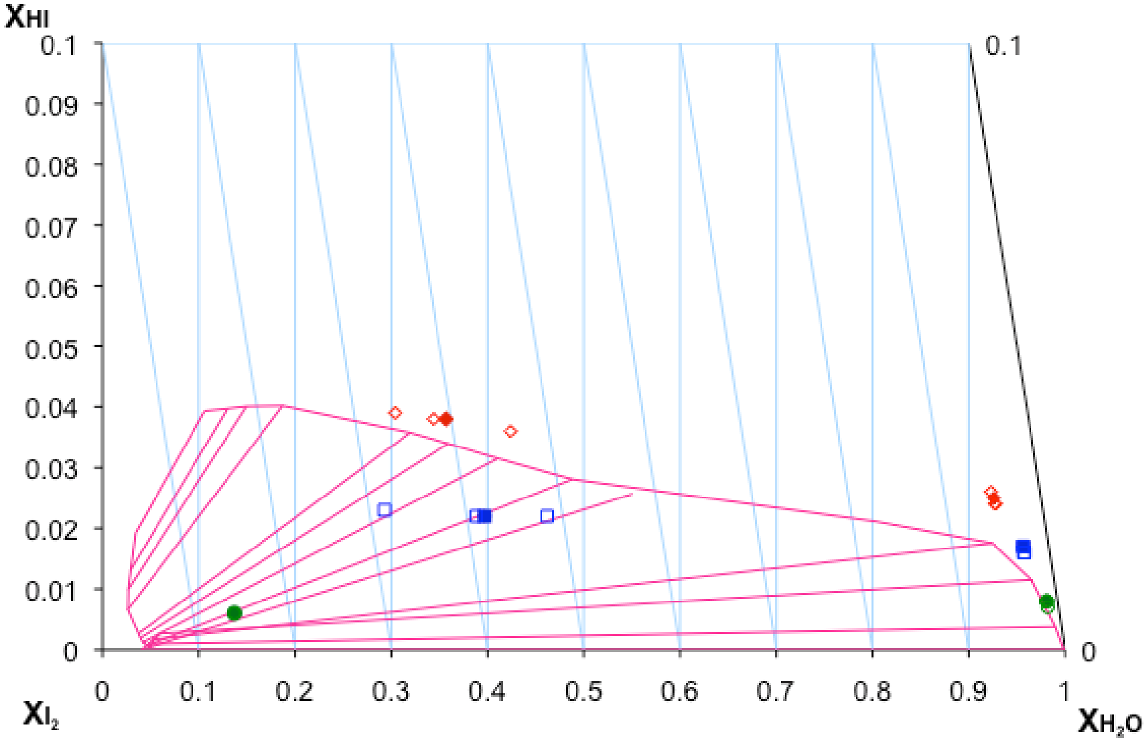

Figure 3.6 Ternary diagram for the system I_2-HI-H_2O at 160°C. Pink solid (—) lines are the model prediction by Murphy and O'Connell [4]; Outlined squares (□) denote CFA 21 subsamples for both the top-phase (right side of the diagram) and the bottom-phase (left side of the diagram), while solid squares (■) denote their average value. Outlined circles (○) denote CFA 22 subsamples and solid circles (●) their average value. Outlined diamonds (◇) denote CFA 23 subsamples and solid diamonds (♦) their average.

PHASE EQUILIBRIUM MEASUREMENTS AT OTHER TEMPERATURES

In addition to the runs at 160°C, other temperatures were also evaluated. A table summarizing all the experiments conducted in the CFA is shown in Appendix G. The lowest operating temperature was 120°C and it was found to be too low for an optimum operation of the system. Because 120°C it is too close to the melting temperature of iodine (113°C), solid plugs of iodine were experienced.

At 140°C, a 10% w/w HI feed was tested. During this experiment a single dark phase was observed in the view cell using the IR camera. Overall feed compositions tested at this temperature are shown in Figure 3.7. From the envelope predicted by the model by Murphy and O'Connell [4] we were expecting to observe two-phase LLE behavior for the feeds with H_2O content lower than 0.3 mol fraction. We now believe that because the iodine-rich and water-rich phases have a tendency to look similar to each other when higher HI content is present, we were unable to identify the separate phases. These experiments should be performed again, keeping the top three-way valve (V_4) closed and observing whether a lighter phase accumulates in the top of the view cell. From our experience, when working with aqueous HI-H_2O feed solutions with HI contents higher than 5% mol, it is easier to identify a lighter phase accumulating on top of the heavy phase.

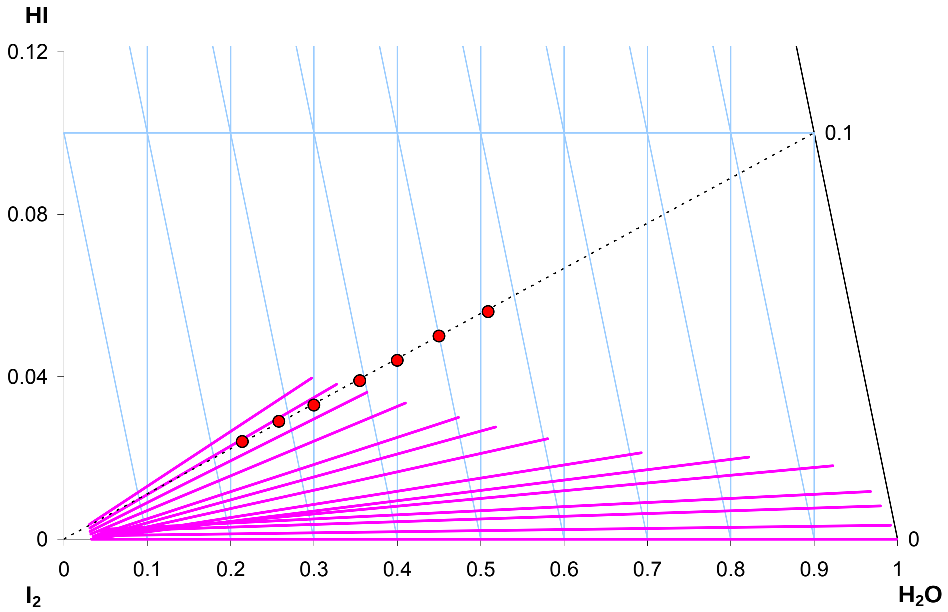

Figure 3.7 HI-I_2-H_2O ternary Diagram at 140°C. All data are in mol fraction. Pink solid (—) lines are the model prediction [4]. Circles (●) denote total feed compositions for when one phase was observed in the view cell.

Experiments at 225°C, with 2.5 mol % HI in the aqueous feed, were also carried out but were inconclusive. Although the runs themselves proceeded smoothly and the apparatus performed well, we were unable to clearly establish how many phases were present in the view cell. Different overall flow rates were tried in order to locate the two-phase region, but without success. The contents of the view cell were dark and unstable, making observation of the LLE interface difficult. The instability could have been caused by an inadequate heating or mixing of the components. At this higher temperature, our calculations indicate that additional preheating line length for the aqueous phase would need to be installed.

INFLUENCE OF TIME AFTER THE COLLECTION OF THE SAMPLES

To check if there was some decomposition of the samples with time, iodine was re-titrated from the same sample at two different time intervals: 11 days after collection and around five months after collection (samples had been homogenized and stored in a refrigerator). Results are shown in Table 3.8.

Table 3.8 Iodine titration over time of the Top 1 sample collected on CFA 21

Top 1 May-12-09	**Collection Date May-12-09**		
	w/w fraction iodine		
Sub-Sample	**May-14-2009**	**May-25-2009**	**Oct-27-2009**
S1	0.265	0.259	0.262
S2	0.260	0.261	0.276
S3	0.259	0.255	0.269

Even after five months in storage, samples do not seem to decompose in a noticeable way.

HI ONLY RUN

In order to test both the IC pump and the quality of our sample collection scheme, a test run (CFA 25) was performed using the CFA. During the run, only HI solutions were pumped, with all other conditions being maintained as for a regular run (i.e., temperature of the oven, heating of the lines and valves outside the oven, and temperature of the cold bath to collect the samples). An HI solution with a concentration of 2.9 w/w % HI (5.5 mol% HI) was fed to the system at a flow rate of 1 mL/min. The weights of the samples obtained are presented in Table 3.9.

Table 3.9 Samples collected on CFA 25 (HI only) run

Collection time	30 min each		
Expected total weight of each sample from IC pump setting	**38.1 g**		
	Sample 1	**Sample 2**	**Sample 3**
Top phase sample weight (g)	7.65	20.14	9.82
Bottom phase sample weight (g)	29.08	16.62	30.62
Total weight (g)	**36.73**	**36.76**	**40.44**
Difference from estimate (g)	1.37	1.34	-2.34
% Error	3.59	3.51	-6.14

*where % error is defined as $\frac{(\text{expected} - \text{measured})}{\text{expected}} \times 100$

For 30 minutes of sample collection, taking the density of the HI-H_2O solution to be 1.27 g/mL, the total mass of sample collected should be 38.1 g. The difference between this value and the total weight is shown in the last row of Table 3.9 and represents around 3-5% of the total weight. The HI concentration of the feed and each top and bottom sample, obtained by titration, is presented in Table 3.10.

Table 3.10 Concentration of samples for CFA 25

mol fraction HI content						
Feed 0.055						
Phase	Sample 1		Sample 2		Sample 3	
	X_{HI}	%error	X_{HI}	%error	X_{HI}	%error
Top	0.0436	20.21	0.0507	7.23	0.0473	13.47
Bottom	0.0519	5.14	0.0507	7.19	0.0516	5.58

*where % error is defined as $\frac{(feed - sample)}{feed} \times 100$

The reduction of HI content in all collected samples could be the result of loss of sample, the reaction of HI during the experiment, and/or experimental error.

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CHAPTER IV

CONCLUSIONS

We have constructed a new, unique, continuous-flow apparatus, designed for obtaining data for highly corrosive systems. The apparatus is fully functioning and has been used to measure liquid-liquid equilibria (LLE) for aqueous mixtures of HI with iodine, which is a solid at room temperature. For the water-rich, top-phase samples obtained, the iodine and HI compositions were obtained via titrations using sodium thiosulfate and sodium hydroxide, respectively. For the iodine-rich bottom phase, phase compositions were deduced from an overall mass balance. This chapter presents conclusions drawn from this study.

CONTINUOUS-FLOW APPARATUS

The continuous-flow apparatus (CFA) designed and constructed for this work is rated for temperatures of 350°C and pressures of 150 bar. In the course of the development of this apparatus, tantalum (Ta) and its tungsten (W) alloys were found to be capable of withstanding the aggressive chemicals and conditions that exist for the I_2-HI-H_2O system. For this reason, Ta valves and fittings were fabricated at Clemson University and found to perform as well as their analogous stainless steel (ss) counterparts. Graphite and borosilicate were also found to work well at high temperatures. For low-temperature applications with these chemical species, PEEK and PFA polymers were found to work well.

We have successfully demonstrated the indirect pumping of molten I_2 with a ~700 mL Ta-10W alloy reservoir, using water being delivered from an Isco syringe pump as the working fluid.

The mixing equilibrium section currently used in the CFA was proven to be adequate, as large changes in flow rates have no impact on the observed phase boundaries (See Table 2.3).

Deterioration of the original aluminosilicate windows (Hoya Optics, Almax II) for the view cell was observed at temperatures of 270°C in the presence of the binary I_2-H_2O. On the other hand, borosilicate windows have worked flawlessly with ternary mixtures of I_2-HI-H_2O at temperatures as high as 225°C. Even after 17 runs, no signs of wear are noticeable.

For this work, the infrared setup with the electro-viewer was successfully used to observe VLE, LLE and VLLE of the systems studied at a maximum concentration of 2.5% mol fraction HI in the aqueous feed solution at temperatures up to 200°C, and at a maximum concentration of 5% mol fraction HI in the aqueous feed at temperatures up to 160°C. Application of IR at higher temperatures and concentrations might be possible, but has not yet been tested.

ANALYSIS TECHNIQUES

Good reproducibility was observed for the HI and I_2 concentrations of the samples obtained for the ternary I_2-HI-H_2O experiment, as seen in Table 3.4. Iodine concentrations, taking into account all sources of error, are estimated to be accurate to better than 5% deviation error. HI concentrations are estimated to be accurate to within 5% deviation error for solutions containing at least 0.02 mol fraction HI and to within 9% error for lower HI concentrations.

Solutions of 10% KI in water were found to be suitable as a solvent for the top phase samples of the ternary I_2-HI-H_2O system. Homogenized samples appear to be stable for long periods of time (See Table 3.8).

In the early stages of this work, difficulties in obtaining reproducible phase compositions in the collected samples were encountered. The reason for this problem was that, upon exiting the view cell, the streams cool and subsequently phase-separate to form two liquid phases. Because this mixture is not homogeneous, the two phases travel through the tubing at different instantaneous rates, or in slugs. For a particular segment of time, more of one phase than of the other may be collected because of holdup of one of the phases. In order to minimize deviations in phase compositions due to these two-phase flow effects, relatively large sample sizes (at least 30 minutes collection time) were collected in order to average out the fluctuations in flow of the two phases. Long periods of sample collection resulted in good reproducibility between the samples for each experiment (See Table 3.4).

PHASE BEHAVIOR

The first observations for LLE for the binary I_2-H_2O above 225°C are presented. LLE was clearly observed at temperatures up to and including 300°C, contradicting previous expectations in this area [1, 2]. Based on our observations, we estimate that the upper critical solution temperature will occur at 315 ± 5°C.

LLE phase boundaries for the ternary I_2-HI-H_2O were mapped for the water-rich region at temperatures of 160 and 200°C. From the results at these two temperatures, we observed that the region of immiscibility decreases with increasing temperature.

Existing models for the ternary I_2-HI-H_2O, which are based on VLE data, are inadequate for the prediction of LLE. Analysis of the top-phase, water-rich samples, combined with an overall mass balance on the system, indicates that HI concentrations in the bottom, iodine-rich phase are significantly higher than what predicted by the best current models.

CHAPTER V

RECOMMENDATIONS

Recommendations for improvement of the current CFA and for future work with the ternary I_2-HI-H_2O system are presented in this chapter.

CONTINUOUS-FLOW APPARATUS

During the course of our experiments, overall mass balances were conducted on the I_2-HI-H_2O system. Although the weights of the samples collected during these experiments agreed, within experimental error, with the expected weight of the combined flow rates delivered by both the ISCO and the IC pumps (Table 3.7), we recommend that experiments be conducted such that only iodine is delivered into the system, in order to corroborate the accuracy of the indirect method of pumping iodine.

The cause of the reduced HI content in the samples collected during run CFA 25 (See Table 3.9) need to be determined, as it could be having a significant impact on our reported experimental compositions. We recommend performing similar "HI solution only" experiments, but at lower oven and heat-tracing temperatures. This action will help to isolate the problem as being related to the reaction/volatility issues.

Even though the mixing/equilibrium section has proven to perform adequately, we recommend improving the current configuration by installing two more mixer/splitters, as shown in Appendix H. This will help for studies of the low water content side of the ternary diagram, where the feed flow rates coming from the iodine and HI solution are highly dissimilar and mixing problems are more likely to occur, as the momenta of the phases are no longer similar [3]. To validate the performance of the mixing/equilibrium section, samples from one-phase experiments can be collected and analyzed. If good mixing is attained, then variation from top- and bottom-phase samples should be minimal.

We recommend that the length of the heating section of the iodine tubing be increased to 24 ft before conducting experiments at temperatures higher than 200°C. The current length (15 ft) is adequate to preheat the iodine to within 1°C of an oven temperature of 200°C at a flow rate of 1.5mL/min (90mL/hr). Here we note that the heating section for the HI-H_2O solution is already of adequate length (i.e., 20 ft) and can preheat the same flow rate (1.5 mL/min) to within 0.1 °C of oven temperatures up to 350°C.

We recommend calibrating the RTD currently in the system against our Rosemount primary standard, as such a calibration has not been done for the actual RTD.

During the operation of our CFA, significant deviations in the system pressure (e.g., caused by too large a change in a micrometering (MM) valve setting) will cause iodine from the reservoir to flow into the view cell at a faster rate than the one set by the pump. Thus, such changes should be minimized and kept below ± 15 psi.

The modifications performed on the stem of the tantalum MM valve greatly improved pressure control in the system. We therefore recommend that for any future valve-stem fabrication, the angle for the tip of the stems to be set at 1°. (Refer to Figure 2.4)

Even at room temperature, HI will decompose into iodine and hydrogen after long periods of time. Therefore, it is crucial that after every run all the lines in contact with HI should be cleaned with water. Hydrogen will cause the tantalum to become brittle over time. This represents a safety issue, as embrittled Ta lines could eventually rupture during system operation.

The 1/8″ tantalum tubing connecting the bottom of the iodine reservoir to the oven goes through a tee. One of the sides of this tee is connected to a Hastelloy

C-276 valve that has never been used. The tantalum tee was found very likely to have leaks, so we recommend replacing it by a 1/-1/8 tantalum union, eliminating the connection to the Hastelloy C-276 valve.

SAMPLE ANALYSIS

To increase the accuracy of titrations for the determination of HI content, a less concentrated solution of NaOH (less than 0.2 M) should be used (i.e., NaOH , 0.0100 N).

The analysis of the bottom phase is crucial for the construction of accurate equilibrium tie-lines for the ternary I_2-HI-H_2O. For the homogenization of the bottom phase, we recommend testing a more concentrated solution of KI. This might lower the quantity of solvent needed for homogenization and could make the analysis of the HI feasible with the titration method.

To enhance the performance of the current sample-collection setup, the samples can be collected in jars containing solutions of NaOH with a known concentration. The NaOH solution should be added in excess to the glass jars prior to the collection of the samples. After collection, the excess NaOH solution could be titrated using a primary standard (i.e., Oxalic acid solutions) and the amount of HI back calculated from the reacted NaOH.

PHASE BEHAVIOR

For CFA experiments at temperatures above 160° or with HI feed compositions above 5 mol %, the appearance of the water-rich phase under the IR viewer will be more similar to the iodine-rich phase than for lower HI concentrations. If difficulty in establishing LL the interface is encountered, we recommend installing a stronger light source for our IR viewer so that cell contents are more easily visible.

The pressure is not a variable that should affect the LLE behavior of the system, because our two liquid phases are essentially incompressible. Nevertheless, we recommend testing the same feed at two different pressures in order to verify this expectation.

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APPENDICES

APPENDIX A. EXPERIMENTAL PROCEDURE FOR THE CFA

A detail schematic of the apparatus is given as Figure A.1, and it is assumed that the reader is referring to it unless otherwise noted.

PREPARATION

Iodine reservoir refill

Approximately every two runs the iodine reservoir must be refilled. To check if there is enough iodine in the reservoir, disconnect the thermocouple from the tantalum cross on top of the iodine reservoir (see Figure A.2) and insert a piece of 1/16” o.d. tantalum tubing through the tantalum cross, observing the length of tubing necessary to touch the level of solid iodine. For a regular run (only one point tested) it is recommended that the solid iodine level be at least above the fourth heating band in the reservoir, which means that the length of tantalum tubing until it touches the solid iodine level should be around 22 inches, as measured from the NPT fitting (see Figure A.2)

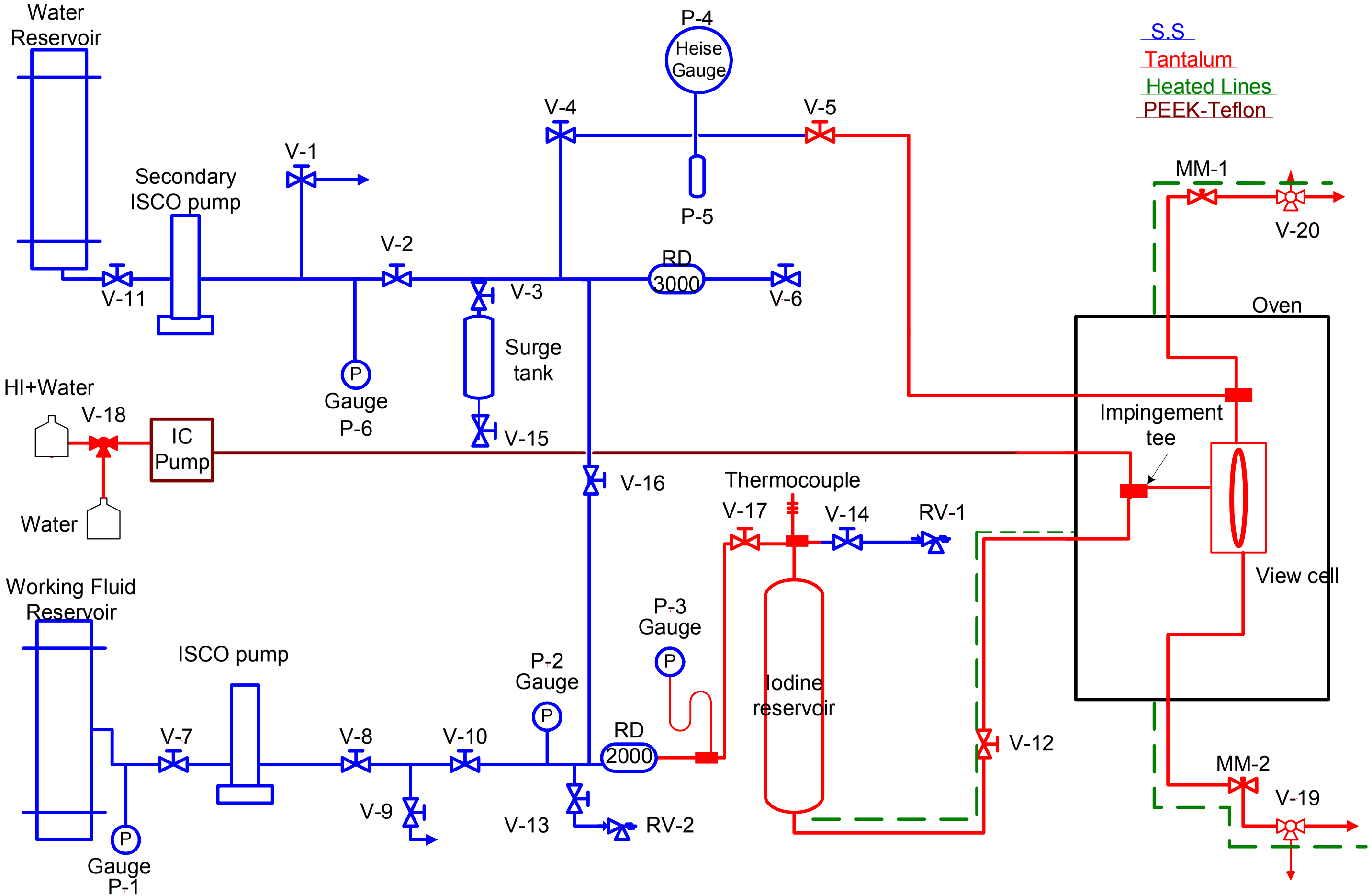


Figure A.1 Detailed schematic of the Continuous-Flow Apparatus

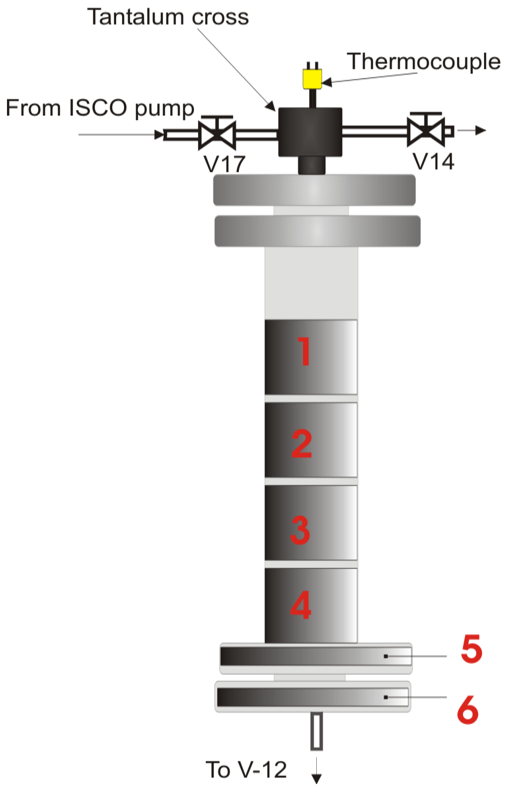


Figure A.2 Heating zones in the iodine reservoir

To refill the iodine reservoir, disconnect the tantalum cross on top of the iodine reservoir at the NPT threads (refer to Figure A.3). Next, remove the water sitting on top of the solid iodine using ¼ " o.d. PFA tubing by means of Pascal's principle: insert one end of the PFA tubing full of water on top of the reservoir while placing the other end at a lower height inside a glass jar to collect the water (1L jar). Allow the water to drain into the glass jar.

Then, weigh approximately 900 grams of prilled solid iodine into a glass jar and slowly transfer them to the open end of the reservoir using a plastic funnel. The level of the iodine in the reservoir must carefully monitored, using the 1/16" tubing, to prevent it from going above the middle of the second heating band (iodine will expand ~30% while melting); this is approximately 15 inches, as measured from the tantalum cross. Once the desired level of solid iodine is achieved, the tantalum cross is connected again after putting new Teflon tape on the NPT threads.

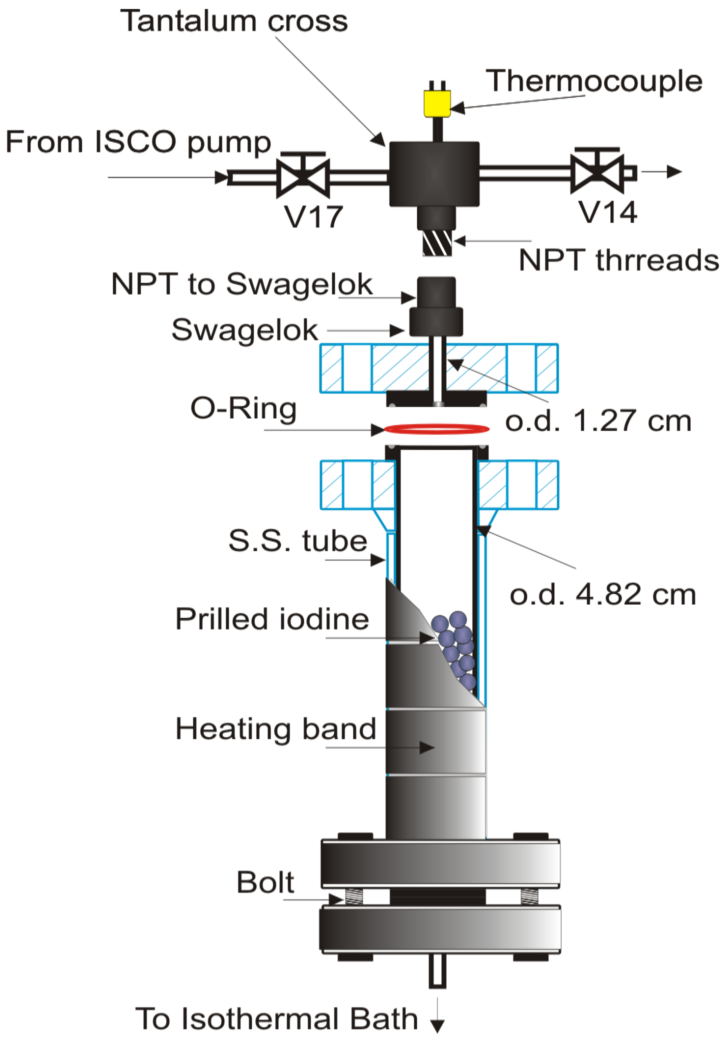


Figure A.3 Detailed schematic of the iodine reservoir

PRESSURE TESTING

At this point the reservoir must be hydrostatically pressure-tested with water at pressures 50% above the expected operating pressure of the run, keeping in mind that the maximum operating pressure of the reservoir is 1500 psig.(so the maximum hydrostatic pressure is 2250 psig). To do this the initial state of all valves is closed. Set the maximum pressure limit for the ISCO pump to 1500 psig. Next, open valves V-7, V-8, V-10 and V-17 and pump water using the ISCO pump at a flow rate of 10 mL/min to build the pressure needed. Typically, pressure-testing is at 1500 psig and pressures above 2000 psig should be avoided (In case a pressure between 1500 and 2000 psig is needed, the maximum pressure limit for the ISCO pump should be set to 2000 psi.) Once the pressure reading of gauge P3 is at 1500 psig (or the desired pressure), stop the ISCO pump and monitor the pressure drop. When the iodine reservoir has just been filled with the solid I_2 prills, a considerable pressure drop normally occurs even if no leaks are present , as the prills become more closely packed. If leaks are observed, fix them and increase the pressure again by pumping more water using the ISCO pump. Note that water leaks are harder to observe, and sometimes an hour must pass before a drop is noticeable, so allow enough time for this test. If desired, valve V-8 can be close to isolate the Isco pump. The tantalum cross on top of the iodine reservoir is likely to present leaks. (Don’t over-tight the tantalum fittings. Tantalum is a soft material, and if over-tighten the parts will deform.) After pressure testing, V-14 is opened to release the pressure. Close all valves.

The rest of the system should also be pressure-tested at this point. For this purpose a nitrogen gas cylinder tank is connected to valve V-1. Caution: Before connecting the nitrogen tank to valve V-1, make sure the gas regulator exit pressure is set to zero psig. Then close the tank valve again before proceeding. Then open valves V-2, V-4 and V-5, with all other valves being closed. Open the nitrogen tank valve and set the regulator to a pressure of 500 psi. Then open V-1 and observe that the pressure of the Heise gauge agrees with the pressure in the tank. Warning: care must be taken not to over-pressurized the system (iodine reservoir pressure rating= 2250 psig; view cell pressure rating=3000 psi); as a precaution for the operator, a curved-shaped piece of polycarbonate is placed on the studs of the view cell prior to pressure testing, held with nuts, to protect the operator from glass pieces should a window break.

With the system at 500 psi, check all fittings, inside and outside of the oven, --including the valves fittings- using Snoop. If no leaks are found, increase the pressure from the nitrogen tank to 1000 psi and monitor the pressure drop in time. 30 psi lost in 2-3 hours is considered typical. If the pressure drops faster, check for leaks at 1000 psi. After pressure testing, close all valves.

THE DAY BEFORE A RUN

Oven heating

After pressure testing, the heating of the oven can start. Before turning the oven on, the view cell must be confirmed to be empty. If there is liquid, it should not be filled to more than 1/4 or 1/3 of its content to avoid overpressurization during liquid expansion heating. If more liquid is present, it has to be purged by heating the copper block (not shown) and valves V-19, V-20, MM-1 and MM-2, and lines exiting the oven to a temperature of at least 130°C (temperatures above 150°C should be avoided in order to not damage the heating tapes; for more details about heating, refer to the section of "heating of lines, valves and copper block" later in this same appendix). Nitrogen gas can be used to help push the liquid from the view cell into the lines after all lines and valves have been heated to temperature. Warning: Note that if the view cell is full of liquid and the oven is turned on, a huge pressure increase will be generated while heating, which will cause the view cell to rupture.

Before turning on the oven, all valves should be in the closed position. Next, valves V-20, V-19, MM-1 and MM-2 are opened, and the procedure to turn on the oven found in Appendix B can be followed. The oven needs approximately 6 hours to stabilize, so it is recommended to turn it on the day before an experiment and let it reach the desired temperature overnight.

Preparing pumps

The water reservoir that feeds the secondary ISCO pump should be refilled following the instructions given in Appendix C. The ISCO pump used to deliver the working fluid has two separate cylinders. The procedure to refill the ISCO pumps is described in Appendix D.

Checking heating tapes

Check that all the heating tapes located in the lines outside the oven are working. For this, turn them on and check if they are heating (this test is really quick, just to check if they are turning on. It should not be longer than 1 minute for each line. Heating of the solid iodine inside the tubing should be avoided, as it can expand and burst the lines). Replace all heating tapes that are not working.

RUNNING THE CFA

Heating of the iodine reservoir

Proper heating of the iodine reservoir is key to avoid plugs inside it that could cause an overpressure and subsequent rupture of this unique and expensive unit. First, proper operation of the relief valve RV-1 is checked. For this, with all other valves closed (except 3 way-valves V-19 and V-20 and MM valves MM-1 and MM-2), valves V-7, V-8, V-10, V-17, and V-14 are opened, and the ISCO pump is set to a flow rate of 2 cc/min and to a pressure limit of 150 psi. RV-1 should open at a pressure of ~100 psi (if the relief valve is opening to a higher or lower pressure, the spring setting of the valve must be adjusted). The purge coming from this valve is collected in a glass jar and should be checked regularly to prevent overflow. The jar is located on the bottom shelf of the black frame, next to the IC pump and it is labeled “From the iodine reservoir”.

As an extra safety feature, in case RV-1 fails, open valve V-13. Valve V-13 opens to a second relief valve, RV-2, that is set to open at a higher pressure than RV-1 (usually, 120 psi). Reduce the flow of water from the ISCO pump, exiting RV-1, to 1 mL/min and maintain it through the entire heating procedure for the iodine reservoir.

The heating of the reservoir is conducted using 6 independent heating bands controlled by an OMEGA CN616 series controller. The heating is carried out stepwise from top to bottom, allowing each zone to reach a uniform temperature before starting to heat the next one (allow about 20 min for zone 1, 25 minutes for zones 2 through 4, and 30 min for zones 5 and 6). This procedure is carried out to avoid the possibility of a solid plug of iodine in the top of the iodine reservoir that would inadvertently pressurize a melting, expanding plug of iodine in the bottom, causing the reservoir to burst. For instructions on how to operate the OMEGA controller see Appendix E.

Pressure transducer (P5)

The power source for the pressure transducer (P5) needs to be on at least one hour before the measurements start. So turn on the power source and set it to 18 V (Calibrations were made at this voltage). The manual for the pressure transducer can be found at www.heise.com.

Coolant

Turn on the Neslab chiller bath for the coolant of the samples, located to the right of the oven. For this check that the drain valve of the bath is closed. This valve is located to the left of the bath. Then pour a propylene glycol mixture with water (~ 50% water) until the level shown in the inside of the bath is reached.

Turn on the bath using the switch located to the left side of the bath. As the pump starts to fill the plastic containers where the jars for the sample containers will be, the level in the bath will go down. Pour in more propylene glycol/water mixture until proper level is maintained. Set the temperature of the bath to -5°C. Allow enough time (one hour) for the propylene glycol/water mixture to cool down.

Heating of lines, valves and copper block

Heating of the lines outside the isothermal bath is conducted using electrical tapes of two types: silicone coated (Glas-col, part No 103A DET0.254), used mainly for 1/16″ OD tubing, and fiber glass (part No BWH051-040 and BWH051-080). The main difference is that the silicone coated tapes have a lower temperature rating (they should not be used above 160ºC). The tapes are connected to Minitrol controllers, with the setting depending on the length of each tape.Table A.1 shows some guidelines for Minitrol controllers. These values should not be taken as absolutes; every tape should be monitored so as to be set to the desired temperature.

Table A.1 Guideline settings for silicone tape connected to Minitrol. These settings should not be taken as absolute. The desired setting should be reached slowly, for example, by increasing the dial by one unit every 10-15 minutes

Length of the tape (ft)	Minitrol setting
8	7.5-8
4-6	3-5.5
2	Low-1.5

The heating of the lines outside the oven should be done stepwise after the heating of the iodine reservoir is completed (30 minutes after turning on zone 6, see Figure A.2), starting from the tape on the tubing on the bottom of the iodine reservoir to the tape placed in the tubing that goes through the copper block. Each tape must be allowed to reach its final temperature before starting the next one. For the heating tapes connected to Minitrols, the desired setting should be reached slowly, for example, increasing the dial by one unit every 10-15 minutes.

The valves and copper block are heated using cartridge heaters connected to variacs. Table A.2 show the setting for variacs used in the actual setup of the experiment.

Table A.2 Current settings for the variac used in the CFA

Location of the cartridge heater	Current variac setting
Copper block	56
Reservoir on/off	58
3-way valves	46
Micrometering valves	50

For the lines exiting the oven, the tapes on the tubing that connect to the glass sampling jars should be heated first, along with the 3-way valves V-19 and V-20, followed by the tape on the lines coming from the oven and the MM lines (if only one heating tape is used from the exit of the oven to the top of the sample collection jars the tape, the MM valve and the 3-way valve should be heated at the same time). It is important to check that the micrometering valves and 3-way valves are open.

After checking that the iodine reservoir, the tubing outside the oven, the copper block, and the valves are at a temperature of at least 130°C, the experimental run can start.

EXPERIMENTAL RUN

Set up the IR viewer, placing it in front of the view cell window.

Close 3-way valves V-19 and V-20. Open the side of the 3-way valve V-18 (located in the last shelf of the frame) that is connected to the HI/ H_2O solution jar (this jar has a rubber stopper with two lines: the PEEk line, connected to the IC pump, and a 1/16″ Teflon line, that has a constant flow of nitrogen to create a small pressure in the jar, that will allow correct operation of the IC pump). Prime the IC pump (see Manual) and set the IC pump to the desired flow rate (see

Appendix D) and to a maximum operating pressure of 1500 psi. Start pumping the HI aqueous solutions (or the water for the binary experiments) into the view cell. Once the accumulation of HI is observed in the view cell, the flow of iodine can start. For this matter, set the ISCO pump to the desired flow rate for the experiment and to a maximum pressure limit of 1500 psi. Close both V-13 and V-14, which are the valves connected to the relief valves (RV-1 and RV-2) to build pressure in the iodine reservoir and help the start of the flow into the oven. Beware that the pressure will rise quickly. Once the pressure is around 500-600 psi, open valve V-12 (use thermal protection as the handle might be hot) to allow the flow of iodine into the oven. Immediately after, build pressure into the Heise gauge by pumping water using the secondary ISCO pump. For this open valves V-2 and V-4. Once the pressure is at 1000 psi, turn off the secondary ISCO pump, close valve V-2 and open valve V-16, which connects Heise gauge P4 and pressure transducer P5 to the line with the iodine reservoir. A higher pressure is initially required in P4 and P5 to avoid backflushing of contents from the iodine reservoir into the stainless steel (ss) lines.

Allow the iodine and aqueous HI solutions to fill the view cell. Once the pressure in the view cell, reading from the Heise gauge P4, is approximately 100-200 psi above the water vapor pressure at the operating temperature, partially close (¼ of a turn open) MM valves MM-1 and MM-2 and slowly open one side of the 3-way valves V-19 and V-20. The flow out of the top and bottom 3-way valves should be manipulated in such a way that the interface is maintained at a level that is not changing with time, preferably near the middle. Allow the system to remain in steady state (interface is not moving) for at least 20 minutes before starting the collection of the samples.

For the sample collection, using a screwdriver (i.e. P1 Phillips screw driver, Craftsman) puncture the septum seal of the cap of a 250-mL glass jar (Fisher, Part No. 05719450). Weight the jar along with its cap and record the weight in the cap using a marker. Connect it to the exit tubing coming from the 3-way valves. When system reaches steady-state, close the side of the 3-way valve V-20 that was opened while system was reaching steady-state and open the other side. Repeat for 3-way valve V-19. A stream of dark purple sample will start flowing into the glass jar immediately after the 3-way valves are opened. Iodine will start to condensate in the jar walls. Record the time the sample collection starts and collect sample for 30-45 minutes.

In the mean time, place new weighed glass jars on the closed side of the 3-way valves V-19 and V-20.

After 30-45 minutes of collecting sample, change the side of the 3-way valves. That is, let the sample that has just been collected rest in the chiller bath for at least 20 minutes to allow the contents (especially the HI, b.p. -35.5°C) to completely cool down. Afterwards, disconnect from the tubing exiting the 3-way valve and immediately seal the septa opening with tape, to avoid loss of any any sample material. Weigh and store in the refrigerator.

Collect triplicate samples of the top and bottom phases for each experiment. At the end of the run, homogenize all top samples with KI solution. Be sure to clean the lid of the glass jar of all solidified iodine with the KI solution. Approximately 170 grams of KI are needed to homogenize a top-phase sample weighing around 50 grams (This means that by adding about 170 mL of KI, the glass jar will be almost completely full).

SHUT-DOWN PROCEDURE

After the samples required have been collected, the shut-down procedure is performed as described below.

Connect new jars for purging purposes to 3-way valves V-19 and V-20.

Close valve V-12 and slowly open valve V-14 (Check that the jar collecting this purge is not full). Turn off the 6 heating bands for the reservoir by turning off the two black switches located on the gray box of the OMEGA CN616 series controller. Also turn off the heating tapes heating the tubing connecting the bottom of the reservoir to the copper block, and the cartridge heater for V-12. Set the flow rate of the ISCO pump pumping the working fluid to 1 mL/min and set the maximum pressure in the pump to be 150 psi.

Stop the flow rate of the HI aqueous solutions. Close the side of the 3-way valve V-18 (located in the last shelf of the frame, close to the IC pump) connected to the HI/H_2O jar and open the one connected to the H_2O jar (as with the HI/H_2O jar, the water jar is closed with a rubber stopper that has a Teflon line delivering a flow of nitrogen on top of it). Prime the pump. Start pumping water at a flow of 7 mL/min. Open both MM valves and both sides of V-19 and V-20, so that the water being pumped cleans all the tubing.

Run the secondary ISCO pump water at a flow rate of 5 mL/min into the view cell and out of the 3-way valves. After 5 minutes, close V-16 and open V-5. This will allow water to clean the Heise gauge and the lines connected to the top of the view cell.

Once the view cell is full of clean water (20-30 minutes), shut down the secondary ISCO pump and the IC pump. Empty the contents of the view cell by opening fully MM-2 and valve-19. Turn off the rest of the heating tapes and cartridge heaters. Close valve V-5.

Turn off and store the IR viewer.

Turn off the chiller bath for sample collection turning off the switch located to its left. Open the purging valve to remove the propylene glycol/water mixture to store in a separate container. The purging valve is located to the left of the cold bath.

Turn off the oven, pushing down the red main power switch to the right. Unplug the oven from the main chord.

Turn off the ISCO pump and close valve V-17. Open valve V-13.

Leave the nitrogen for the oven flowing until the oven is at room temperature (i.e. next day).

APPENDIX B. TURNING ON THE OVEN

1. Make sure the items inside the oven are clear from the fan blade (i.e. if pressure tested, take out the polycarbonate protection of the view cell). Close the door and clamp shut.

2. Make sure the view cell is empty or no more than quarter full with liquid. If there is liquid inside it must be taken out before turning on the oven to avoid over pressurizing the view cell during heat-up.

3. Turn on the nitrogen flow into the oven at a minimum flow rate of 10L/min to displace the oxygen inside and prevent the oxidation of the tantalum. Be sure to confirm that the nitrogen is actually entering the oven by checking the line delivering the nitrogen ahead of time.

4. Plug in the electrical cord for the oven.

5. Set RTD decade resistance box on the oven front panel to the desired temperature. A table of temperature vs. resistance is pasted on the oven, but is off several degrees from the actual temperature, so it should be taken as a guide of the desired temperature only. It can also be found in the Omega Temperature catalog.

6. Set the oven over-temperature controller (blue box on front of the reservoir) 100ºC above the operating set point to prevent temperature overrun in case the main controller fails.

7. Turn oven ON switch at control box located to the right of the oven.

NOTE: “Main Power”, “Fan”, “Nitrogen”, and “Lost Power” lights will come on immediately, and heaters will turn on approximately ten seconds after oven has been turned on (you will hear a click when they engage). However, on a few occasions, an error with the controller unit for the oven has occurred, preventing the oven heaters from turning on. When the main power switch (fuse box) is moved to the “on” position, the oven fan will not turn on and the “Halt”, “Memory”, and “Force” lights on the oven controller are on (red color). In this case, the computer controller needs to be rest. This problem has been eliminated by turning the key on the controller to the “Disable Outputs” position and waiting 10-30 minutes (note that main power is “on”). After that time, the “Halt”, “Memory”, and “Force” lights should be off and the “Run” light should be on (green color). When the key is turned back to the “Run” position, the fan should turn on, followed by the heaters after about 10 seconds.

8. Allow oven to heat up to the desired temperature (6 to 8 hours).

9. Hutchenson’s PhD dissertation has a detailed schematic of the oven, and there is also a notebook on the electronics in Dr. Thies’s office.

APPENDIX C. REFILLING WATER RESERVOIRS

Water reservoir 1 is labeled "water for Isco pump", and water reservoir 2 is labeled "water for IC pump". The valves used to do this are located on the left side of the frame that holds the pumps. The filling should be done separately, meaning, first for one of the reservoirs and then for the other one.

1. Open the vacuum valve to the fill the desired reservoir.
2. Turn on the vacuum pump by turning on the black switch located in its power chord. The vacuum pump is in the countertop across from the ISCO pumps.
3. When the reservoir is full, turn off the pump. Close the vacuum valve, close the nitrogen valve, and open the vacuum vent, located behind the PC monitor. The vacuum pressure can be read at the gauge located on top of the PC monitor.

APPENDIX D. PUMPS

TURNING ON THE ISCO PUMP AND ITS CONTROLLER

There are dual Isco pumps for the water into the iodine reservoir, located in the last level of the frame. They work using the same controller that is in the second level, from top to bottom, in the frame.

1. To set a flow rate you have to choose which pump you want to run (A or B) This option will appear on the bottom of the controller. Once you choose the pump, you can set the flow rate by pressing the “flow rate” button and then keying in the flow rate.

2. Set the pressure by selecting the “Limits” option in the controller. Press 1 two times, and introduce the limit using the numbers. **Be sure that the shut down option is ON** (This will make the pump to turn off once it has reach the pressure limit). You may choose to turn on the alarm if you want. While heating the reservoir set a limit of 150 psi. When operating the CFA set a limit of 1500 psi max.

- CAUTION

You have to set the limits for BOTH pumps, they are independent.

When you set the limit for one of them the other one does NOT change!

TURNING OFF

1. Turn off the pump and its controller using the red switch on both units.

REFILLING ISCO PUMPS

1. Open the nitrogen valve labeled "Ethanol & Water Res. 1) to allow a flow of nitrogen to the top of the water reservoir (Ethanol is no longer used in our experiments, but the previous labels are still there).
2. Open the *"refill ISCO pump"* (V-7) valve
3. Push the refill button on the controller. Chose the pump you want to refill. You may refill one pump while the other one is running. Typical refilling flow rate is 20 mL/min, but you may change it in the same way you change the flow rate while running.

At any point you can see the conditions for each pump in the controller by choosing the pump you are interested in. The manual for the dual Isco pumps is located on top of the pump controllers.

IC PUMP

1. Turn on the pump with the button to the left of the pump.

2. The pump should be in direct control

3. To set the flow rate put the cursor over the flow rate value on the screen and key in the new value using the numbers to the left.

4. In the same way set a limit pressure of 1500 psi (The view cell is rated to ~3000 psi). Beware that the pressure transducer in the IC pump does not display an accurate reading of the system pressure while the pump is running. Nevertheless, after the stopping the pump, the reading of the pressure is displayed. Also, even though the reading of the system is not shown while running, the alarm for over-pressure works. This is the only safety feature in the HI line connecting to the view cell.

5. Turn on the flow by pushing the “on/off” button so that the light is on the “on” side.

6. The manual for the IC pump is located on top of the computer (CPU).

APPENDIX E. CONTROLLER FOR THE HEATING BANDS ON THE IODINE RESERVOIR

TEMPERATURE SETTING

(see page 24 in the Temperature Controller manual, which is located on top of the controllers box)

- Hold to the ► and ● buttons until the function number appears
- Select function 72
- Confirm function 72
- Select 36 for set point
- Use the ● button to change zones (1, 2, 3, 4, 5, 6)
- Using the ► and the ▲and ▼ buttons, set the desired temperature for each zone. When a particular zone is desired to stay cold, set the temperature to 25°C.
- When the zones are set to the desired temperature, hold the ► and ● until zero.
- Turn "ON" both switches for the heating band.

ALARMS

(Alarm 1 is set as the High limit and Alarm 2 is set as the Low limit)

- Hold the “SET” button until zero
- Push the “SET” button again to go to the list of parameters
- Set: SP, A1 and A2
- Use the up and down buttons to obtain the desired temperature or delta of temperatures (for the set points and alarms respectively).
- Push the “SET” button again to select the temperature.
- Hold the “SET” and down button to go back to the Start menu.

APPENDIX F. SAMPLE CALCULATION OF MASS BALANCE FOR TERNARY EXPERIMENTS

For the conversion from weight fraction to mol fraction the following molecular weights were used:

Molecular weights	
HI	127.908
H_2O	18.016
I_2	253.809

Table F.1 Conditions for run CFA 21

CFA 21

Date: May-12-2009

Feed		
HI-H_2O feed concentration	0.147	weight fraction HI
HI-H_2O flow rate	1	mL/min
HI-H_2O density	1.114	g/mL
I_2 flow rate	1	mL/min
I_2 density (135°C)	3.917	g/mL

The grams of each compound delivered to the system can be found by Equation F.1

$$\text{grams compound} = \rho \bullet C \bullet F \qquad \text{Equation F.1}$$

Where ρ is the density (g/mL) of the solution being pumped, C is the concentration of the compound in the solution (weight fraction), F is the flow rate of the pump (mL/min), and t is the time (min) the compound was delivered. For one minute of operation using the conditions in Table F.1 the grams of each compound delivered and their concentrations are shown in Table F.2

Table F.2 Composition of the feed delivered for CFA 21

For one minute	grams	w/w fraction	mol fraction
HI	0.164	0.033	0.018
H_2O	0.950	0.189	0.759
I_2	3.917	0.779	0.222

The weight of Sample 1 from CFA 21 is shown in Table F.3

Table F.3 Weights of the top and bottom samples for Sample 1 in CFA 21

Sample 1	
Top weight	47.6 g
Bottom weight	140.53 g
Total weight	188.13 g
Collection time	38 min

An overall mass balance gives the total grams of each compound that were delivered to the system, using Equation F.2

mass $\text{compound}_{\text{feed}}$ = total weight•concentration of $\text{compound}_{\text{feed}}$ Equation F.2

Where the total weight is the sum of the top and the bottom samples and the concentration of compound in feed is taken from Table F.4 for each compound.

Using Equation F.2, Table F.4 is generated

Table F.4 Overall mass balance for CFA 21

HI (grams)	6.121
H_2O (grams)	35.536
I_2 (grams)	146.473

From the titrations performed to the top water-rich phase, the concentration of the top phase is known and presented in Table F.5.

Table F.5 Compositions for the top phase-Sample 1 for CFA 21

	Top composition (from titrations) w/w fraction	Mass of each compound in sample (grams)
HI	0.081	3.852
H_2O	0.661	31.456
I_2	0.258	12.292

Recall that the water composition was calculated by difference.

The mass of each compound present in the sample was calculated using Equation F.3:

$$\text{mass of compound}_{\text{top phase}} = C \bullet \text{top weight} \qquad \text{Equation F.3}$$

Where C is the composition for each compound taken from the second column of Table F.5 and the top weight is the mass of the top sample taken from Table F.3.

From the total mass of each compound delivered to the system and the mass of each compound that exited in the top phase, we can calculate the mass of each compound that exited in the bottom phase, following Equation F.4

$$\text{mass compound}_{\text{bottom phase}} = \text{mass compound}_{\text{feed}} - \text{mass compound}_{\text{top phase}} \qquad \text{EquationF.4}$$

With the mass of each compound in the bottom phase being calculated from Equation F.4 , Table F.6 is generated.

Table F.6 Calculated concentration for the bottom phase

Bottom composition			
Compound	Mass (grams)	w/w fraction	mol fraction
HI	2.269	0.016	0.023
H_2O	4.080	0.029	0.293
I_2	134.18	0.955	0.684

APPENDIX G. CFA EXPERIMENTS

Run	Date	T (°C)	Mol fraction of HI in the feed	Comments
CFA1	Aug-08-08	160	0.025	First attempt with HI. No significant results
CFA2	Aug-12-08	160	0.025	Bursting of 1/8 Ta line while heating
CFA3	Aug-13-08	160	0.025	First observations of two phases. Had to stop due a plug in bottom line
CFA4	Aug-15-08	160	0.025	Located the interface for 0.025 HI
CFA5	Sep-15-08	160	0.025/0.05	Confirmation of interface for 0.025 HI and first attempts with 0.05
CFA6	Oct-03-08	160	0.05	Located the interface for 0.05 HI
CFA7	Oct-10-08	160	0.1	Ran out of iodine
CFA8	Oct-15-08	160	0.1	Tried 4 points for the ternary, all one phase
CFA9	Oct-17-08	160	0.1	Tried 4 points for the ternary, all one phase
CFA10	Oct-22-08	160	0.1	Tried 2 points for the ternary. Then I ran out of iodine
CFA11	Oct-24-08	120-140	0.1	No significant results. Some issues
CFA12	Nov-03-08	140	0.1	IC pump leaked.
CFA13	Nov-05-08	140	0.1	Tried 7 points for the ternary, all one phase
CFA14	Nov-06-08	180	0.025	Ran out of iodine
CFA15	Nov-12-08	200	0.025	Located the interface for 0.025 HI
CFA16	Dec-04-08	160	0.025/0.05/0.075	Collected samples of the two phases for 0.025 and 0.05. Two-phases not observed for 0.075
CFA17	Dec-12-08	200	0.025	IC pump is not working. Check valves are not good.
CFA18	Apr-03-09	225	0.025	Problems with coolant pump and heating tapes.
CFA19	Apr-08-09	225	0.025	Content of view cell really dark. Unable to determine if one or two phases were present.
CFA20	Apr-10-09	200	0.025	Content of view cell really opaque. Unable to determine if one or two phases were present.
CFA21	May-12-09	160	0.025	Collected samples of the two phases.
CFA22	May-15-09	160	0.01	Collected samples of the two phases.
CFA23	May-29-09	160	0.05	Collected samples of the two phases.
CFA24	Jun-17-09	160	0.035	Problems with heating tapes
CFA25	Jul-09-09	160	0.035 and ~0.05	Run with only HI. Then collected samples of one phase for the 0.035 HI.
CFA 26	Oct-20-09	160	0.1	2 phases observed. Big leak coming from feed thermocouple avoid the collection of samples
CFA 27	Oct-25-09	160	0.035	Collected samples of the two phases.

APPENDIX H. PROPOSED MIXING EQUILIBRIUM SECTION

The mixing equilibrium section currently in the system and that was used for the experiments described in this thesis is shown in Figure H.1

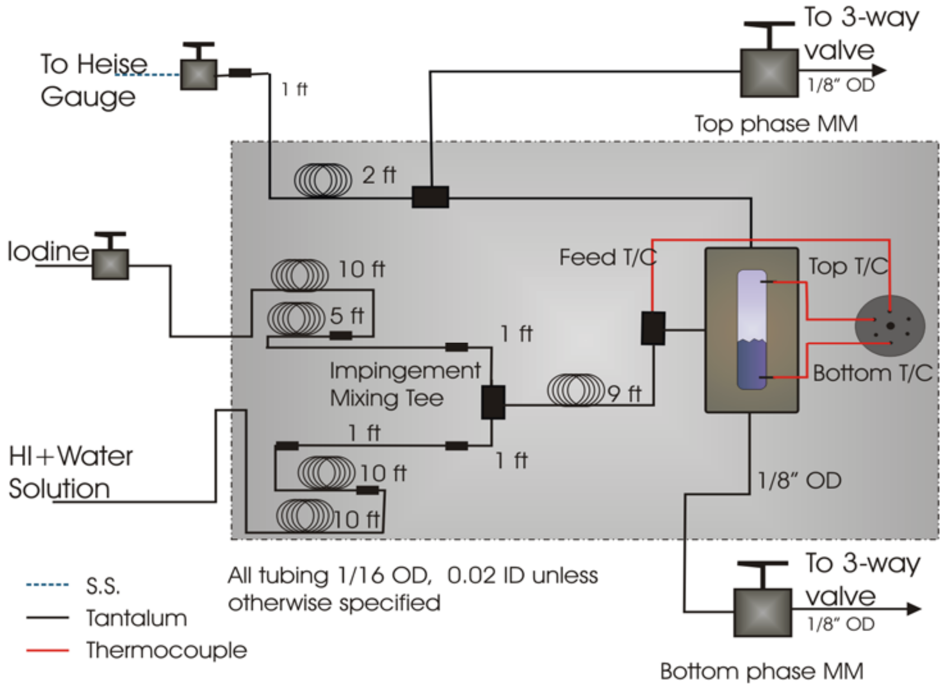
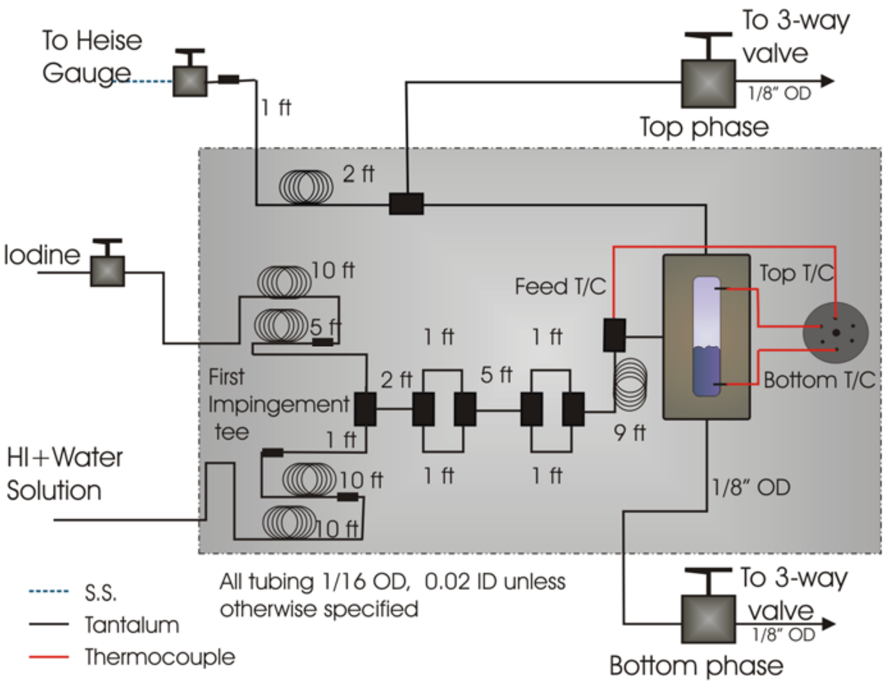


Figure H.1 Mixing-equilibrium section used in the experiments presented in this thesis

An improvement to this set up is shown in Figure H.2



All tubing 1/16 OD, 0.02 ID unless otherwise specified

Figure H.2 Proposed mixing-equilibrium section

APPENDIX I. PERMISSION TO REPRINT TABLE 1.2

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