# HYDROCARBON-WATER SOLUBILITIES AT ELEVATED TEMPERATURES NEAR THE THREE-PHASE EQUILIBRIUM PRESSURE

By

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EQUILIBRIUM PRESSURE

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# PREFACE

The purpose of this work was to establish a reliable experimental apparatus and procedures for measuring liquid-liquid equilibrium data at ambient and elevated temperatures and pressures. A continuous flow apparatus has been designed and constructed to obtain mutual solubilites at temperatures from ambient to 623 K and pressures up to 13.8 MPa. The accuracy of the apparatus and methods used was determined by measurements on the well-documented benzene-water system. Mutual solubility data have also been measured for the aqueous binary systems involving decane and 1-hexene at temperatures up to the three-phase critical end point.

I would like to thank my primary advisor, Dr. Khaled A.M. Gasem, for his knowledge and enthusiasm for chemical engineering. His fervency for chemical engineering seems to know no bounds. I am also appreciative of Dr. Robert L. Robinson, Jr., for his patience and guidance, as his comments were invaluable to the success of this study. I am grateful to Dr. Jan Wagner, as well, for his help in making the apparatus used in this study a possibility, as the credit for the design of the apparatus goes to him. His experience and knowledge of liquid-liquid equilibrium were of great assistance throughout this study. Mr. Charles Baker, Laboratory Manager, and the rest of the Chemical Engineering staff were also of great assistance throughout my graduate study. Their efforts are greatly appreciated.

I would like to express my deepest appreciation for my parents, Sherwin and Carol, who never stopped encouraging me during what seemed, at times, to be an insurmountable task. I am sure I would not have accomplished what I have had it not been for their support and prayers.

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# CHAPTER I

# INTRODUCTION

## Significance

Phase equilibrium data are essential for the proper design and operation of many chemical engineering processes. Separation processes such as distillation, adsorption and solvent extraction are some of the more prevalent applications. Where there is a lack of experimental data, thermodynamic models are used to predict the phase equilibrium. The accuracy of these models is dependent upon the quality, as well as the quantity, of the experimental data used in the model development.

Despite the fact that sufficient literature data are available for select binary systems at ambient or near ambient temperatures, there is still a deficiency in mutual solubility data at elevated temperatures. Experimental studies such as this one, which are focused on obtaining the necessary equilibrium data, are needed for this reason.

## Objectives

The purpose of this study was to develop an apparatus, with operating procedures and sampling and analytical techniques, which would yield reliable liquid-liquid equilibrium data at ambient and elevated temperatures. This required being able to control the hydrocarbon-water interface, which was difficult to do at elevated pressures with the apparatus used in the study by Chen and Wagner *(11, 12, 13)*. An additional objective of this study was to perform an error analysis to determine the amount of uncertainty in the measurements.

Once the apparatus and methods were established, the objective was to obtain mutual solubility data for a number of binary systems. The three systems studied included an aromatic (benzene), an alkane (decane), and an olefin (1-hexene). The benzene-water system was used to verify the data obtained with this apparatus. The decane-water and 1-hexene-water systems were studied to complement the limited existing data.

**Organization of the Thesis**

Following this introduction, a review of the literature is given in Chapter II. The literature review was conducted for temperatures extending from 293 K to the three-phase critical temperature of each system and pressures to the three-phase equilibrium pressure. The various analysis methods employed and the types of apparatus used are also considered. A detailed description of the experimental apparatus is given in Chapter III. The experimental methods and techniques are discussed in Chapter IV, including sample preparation, sample collection, instrument calibration, and sample analysis. In Chapter V, the experimental data are presented and discussed, along with the expected uncertainty in the measured values. Conclusions and recommendations are made in Chapter VI. The appendices follow. In Appendix A, a standard operating procedure is given to accompany the new apparatus. The calibration technique and the calibration data are given in Appendix B, and the propagated error analysis used to weight the calibration data is shown in Appendix C. A description of how the solubilities were calculated is given in Appendix D and Appendix E shows how the trace amount of water in the ethanol was accounted for in the sample analysis. A complete propagated error analysis of the experimental solubility data is presented in Appendix F.

A manuscript format was followed in preparing this thesis, and Chapter V is written in the form of a manuscript, complete with an independent set of tables, figures, nomenclature, and references.

# CHAPTER II

# LITERATURE REVIEW

The amount of liquid-liquid equilibrium data available in the literature varies among binary systems. There is an abundance of such data for the benzene-water system, but literature data are limited for the decane-water and 1-hexene-water systems. The majority of the available data have been collected at low temperatures, primarily at the ambient temperature of 298 K. Only a few studies have measured the mutual solubilities at elevated temperatures and pressures.

## Benzene-Water System

Most of the literature data for the solubility of benzene in water at atmospheric pressure are in agreement. The data of Kudchadker and McKetta *(25)*, Krasnoshchekova and Gubergrits *(24)*, Schwarz *(33)*, and Sanemasa et al. *(32)* disagree significantly with the other studies.

The reported values of water solubility in benzene at atmospheric pressure are in fair agreement. The data of Englin et al. *(16)* and Bittrich et al. *(5)* are significantly lower than the values given by other studies. Hefter *(22)* notes that the more recent water solubility in benzene data have a tendency to be higher than the overall average, with smaller standard deviations.

The reported mutual solubility data for the benzene-water system at elevated temperatures and pressures are in fair agreement. Not only is there a limited amount of literature data on the mutual solubilities of benzene and water at elevated temperatures and pressures, almost all of the data have been collected at different conditions. This makes it difficult to evaluate the data. The studies of Anderson and Prausnitz *(1)*, Tsonopoulos and Wilson *(38)*, and Chandler et al. *(9)*, which are along the three-phase equilibrium curve, exhibit fair agreement.

### Decane-Water System

There is poor agreement among the seven studies reporting the solubility of decane in water at atmospheric pressure. Three studies report the solubility of water in decane at atmospheric pressure. The data of Schatzberg *(34)* and Ng and Chen *(29)* are in agreement, but the datum of Becke and Quitzsch *(3)* is significantly higher.

Only Guerrant *(21)*, Ng and Chen *(29)* and Economou et al. *(15)* have reported decane solubilites in water at elevated temperatures and pressures, but none of the data have been collected under comparable conditions. Four studies (Guerrant *(21)*, Namiot et al. *(28)*, Skripka *(35)*, and Economou et al. *(15)*) report water solubilities in decane at elevated temperatures and pressures and they are in reasonable agreement.

### 1-Hexene-Water System

The available literature data on the 1-hexene-water system are severely limited. Four separate studies exist at ambient temperature for the solubility of 1-hexene in water. The datum of McAuliffe *(26)* appears to be slightly low. Only Economou et al. *(15)* reports measurements at elevated temperatures. For the solubility of water in 1-hexene, Englin et al. *(16)* and Budantseva et al. *(7)* each report a single measurement at ambient conditions and Economou et al *(15)* reports several measurements at elevated conditions. The two studies under similar conditions (Englin et al. *(16)* and Budantseva et al *(7)*) are in reasonable agreement.

## Experimental Methods

Many different methods have been employed to collect liquid-liquid equilibrium data. A majority of the studies employ static cells to achieve equilibrium. Those investigations using a static cell include McAuliffe *(26, 27)*, Karlsson *(23)*, Franks *(17)*, Franks et al. *(18)*, Goldman *(20)*, Guerrant *(21)*, Anderson and Prausnitz *(1)*, Polak and Lu *(30)*, Chandler et al. *(9)*, Krasnoshchekova and Gubergrits *(24)*, Ng and Chen *(29)*, and Schatzberg *(34)*. Saturated solutions are prepared in the equilibrium cell, agitated for some time, and then allowed to separate gravimetrically before analysis. The investigations by Wang and Chao *(40)*, Chen *(10)*, Chen and Wagner *(11, 12, 13)*, Bennett *(4)*, and Stevenson et al. *(37)* use continuous flow apparatus, similar to the one in this study, to obtain liquid-liquid equilibrium data.

An advantage a continuous flow apparatus has over a static equilibrium cell is that phase compositions can be measured much more rapidly *(37)*. Thermal decomposition of the hydrocarbon is minimized with a continuous flow apparatus, as well *(37, 40)*.

There have been a variety of analysis techniques used to analyze the samples. The more common techniques include volumetric analysis (Guerrant *(21)* and Umano and Hayano *(39)*), Karl Fischer titration (Polak and Lu *(30)*, Karlsson *(23)*, Tsonopoulos and Wilson *(38)*, and Stevenson et al. *(37)*), ultraviolet spectrophotometry (Bradley et al. *(6)*, Franks et al. *(18)*, and Arnold et al. *(2)*), and gas chromatography.

The studies that utilized gas chromatography included Chen and Wagner *(11, 12, 13)*, Chen *(10)*, Bennett *(4)*, Polak and Lu *(30)*, McAuliffe *(26, 27)*, Franks et al. *(18)*, Anderson and Prausnitz *(1)*, Tsonopoulos and Wilson *(38)*, Chandler et al. *(9)*, and Stevenson et al. *(37)*.

## Summary

The availability of liquid-liquid equilibrium data at elevated temperatures is limited for most systems. The benzene-water system is an exception and is used as the benchmark when testing this new apparatus. The benzene-water system has been thoroughly investigated, with a majority of the data collected at, or near, 298 K. There are limited literature data available for the decane-water system and there are very few literature data available for the 1-hexene-water system.

Many methods have been used to collect liquid-liquid equilibrium data. Static cells and continuous flow apparatus are two of the most common methods. The analysis techniques used to analyze the samples have also varied among studies.

# CHAPTER III

## EXPERIMENTAL APPARATUS

A continuous flow apparatus has been designed and constructed to obtain mutual solubilities of two liquid phases in equilibrium at elevated temperatures and pressures. This apparatus is similar to the apparatus constructed by Chen and Wagner *(12)*, with a few improvements. The major improvement is the ability to accurately control the hydrocarbon-water interface at elevated pressures. This minimizes the possibility of entrainment and allows mutual solubilities at elevated temperatures and pressures to be measured.

The experimental apparatus may be described briefly as follows. Two well-mixed liquids are supplied to a phase separation cell, where the phases separate gravimetrically, exit the cell, and are collected. The phase separation cell is located in a convection oven where the final mass transfer between phases takes place. A pressurized nitrogen source is used to pressurize the apparatus and a backpressure regulator controls the pressure.

The apparatus used in this study consists of four sections: a feed section, an equilibration section, a separation section, and a sampling section. The feed section supplies two pure, partially miscible fluids at a constant flow rate to the equilibration section. In the equilibration section, the two fluids are thoroughly mixed and allowed to come to equilibrium. The separation section is designed to allow the equilibrium phases to separate for sample collection. The sampling section is where the two separated phases are collected. The total volume of the apparatus is approximately 120 $cm^3$. A schematic drawing of the apparatus is shown in Figure 1.

The feed section contains two reservoirs for the pure liquid feed stocks and a LCD Analytical Type NSI-33R duplex miniPump (DP1, the abbreviations correspond to Figure 1). The two liquids are a hydrocarbon and water. The duplex miniPump supplies the liquids at a constant total flow rate of 4.0 $cm^3$/min with equal parts (2.0 $cm^3$/min) of hydrocarbon and water. The flow rate was varied to determine the effect it has on the solubilities and no significant variation was seen in the solubilities when the flow rate was between 1.5 and 4.5 $cm^3$/min. Flow rates in this range reduce the formation of emulsions in the apparatus and allow sufficient time for the two liquids to reach equilibrium in the equilibration section. The residence time of the system is 30 min.

The equilibration section provides the necessary mixing for the two liquids to reach equilibrium at the experimental temperature. Immediately following the duplex miniPump is a Whitey three-way valve (V1). This valve functions as a bypass valve, should the pump need to be primed. The two liquids then pass through approximately 6.8 m of 0.318 cm-o.d. stainless steel tubing followed by 3.1 m of 0.835 cm-o.d. stainless steel tubing packed with 1.0 mm glass beads. Next, the liquid enters a 1.0 m section of 0.318 cm-o.d. stainless steel tubing before entering the oven. The oven is a Hotpack Digimatic Model 213024, with a maximum temperature rating of 623 K. The temperature inside the oven is controlled within ±0.1 K of the set point, as determined by the manufacturer. A J-type thermocouple, calibrated against a Minco platinum resistance thermometer that is NIST traceable, is used to measure the phase separation cell temperature. Inside the oven, 15.2 m of 0.318 cm-o.d. stainless steel tubing is used to

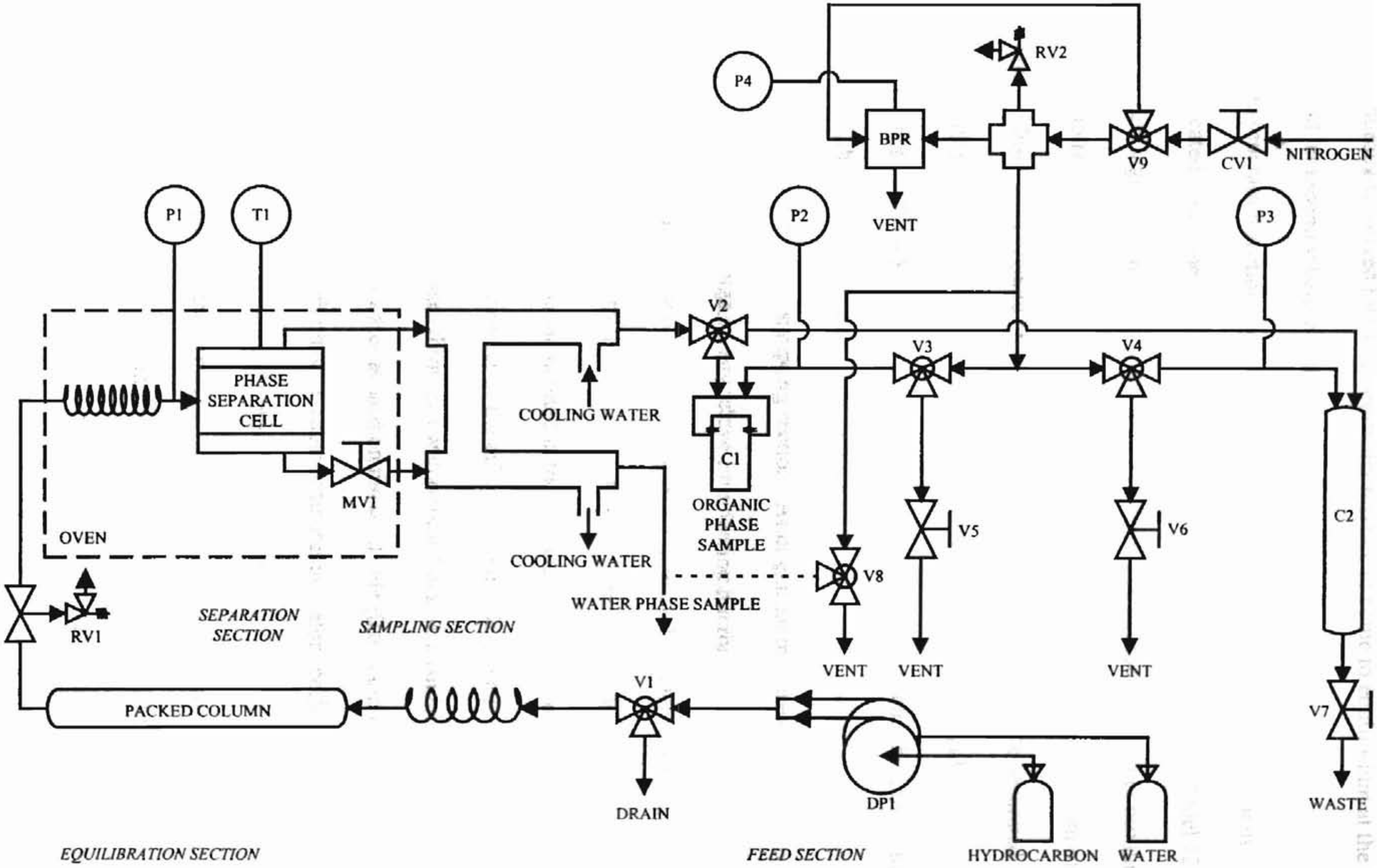

**Figure 1.** Diagram of the Continuous Flow Apparatus

allow the thoroughly mixed hydrocarbon-water mixture to come to equilibrium at the experimental temperature before entering the separation section.

The separation section consists of a phase separation cell (labeled as such in Figure 1) located inside the oven. This cell is a 316 stainless steel Jerguson Model 12T40 Liquid Level Gage with an internal volume of 19 cm$^3$. The hydrocarbon-water mixture separates into two phases inside the cell. The water phase exits through the bottom of the cell, and the less dense organic phase exits through the top of the cell. The separated phases exit the phase separation cell through individual 0.159 cm-o.d. stainless steel capillary tubing. Capillary tubing is used to minimize dead volume, and thus, minimize the effects of phase separation on sample composition.

The final section is the sampling section. After exiting the phase separation cell, the water phase passes through an Autoclave Engineering micrometering valve (MV1). This valve is located inside the oven and controls the flow of the water phase out of the phase separation cell. By controlling the water phase effluent rate, equal amounts of hydrocarbon and water may be maintained in the cell and thus, the hydrocarbon-water interface may be kept near the center of the cell. This minimizes the possibility of entrainment. Each phase passes through a water-cooled heat exchanger 20.3 cm in length prior to being collected. Tap water is used on the shell side (0.635 cm-o.d. stainless steel tubing) to effectively cool each phase to room temperature before collection. This helps to prevent the sample from volatilizing into the vapor phase.

Elevated pressures in the apparatus are established using pressurized nitrogen gas to create a backpressure on the system. A Grove Mity Mite S-91XW backpressure regulator (BPR) is used to control the pressure in the high-pressure sampling cell (C1).

To protect against overpressure, a spring-loaded Nupro relief valve is placed at each possible source of pressure. One relief valve (RV1) is located on the liquid mixture feed line, upstream of the oven, and a second relief valve (RV2) is located on the nitrogen stream line. The sample is collected in a glass bottle, which is placed in a 300 $cm^3$, sightless, high-pressure sampling cell (C1), pressurized by the nitrogen gas. The cell pressure is measured at the feed port of the phase separation cell with a Sensotec STJE pressure transducer and 450D readout. The maximum pressure of the system is limited by the pressure transducer, which has a pressure limit of 13.8 MPa (2000 psia). The relief valves are set at 12.4 MPa (1800 psia).

A Whitey three-way valve (V2) is located between the phase separation cell and C1. This valve is used to divert the flow of the organic phase sample to a 400 $cm^3$, sightless, high-pressure, collection cell (C2), used for waste collection. This allows continuous flow through the system at elevated pressures while changing the sample bottles. The blanket of nitrogen gas pressurizes C2. Two Whitey three-way valves are used to isolate C1 and C2 from the system so the nitrogen gas may be vented. The valve V3 is used to close C1 and the valve V4 is used to close C2. This allows C1 or C2 to be lowered to atmospheric pressure while maintaining a constant elevated pressure inside the apparatus. A detailed description of the standard operating procedures is given in Appendix A.

# CHAPTER IV

# EXPERIMENTAL METHODS AND TECHNIQUES

The experimental procedure includes preparing and collecting the samples, calibrating the instrument used for analysis, and analyzing the samples. To prepare for sample collection, and eventual sample analysis, a solvent was added to the sample bottles. A gas chromatograph (GC) equipped with a thermal conductivity detector (TCD) was used for the analysis. This instrument was calibrated by a serial dilution technique. A weighted-least-squares regression was used to fit the calibration data and generate a calibration curve. The calibration curve was utilized during the sample analysis to determine the concentration of the sample.

## Sample Preparation

Prior to sample collection, a known amount of solvent, by weight, was added to the sample bottles in preparation of sample analysis. The solvent used in the water phase samples was either decane or 2,2,4-trimethylpentane, depending on the system being studied. Decane was used as the solvent when the hydrocarbon of interest was benzene or 1-hexene and 2,2,4-trimethylpentane was used as the solvent when the decane system was studied. The purpose of the solvent used in the water phase was to extract the hydrocarbon from the water so it could be analyzed in the absence of water. A reproducible analysis was achieved by excluding water from the analysis. Water was the solute of interest in the organic phase so it could not be excluded from the organic phase analysis. Therefore, ethanol was used as the solvent in the organic phase samples. The purpose of the ethanol was to homogenize the sample and allow the water to be analyzed in the presence of the hydrocarbon.

To determine the amount of solvent to be added to the sample bottles, solutions of known concentration were prepared and analyzed prior to collecting the samples. For each system studied, two solutions were prepared for each phase. One mixture had a composition that would be expected at the low experimental temperatures (a low concentration solution) and the other had a composition that would be expected at the elevated experimental temperatures (a high concentration solution). Incremental amounts of solvent were added to both the low concentration and the high concentration solution. After each addition, the mixtures were analyzed to determine the effect of solvent on the measured mole fractions. The measured concentrations gradually increased until a plateau was reached, which was near the known concentration of the mixture. The plateau in concentration demonstrated the optimum amount of solvent to be used.

For the organic phase of each system studied, a solvent-to-sample ratio of 0.8 was sufficient to completely homogenize the solution throughout the temperature range studied. The fact that the optimum solvent-to-sample ratio is the same for all three systems may be because the concentration of water in hydrocarbon is of the same order of magnitude for all three systems.

The amount of solvent needed to completely extract the hydrocarbon of interest from the water phase varied among the systems studied. In the benzene-water system, the solvent-to-sample ratio used throughout the temperature range studied was 0.7. The optimum solvent-to-sample ratios for the decane-water system and the 1-hexene-water system were 0.003 and 0.08, respectively.

### Sample Collection

The samples were collected after adding the solvent to the sample bottles to minimize sample contact with the atmosphere and to keep from disturbing the sample after it was collected. Three samples of each phase were collected successively at each temperature. The organic and water phases were collected simultaneously and at a pressure slightly above the three-phase equilibrium pressure.

### Instrument Calibration

A Hewlett-Packard 5890A gas chromatograph (GC), equipped with a thermal conductivity detector (TCD) and a Hewlett-Packard 3392A integrator, was used to analyze the samples. A 1.8-m x 0.32-m stainless steel column packed with GasChrom 254 was supplied by Alltech. High purity helium was used as the carrier gas. The GC was calibrated by a serial dilution technique (see Appendix B for details). Multiple calibration standards were prepared (by weight) and analyzed with the GC. The range of calibration standards encompassed the experimental concentration range. The calibration standards and samples were analyzed at the GC operating conditions listed in Table 1. A temperature program was used in the GC analysis to provide the most accurate and reproducible analysis in a reasonable amount of time. Each set of parameters was optimized individually. Sample volumes of 0.003 $cm^3$ (3 $\mu$L) were injected into the GC.

**Table 1.** Gas Chromatograph Operating Conditions

| | Benzene-Water System | |
|---|---|---|
| Variable | Water Phase | Benzene Phase |
| Detector Temperature, °C | 300 | 300 |
| Injector Temperature, °C | 250 | 250 |
| Initial Oven Temperature, °C | 225 | 150 |
| Initial Time, min. | 4.75 | 1.25 |
| Final Oven Temperature, °C | 225 | 250 |
| Final Time, min. | 0.00 | 1.75 |
| Rate, °C/min. | 0.0 | 40.0 |
| Total Gas Flow, $cm^3$/min. | 27.7 | 27.7 |

| | Decane-Water System | |
|---|---|---|
| Variable | Water Phase | Decane Phase |
| Detector Temperature, °C | 300 | 300 |
| Injector Temperature, °C | 250 | 250 |
| Initial Oven Temperature, °C | 200 | 150 |
| Initial Time, min. | 0.75 | 1.25 |
| Final Oven Temperature, °C | 250 | 250 |
| Final Time, min. | 1.50 | 2.00 |
| Rate, °C/min. | 40.0 | 40.0 |
| Total Gas Flow, $cm^3$/min. | 27.7 | 27.7 |

| | 1-Hexene-Water System | |
|---|---|---|
| Variable | Water Phase | 1-Hexene Phase |
| Detector Temperature, °C | 300 | 300 |
| Injector Temperature, °C | 250 | 250 |
| Initial Oven Temperature, °C | 180 | 150 |
| Initial Time, min. | 1.50 | 4.50 |
| Final Oven Temperature, °C | 250 | 150 |
| Final Time, min. | 2.75 | 0.00 |
| Rate, °C/min. | 40.0 | 0.0 |
| Total Gas Flow, $cm^3$/min. | 27.7 | 27.7 |

The calibration curves were prepared from the solute-to-solvent weight ratio as a function of the solute-to-solvent area ratio. The data were regressed with the nonlinear weighted-least-squares Marquardt method *(8)*.

The uncertainty in the weight ratio, which was used as the weighting of each datum, was determined by an analysis of propagated error. This is given in detail in Appendix C. The calibration curves demonstrated good reproducibility. The average deviation in the predicted weight ratio from the actual weight ratio was 1.7% in the benzene-decane calibration, 1.0% in the decane-2,2,4-trimethylpentane calibration, 0.2% in the 1-hexene-decane calibration, and 0.3% in the water-ethanol calibration. Any datum with a deviation greater than two and one half times the standard deviation was not included in the regression.

Each calibration curve was expressed as a second order polynomial:

$$WR = \alpha AR^2 + \beta AR + \gamma \tag{1}$$

where WR is the weight ratio, AR is the area ratio, and $\alpha$, $\beta$, and $\gamma$ are the regressed parameters. The parameters are listed in Table 2. The calibration curves are shown in Figures 2, 3, 4 and 5. A detailed description of the calibration technique and the calibration data are given in Appendix B.

## Sample Analysis

Sample analyses were performed under the same GC conditions as the calibrations. The amount of each component in a sample was given in the GC output as area percent. This refers to the integrated area under the curve for each peak identifying a component in the analysis and is reported as a percentage of the total area. The solute-to-solvent area ratio was found by dividing the solute area percent by the solvent area

**Table 2.** Gas Chromatograph Calibration Parameters

| Calibration | $\alpha$ | $\beta$ | $\gamma$ ($10^5$) |
|---|---|---|---|
| Benzene-Decane | 1.71454 | 1.16198 | 0.367 |
| Decane-2,2,4-Trimethylpentane | 0.33794 | 0.54680 | -0.470 |
| 1-Hexene-Decane | 0.61704 | 1.00002 | 1.061 |
| Water-Ethanol | 1.24061 | 1.13508 | -1.293 |

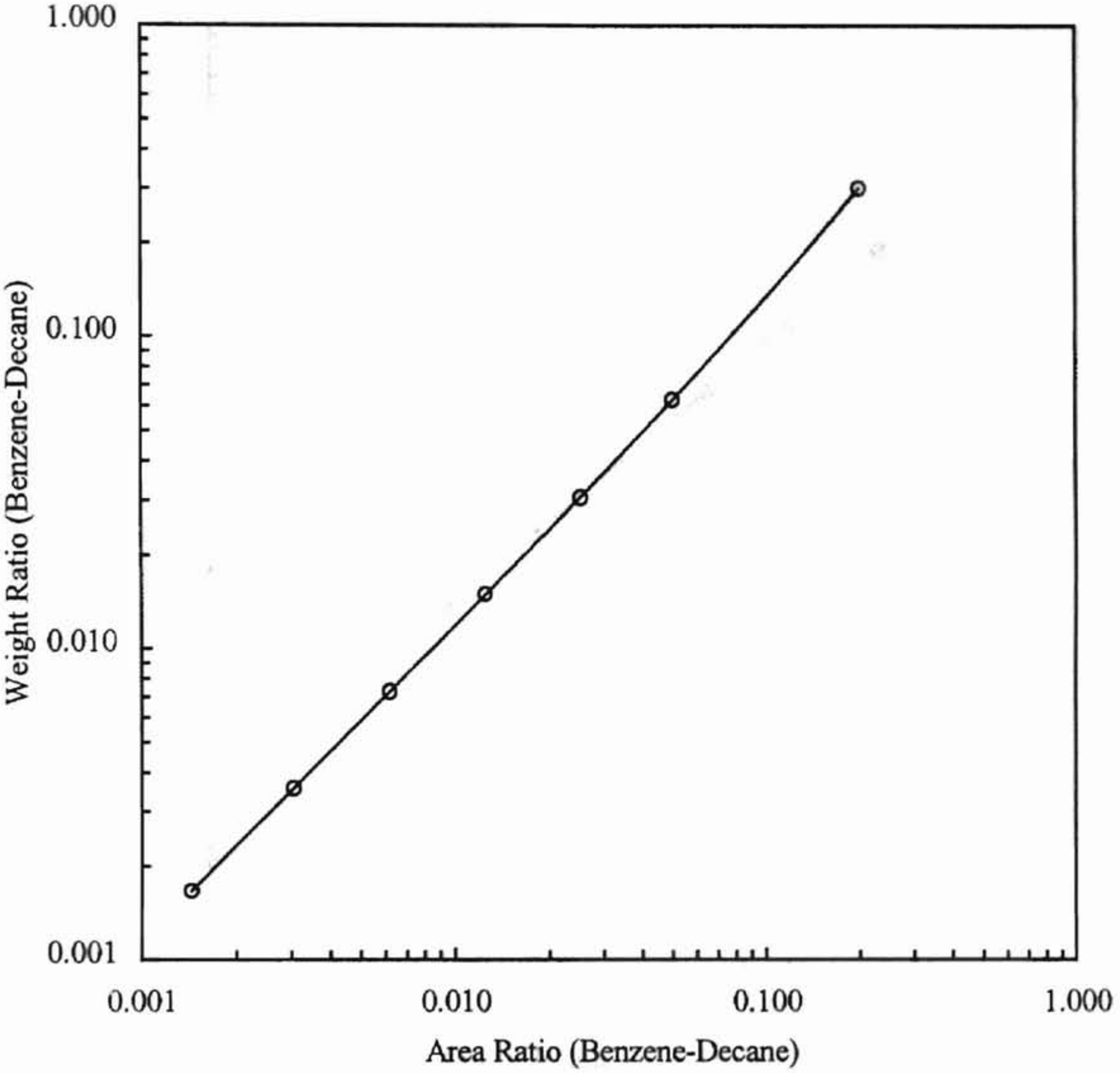

**Figure 2.** Benzene-Decane Calibration Curve

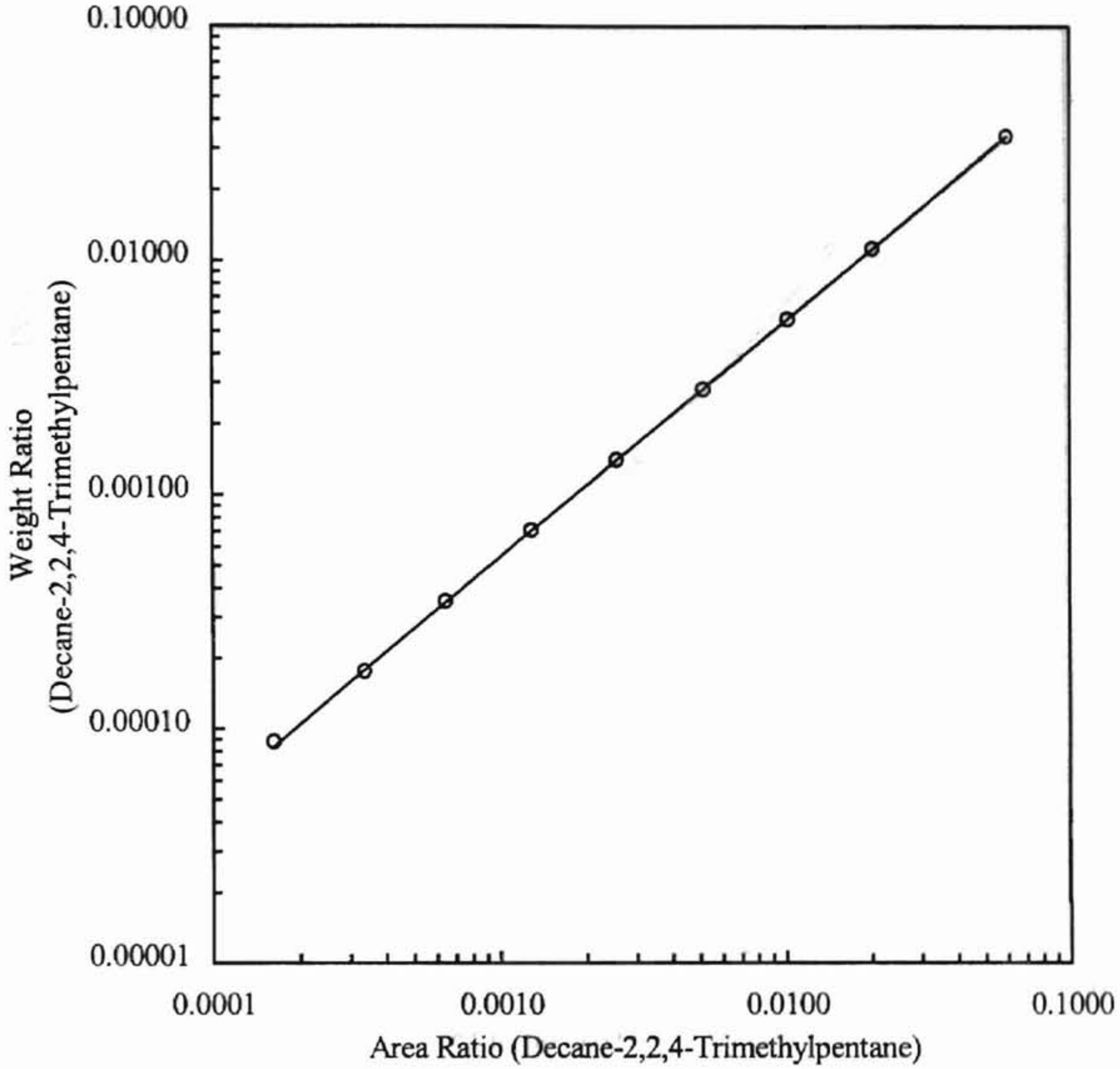

**Figure 3.** Decane-2,2,4-Trimethylpentane Calibration Curve

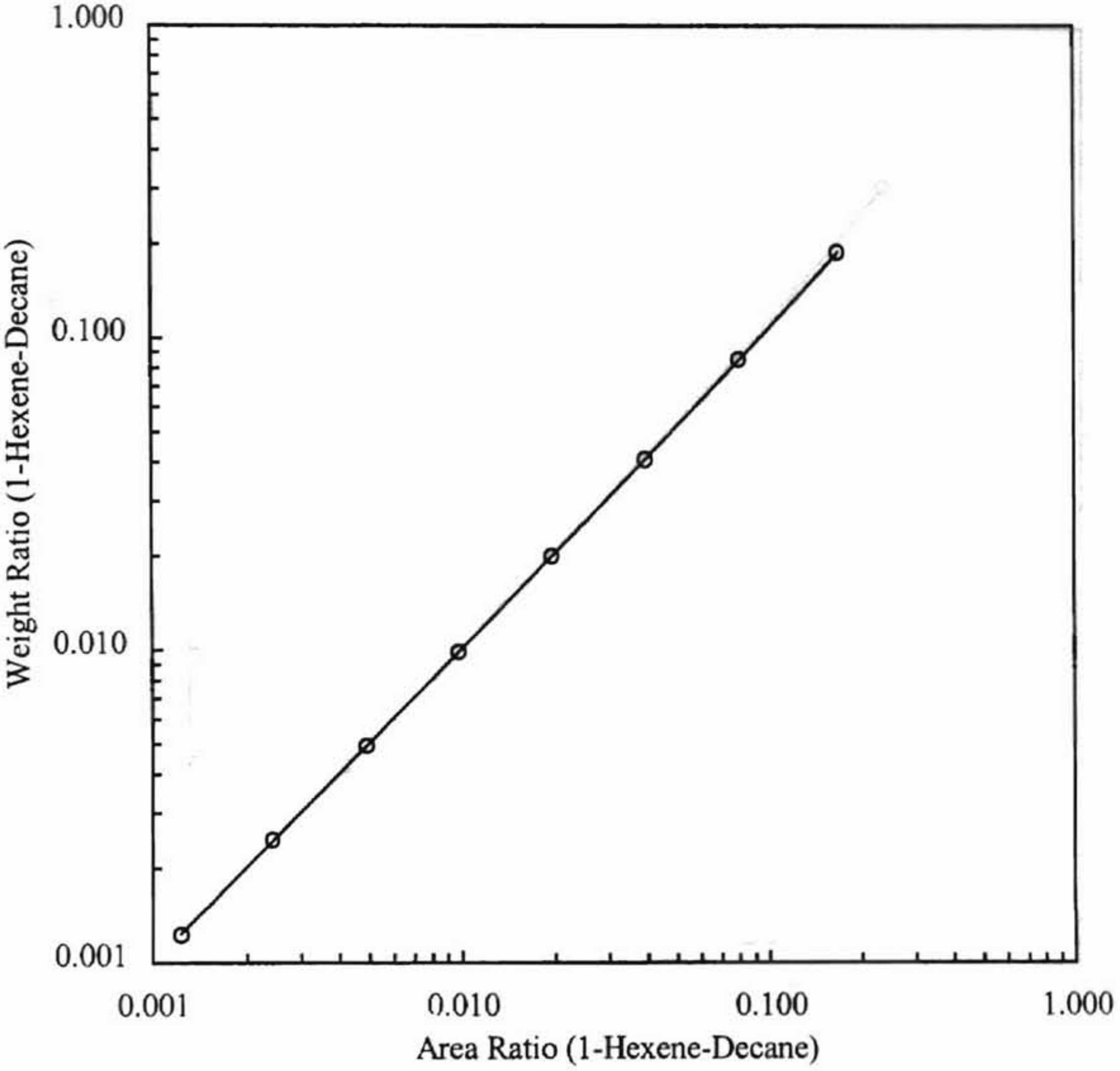

**Figure 4.** 1-Hexene-Decane Calibration Curve

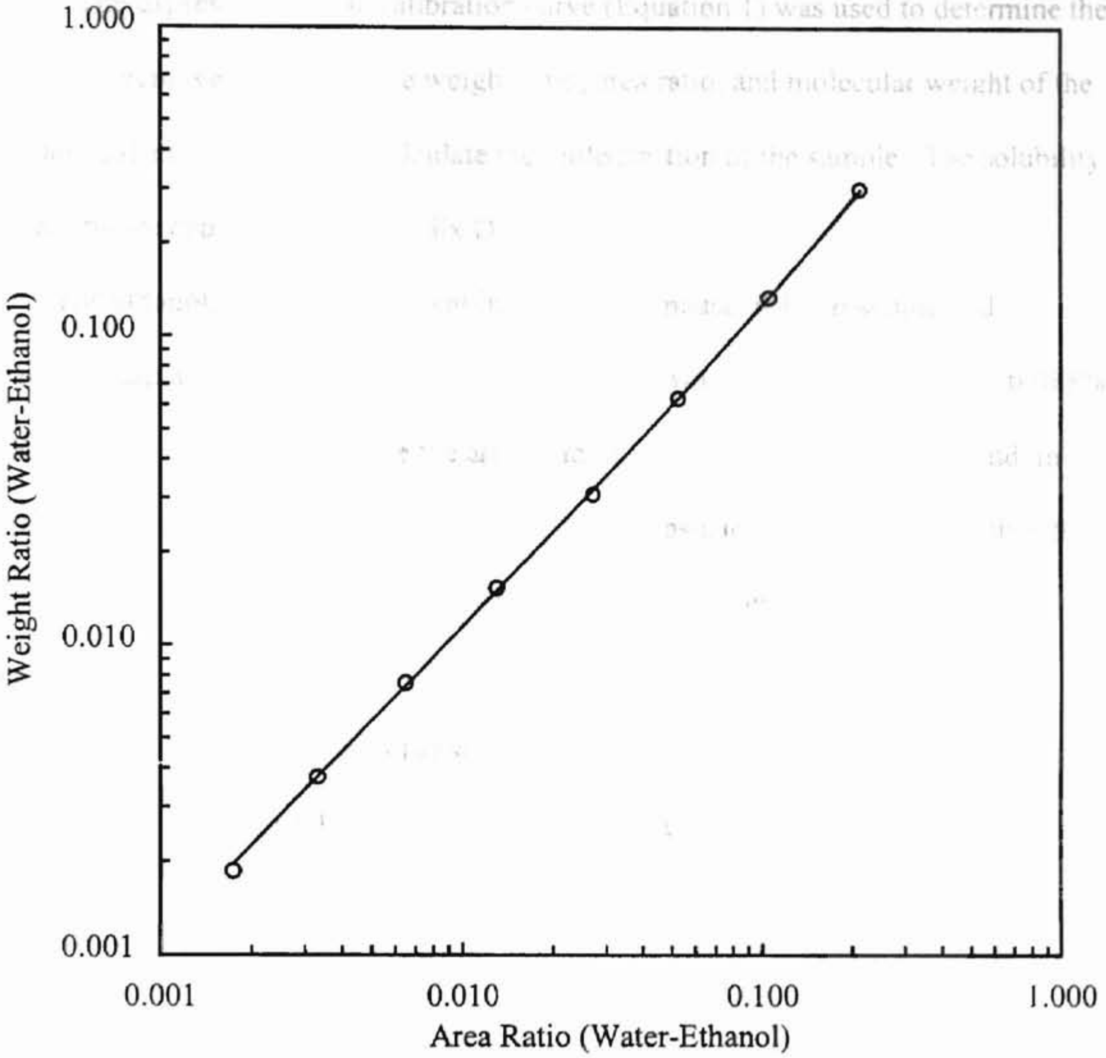

**Figure 5.** Water-Ethanol Calibration Curve

percent. The expression for the calibration curve (Equation 1) was used to determine the solute-to-solvent weight ratio. The weight ratio, area ratio, and molecular weight of the solute and solvent were used to calculate the mole fraction of the sample. The solubility calculations are explained in Appendix D.

The ethanol, used as the solvent in the organic phase, is hygroscopic and contained small amounts of water. (The ethanol had a water content of less than 0.015%, by GC analysis). This could cause the area ratio in the organic phase samples and, in effect, the calculated water solubility in the organic phase, to be slightly higher than the equilibrium value; thus, a correction was required. This correction is described in Appendix E.

A complete description of the sample preparation, sample collection, and sample analysis is given as part of the standard operating procedures in Appendix A. The instrument calibration is given in detail in Appendix B.

# CHAPTER V

# LIQUID-LIQUID PHASE EQUILIBRIA AT ELEVATED TEMPERATURES FOR BINARAY AQUEOUS SYSTEMS CONTAINING BENZENE, DECANE, AND 1-HEXENE

## Abstract

A continuous flow apparatus was designed and constructed to obtain liquid-liquid mutual solubilites at temperatures from ambient to 623 K and pressures up to 13.8 MPa. Mutual solubility data have been measured at temperatures from ambient to near the three-phase critical end point for three hydrocarbon-water systems: benzene-water, decane-water, and 1-hexene-water. The expected uncertainty in the measurements, determined by error propagation, was typically less than 5%. The well-documented benzene-water system was used to benchmark the proper operation of the apparatus used. The mutual solubilities measured for the benzene-water system deviated from the literature values by less than 10%.

## Introduction

Liquid-liquid mutual solubility data for hydrocarbon-water systems are essential for the proper design and operation of many chemical engineering separation processes. A common application is in the removal of water from hydrocarbon process streams in refineries. Environmentally harmful organic substances are removed from wastewater streams in refineries and petrochemical plants through the use of sour water strippers *(60)*. Liquid-liquid extraction processes, based on the equilibration of hydrocarbon-rich and water-rich liquid streams, are also used *(1)*. Increasing environmental concerns have also led to using supercritical water, instead of organics, as the solvent in some reaction processes and extraction methods. These processes include the destruction of hazardous wastes in supercritical water *(55)* and chemical processing in supercritical and near critical water *(30)*.

Many of these processes occur at elevated temperatures and pressures. While there are sufficient data in the literature for most binary systems at ambient or near ambient temperatures, only limited data exist at elevated temperatures.

Liquid-liquid mutual solubilities for the benzene-water, decane-water and 1-hexene-water systems were measured from ambient temperatures to near their three-phase critical end points, as reported in the literature. Roof *(51)* reports the three-phase critical end point to be at 542.6 K for the benzene-water system and at 569.3 K for the decane-water system. For the 1-hexene-water system, the three-phase critical end point is reported by Economou et al. *(20)* to be at 493.3 K.

## Experimental Section

***Materials.*** The 2,2,4-trimethylpentane (99.9+ mole %), benzene (99+ mole %), and decane (99+ mole %) were supplied by Aldrich Chemical Co. The 1-hexene (98+ mole %) was supplied by Phillips Petroleum Co. No further purification of these chemicals was done. Ethanol (USP grade, Absolute-200 Proof), supplied by Pharmco Products, was dehydrated and stored over 4A molecular sieves from Fisher Chemical

Company for at least two months prior to use. The Oklahoma State University Biochemistry and Molecular Biology Department supplied the nanopure, deionized water. High purity helium (99.997 %) and ultra-high purity nitrogen (99.999 %) were obtained from Sooner Airgas, Inc.

Alltech supplied the screw top bottles, with open-hole caps and Teflon liners, used for sample collection. Hamilton 10 $cm^3$ syringes, from Alltech, were used to prepare the calibration standards. They were thoroughly rinsed between uses with acetone (99.7 mole %) from Fisher Scientific. Hamilton 0.01 $cm^3$ (10 μL) syringes were used to inject the calibration standard and samples into the gas chromatograph. Pharmco Products provided the ACS grade methanol, used at times in combination with acetone to clean the apparatus.

***Apparatus.*** A continuous flow apparatus was designed and constructed for liquid-liquid equilibrium measurements at ambient and elevated temperatures and pressures, up to 623 K and 13.8 MPa. A schematic diagram of this apparatus is shown in Figure 1. The apparatus consists of four sections: a feed section, an equilibration section, a separation section, and a sampling section. The feed section supplies two pure, partially miscible fluids at a constant flow rate to the equilibration section. In the equilibration section, the two fluids are thoroughly mixed and allowed to come to equilibrium. The separation section is designed to allow the equilibrium phases to separate for sample collection. The sampling section is where the two separated phases are collected. The total volume of the apparatus is approximately 120 $cm^3$.

In the feed section, a LCD Analytical Type NSI-33R duplex miniPump (DP1, the abbreviations correspond to Figure 1) was used to pump the hydrocarbon and water

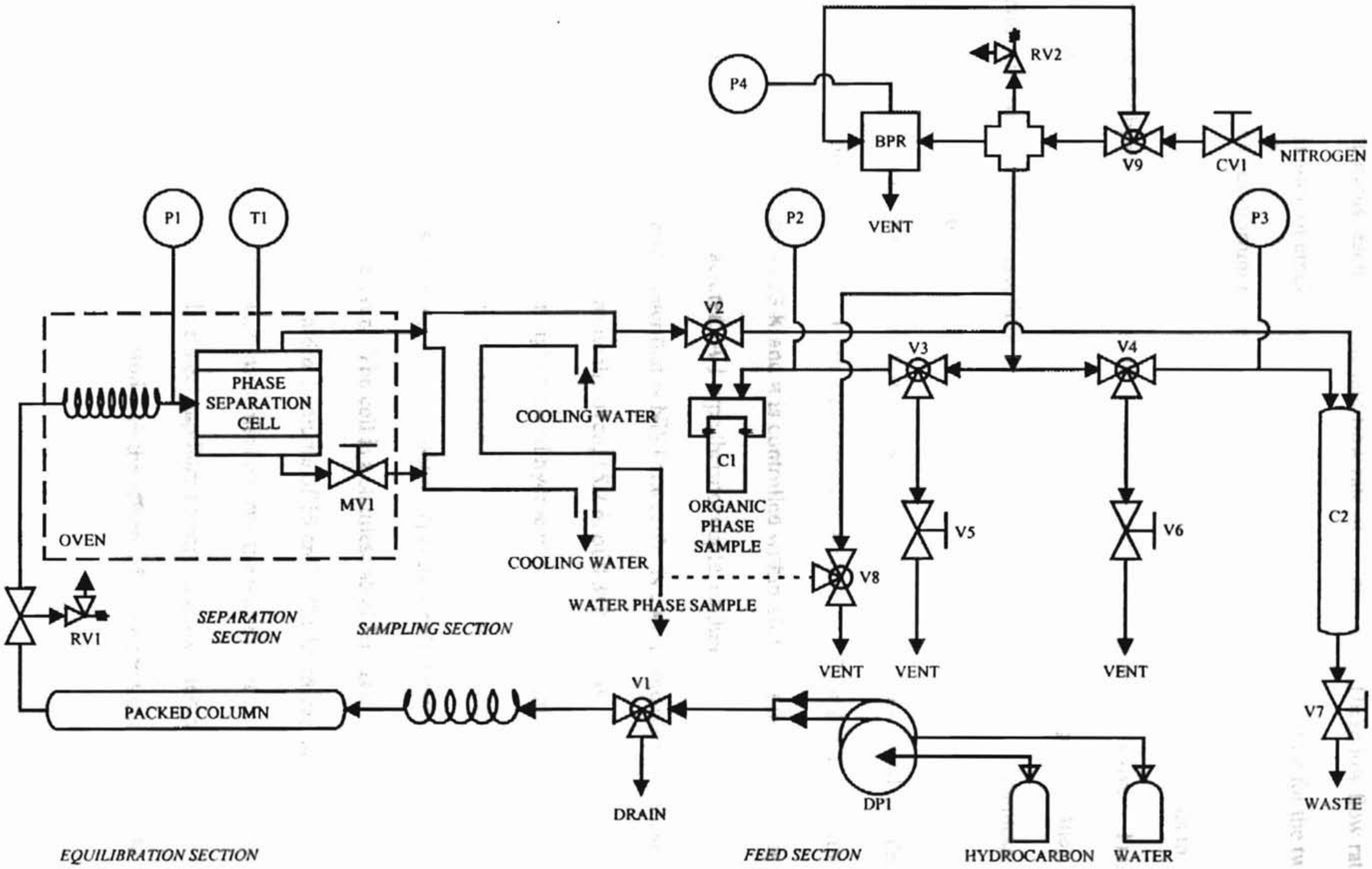

**Figure 1.** Diagram of the Continuous Flow Apparatus

through the apparatus, each at a constant flow rate of 2.0 $cm^3$/min. These low flow rates reduce the formation of emulsions in the apparatus and allow sufficient time for the two liquids to reach equilibrium prior to reaching the phase separation cell.

The equilibration section provides the necessary mixing for the two liquids to reach equilibrium at the experimental temperature. (A Whitey three-way valve (V1) is located directly after the pump and may be used as a bypass valve when priming the pump.) The two liquids pass through approximately 6.8 m of 0.318 cm-o.d. stainless steel tubing followed by 3.1 m of 0.835 cm-o.d. stainless steel tubing packed with 1.0 mm glass beads. Next, the mixture enters a 1.0 m section of 0.318 cm-o.d. stainless steel tubing before entering the Hotpack Digimatic Oven, Model 213024. The maximum temperature of the oven is 623 K and it is controlled within ±0.1 K of the set point, as determined by the manufacturer. A J-type thermocouple, calibrated against a Minco platinum resistance thermometer that is NIST traceable, is used to measure the phase separation cell temperature. Inside the oven, 15.2 m of 0.318 cm-o.d. stainless steel tubing is used to allow the thoroughly mixed hydrocarbon-water mixture to come to equilibrium at the experimental temperature before entering the separation section.

The separation section consists of a phase separation cell (labeled as such in Figure 1) located inside the oven. The cell is a stainless steel Jerguson Model 12T40 Liquid Level Gage and has an internal volume of 19 $cm^3$. The hydrocarbon-water mixture separates into two phases inside the cell, and the phases exit the cell through individual 0.159 cm-o.d. stainless steel capillary tubing. Capillary tubing is used to minimize dead volume, and thus, minimize the effects of phase separation on sample composition.

The final section is the sampling section. An Autoclave Engineering micrometering valve (MV1), located inside the oven, is used to control the flow of each phase out of the phase separation cell. By directly controlling the water effluent with MV1, equal amounts of hydrocarbon and water may be maintained in the cell and thus, the hydrocarbon-water interface may be kept near the center of the cell. This is necessary to prevent entrainment. Each phase then passes through a water-cooled heat exchanger 20.3 cm in length prior to being collected. Tap water is used on the shell side (0.635 cm-o.d. stainless steel tubing) to effectively cool each phase to room temperature before collection. This helps to keep the sample from vaporizing when it is collected. Two spring-loaded Nupro relief valves are used to prevent overpressure, one at each possible source of pressure. One relief valve (RV1) is located on the liquid mixture feed line, upstream of the oven, and the other valve (RV2) is located on the nitrogen stream line. The organic phase sample is collected in a glass bottle placed inside a 300 $cm^3$, sightless, high-pressure sampling cell (C1), which is pressurized by the nitrogen gas. The cell pressure is measured at the feed port of the phase separation cell with a Sensotec STJE pressure transducer and 450D readout. The maximum allowable working pressure of the system is limited by the pressure transducer, which has a pressure limit of 13.8 MPa (2000 psia). The relief valves are set at 12.4 MPa (1800 psia).

A Whitey three-way valve (V2) is located between the phase separation cell and C1. This valve is used to divert the flow of the organic phase sample to a 400 $cm^3$ sightless, high-pressure collection cell (C2), used for waste collection. This allows for continuous flow through the system at elevated pressures while changing the sample bottles. C2 is pressurized with the nitrogen gas. Two Whitey three-way valves are used to isolate C1 and C2 from the system so the nitrogen gas may be vented. The nitrogen gas is vented when the sample bottle is removed from C1 or when C2 is emptied. The Whitey three-way valve (V3) is used to close C1 and the Whitey three-way valve (V4) is used to close C2. This allows C1 or C2 to be lowered to atmospheric pressure while maintaining a constant elevated pressure inside the apparatus.

***Methods and Procedures.*** To prepare the samples for analysis, a known amount of solvent, by weight, was added to the sample bottles prior to sample collection. The organic phase sample was mixed with a nearly equal amount of ethanol. The ratio of the ethanol to the sample, by weight, was 0.8. The ethanol functioned as a homogenizing cosolvent for the sample and assured the sample was a single phase when analyzed. The ethanol contained a small amount of water (less than 0.015%), which was accounted for in the sample analysis.

The water phase sample was mixed with a known amount, by weight, of either decane or 2,2,4-trimethylpentane, depending on the system being studied. Decane was used as the solvent when the hydrocarbon of interest was benzene or 1-hexene and 2,2,4-trimethylpentane was used as the solvent when the decane system was studied. The solvent-to-sample weight ratios of the systems studied were 0.7 for the benzene-water system, 0.003 for the decane-water system, and 0.08 for the 1-hexene-water system. The purpose of the solvent used in the water phase was to extract the hydrocarbon from the water so it could be analyzed in the absence of water.

The samples were collected after adding the solvent to the sample bottles in order to minimize sample contact with the atmosphere and to keep from disturbing the sample after it was collected. At each temperature, three successive samples of each phase were collected. The organic and water phases were collected simultaneously and at a pressure slightly above the three-phase equilibrium pressure.

A Hewlett-Packard 5890A gas chromatograph (GC), equipped with a thermal conductivity detector (TCD) and a Hewlett-Packard 3392A integrator, was used to analyze the samples. A 1.8-m x 0.32-m stainless steel column packed with GasChrom 254 was supplied by Alltech. High purity helium was used as the carrier gas. Sample volumes of 0.003 $cm^3$ (3 $\mu$L) were analyzed.

The GC was calibrated by serial dilution techniques and a calibration curve was generated. The calibration curves were prepared from the solute-to-solvent weight ratio as a function of the solute-to-solvent area ratio. The data were regressed with the nonlinear weighted-least-squares Marquardt method *(12)*. The weighting of each datum was determined by an analysis of propagated error. Each calibration curve was expressed as a second order polynomial:

$$\mathrm{WR} = \alpha \mathrm{AR}^2 + \beta \mathrm{AR} + \gamma \qquad (1)$$

where, WR is the weight ratio, AR is the area ratio, and $\alpha$, $\beta$, and $\gamma$ are the regressed parameters. This expression was utilized in the sample analyses to determine the solute-to-solvent weight ratio. The solute-to-solvent weight ratio, WR, solvent-to-sample weight ratio, SSR, and the molecular weights of the solute, $MW_1$, and solvent, $MW_2$, were used in the following expression to calculate the mole fraction of the solute in the sample.

$$x_1 = \frac{[(WR)(SSR)]/MW_1}{\left\{[(WR)(SSR)]\big/ MW_1\right\} + \left\{1\big/ MW_2\right\}} \qquad (2)$$

A complete description of the apparatus and the operating procedures and techniques is given by Ratzlaff *(47)*.

## Results and Discussion

The mutual solubility data are reported in Table 1 and are presented graphically in Figures 2-19. The uncertainties associated with the data are presented as error bars when the error bar is larger than the symbol. By propagated error analysis, the maximum uncertainty in the water phase measurements ranges from 5 to 20% in the three systems studied. The maximum uncertainty in the organic phase measurements ranges from 2 to 32%. The highest uncertainties are seen in the very slightly soluble decane-water system.

***Hydrocarbon Solubility in Water.*** The hydrocarbon solubility data are correlated by an expression previously evaluated by Benson and Kraus *(7)* and used by Chen and Wagner *(16)*. This expression correlates the mole fraction of hydrocarbon, $x_i$, as a function of temperature, T, as follows:

$$\ln x_i = A + BT^{-1} + CT^{-2} \tag{3}$$

The parameters for each system were determined by a weighted-least-squares regression, in which all the measured data points were included in the initial regression. The results were then analyzed and any data point with a weighted deviation greater than 2.5 times the standard deviation was rejected from the data set. The final regression was performed on the reduced set of data to yield the parameters shown in Table 2. The weighting of each datum during the regression was determined by an analysis of propagated error.

For very dilute solutions (where the activity coefficient for water in the aqueous phase and hydrocarbon in the organic phase may be taken as equal to one), the heat of solution may be expressed by the Gibbs-Duhem equation *(58)*:

$$\left(\frac{\partial \ln x_i}{\partial T}\right)_P \cong \frac{\Delta\overline{H}_i}{RT^2} \tag{4}$$

where $\Delta\overline{H}_i$, the heat of solution, is the difference between the partial molar enthalpy of component $i$ in solution and the pure molar enthalpy of $i$. Thus, $\Delta\overline{H}_i$ is the excess enthalpy of component $i$. The heat capacity of solution, $\Delta\overline{C}_{P_i}$, may be defined as:

$$\left(\frac{\partial \Delta\overline{H}_i}{\partial T}\right)_P = \Delta\overline{C}_{P_i} \tag{5}$$

where $\Delta\overline{C}_{P_i}$ is the difference between the partial molar heat capacity of component $i$ in solution and the pure molar heat capacity of $i$. This is the excess heat capacity. The minimum solubility of hydrocarbon in water is determined when:

$$\left(\frac{\partial \ln x_i}{\partial T}\right)_P = 0 \tag{6}$$

Thus, the minimum temperature may be estimated by setting Equation 4 equal to zero and solving for the temperature. The enthalpies and heat capacities of solution at 298.15 K and the estimated minimum solubility temperatures of the various systems studied are listed in Table 2. Derivative data, such as those calculated in this study from Equations 4 and 5 are very sensitive to the solubility measurements and are, thus, compared to the calorimetric data only to determine the general quality of the solubility data.

***Water Solubility in Hydrocarbons.*** The data for the water solubility in hydrocarbons were also correlated by an equation expressing the mole fraction of water in hydrocarbon, $x_w$, as a function of temperature, as follows:

$$\ln x_w = A + BT^{-1} + C\ln T \tag{7}$$

This empirical equation is a generalized form of the Valentiner equation *(7)* and has been used by many investigators, including Franks et al. *(22)* and Moule and Thurston *(40)*. The water parameters of each system were determined in the same fashion as the hydrocarbon parameters. A weighted-least-squares regression was used and all the measured data points were included in the initial regression. After analyzing the results, any data point with a weighted deviation greater than 2.5 times the standard deviation was rejected from the data set. The parameters shown in Table 3 were determined from the final regression performed on the reduced set of data. The weighting of each datum was determined by an analysis of propagated error.

The heat of solution of water in hydrocarbon can be calculated from Equation 4 and the specific heat of solution from Equation 5, at 298.15 K. These derivative data are presented in Table 3 with the solubility parameters. Water solubilities in the hydrocarbons do not display a minimum solubility temperature.

***Benzene Solubility in Water.*** The measured benzene solubility in water is shown in Figure 2. The abundance of benzene-water data allows for detailed comparisons at temperatures near ambient, but the upper temperature range (>373 K) has not been investigated as thoroughly. The evaluations of Hefter *(28)* and Wagner *(62)* have been used to determine the quality of the data.

Equation 3 was used to correlate the benzene solubility measurements. The measurement taken at 492.8 K was not included in determining the equation parameters since it had a weighted deviation greater than 2.5 times the standard deviation. The weighted deviations are shown in Figure 3, with the exception of the measurement at 492.8 K since it was not included in the regression.

The solubility measurements from this study have an uncertainty of 1.5% or less, as estimated by error propagation, and agree within 10% of the literature data at the lower temperature measurements. In the higher temperature range, where fewer solubility studies exist and there are no "recommended" values, the measurements from this study are within 10% of Anderson and Prausnitz *(1)*. The percent deviations from the correlation are shown in Figure 4.

From Equation 4, the heat of mixing at 298.15 K is 0.96 kJ/mole. This does not agree within uncertainty limits with the calorimetric heat of solution reported by Reid et al. *(49)*, (0.80 ± 0.12) kJ/mole, or with the value reported by Gill et al. *(24)*, (2.08 ± 0.04) kJ/mole. The second derivative property, the specific heat of solution, is 287.0 J/mole-K. This does not agree within uncertainty limits with the calorimetric specific heat of solution reported by Gill et al. *(24)*, (225 ± 5) J/mole-K. From Equations 3 and 6, the temperature at which the minimum solubility of benzene in water occurs is 295 K. This is not consistent within the uncertainty limits with the minimum temperature reported by Gill et al. *(24)*, (289.0 ± 0.2) K.

***Water Solubility in Benzene.*** The solubility of water in benzene is shown in Figure 5. An abundance of solubility data for water in benzene exists in the literature at atmospheric pressures. Hefter *(28)* notes the more recent studies tend to be slightly higher in solubility than previous studies and with considerably smaller uncertainty.

The water solubility measurements were correlated with Equation 7. The measurements taken at 388.0 K and 474.2 K were not included in the regression because their weighted deviations were greater than 2.5 times the standard deviation. The weighted deviations are shown in Figure 6. The weighted deviations at 388.0 K and at 474.2 K are not shown since they were not included in the regression.

The measurements from this study have an expected uncertainty ranging from 1.5 to 10.5%. The low temperature measurements from this study agree within 4% of the single measurements of Polak and Lu *(45)*, Kirchnerova and Cave *(31)*, and Singh and Sah *(56)* at 298 K and are within 8% of the measurements of Goldman *(25)*. At higher temperatures, the measurements of this study are 8% higher, on average, than those of Tsonopoulos and Wilson *(60)* and 13% higher, on average, than those of Anderson and Prausnitz *(1)*. The percent deviations from the correlation are shown in Figure 7.

From Equation 4, the heat of solution is determined to be 21.8 kJ/mole, at 298.15 K. This agrees well with the theory stated by Franks *(23)* that liquid water dissolving into a non-polar hydrocarbon liquid phase is essentially a process of breaking hydrocarbon bonds. The energy associated with a hydrogen bond is 21-29 kJ/mole. The heat capacity of solution at 298.15 K is estimated to be 77.3 J/mole-K, from Equation 5. This is consistent with the solubility derivative datum of Chen and Wagner *(16)* at 298.15 K, which is reported as 78.3 J/mole-K, based on the common uncertainty in heat capacity estimates of at least ±1 J/mole-K.

***Decane Solubility in Water.*** Decane is four orders of magnitude less soluble in water than benzene is. According to Tsonopoulos and Wilson *(60)*, the least soluble hydrocarbons in water are the paraffins and Franks *(23)* reports the solubility of hydrocarbons in water decreases with an increase in paraffin chain length. This low solubility makes it difficult to make accurate measurements. The data from this study are shown in Figure 8. The solubility parameters were regressed using Equation 3. The weighted deviations are shown in Figure 9.

The solubility measurements from this study have an expected uncertainty of less than 3%, with the exception of the four lowest temperature measurements, which have an uncertainty of 10 to 32%. These new data show more scatter about the correlating line and lack the quality and reproducibility the other binary systems demonstrated during this study. This is due to the very low solubilities. The percent deviations from the correlation are shown in Figure 10. The datum of Mackay et al. *(36)* at 298.2 K and the data of Ng and Chen *(43)* at 310.9 K and 394.3 K deviate by more than 500% from the correlation and are not shown in Figure 10.

The heat of solution, at 298.15 K, is 4.41 kJ/mole and the specific heat of solution is estimated to be 722.5 J/mole-K. The minimum solubility is calculated to be at 292 K. There are no literature calorimetric data for comparison.

***Water Solubility in Decane.*** The solubility data for water in decane are shown in Figure 11. These measurements have a maximum uncertainty of almost 20% at the lowest temperature and less than 4% uncertainty at the elevated temperatures. Equation 7 was used to regress the solubility parameters. The weighted deviations and the percent deviations are shown in Figures 12 and 13, respectively. The measurements recorded at 363.2 K and at 440.3 K had weighted deviations greater than 2.5 times the standard deviation and were neither included in the regression nor included in the plot of weighted deviations in Figure 12. The elevated temperature data of Guerrant *(26)* deviate less than 6% from the correlating line. The datum of Becke and Quitzsch *(5)* at 298.15 K deviates from the data of this study by more than 350% and is not shown in Figure 13.

The heat of solution at 298.15 K is calculated to be 26.6 kJ/mole. This value is expected if the energy is a result of the hydrogen bond breaking, but is low compared to the calorimetric heat of solution reported by Nilsson *(44)* of (37.1 ± 1.9) kJ/mole. The heat capacity of solution at 298.15 K, from Equation 5, is 84.1 J/mole-K. There is not a calorimetric comparison in the literature.

***1-Hexene Solubility in Water.*** The literature contains four measurements at ambient temperatures *(11, 34, 39, 42)* and one investigation *(20)* reports several measurements at elevated temperatures. As shown in Figure 14, the measurements of this study are in agreement with the literature data at ambient temperatures and verify the trend in solubility reported by Economou et al. *(20)*. The solubility parameters were regressed using Equation 3. The datum at 434.9 K was not included in the regression since it had a weighted deviation greater than 2.5 times the standard deviation. The weighted deviations are shown in Figure 15, with the exception of the datum at 434.9 K since it was not used in the regression. The maximum uncertainty in the reported measurements is 2%. The percent deviations from the correlating line are shown in Figure 16.

From Equation 4, the estimated heat of solution is –1.38 kJ/mole and the specific heat of solution is 443.1 J/mole-K at 298.15 K. The minimum solubility temperature is 301 K. There are no literature calorimetric data for comparison.

***Water Solubility in 1-Hexene.*** The solubility of water in 1-hexene is shown in Figure 17. Equation 7 was used to correlate the solubility data and all the measurements were used in the regression. No measurement was reported at 353.5 K because it was in obvious error. The weighted deviations are shown in Figure 18. The percent deviations from the correlation are presented in Figure 19. The maximum uncertainty in the solubility measurements is 5%. At 298.15 K, the heat of solution is 23.1 kJ/mole and the specific heat of solution is 77.5 J/mol-K. There are no literature calorimetric data for comparison.

## Conclusions

A continuous flow apparatus was designed and constructed to measure mutual solubilities at temperatures ranging from ambient to 623 K and pressures up to 13.8 MPa. Mutual solubilities for the binary systems of benzene-, decane- and 1-hexene-water have been measured at temperatures from ambient to near the three-phase critical end point. Experimental pressures were slightly above the three-phase values. The measurements were compared with reliable literature data for the well-documented benzene-water system to demonstrate the accuracy of the solubility measurements obtained with the new apparatus; agreement is within 10%. A propagated error analysis was performed and the maximum expected uncertainty in the solubility measurements is about 30%. The maximum expected uncertainty is less than 5% for the majority of the experimental conditions.

Enthalpies of solution for the hydrocarbons dissolving in water, which are estimated from the solubility measurements, do not agree within uncertainty limits with calorimetric measurements from the literature. The enthalpies of solution for the water dissolving in the hydrocarbons were within the range of the hydrogen bonding energies.

## Nomenclature

| | |
|---|---|
| $\alpha, \beta, \gamma$ | constants in calibration correlations |
| WR | weight ratio |
| AR | area ratio |
| A, B, C | constants in solubility correlations |
| $x_i$ | mole fraction hydrocarbon *i* |
| $x_w$ | mole fraction water |
| T | temperature (K) |
| R | ideal gas constant |
| $\Delta\overline{H}_i$ | heat of solution (kJ/mole) |
| $\Delta\overline{C}_{P_i}$ | specific heat of solution (J/mole-K) |

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## List of Tables

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**Table 1.** Mutual Solubilities for Hydrocarbon-Water Systems

Benzene-Water System

| Temperature (K) | Pressure (MPa) | $x_{benzene}$ ($10^4$) | % Uncertainty | $x_{water}$ ($10^2$) | % Uncertainty |
|---|---|---|---|---|---|
| 296.4 | 0.139 | 4.10 | 0.676 | 0.289 | 10.4 |
| 328.5 | 0.139 | 4.90 | 1.54 | 0.656 | 6.09 |
| 358.8 | 0.217 | 7.29 | 0.782 | 1.59 | 4.92 |
| 388.0 | 0.555 | 11.2 | 0.524 | 3.66* | 3.87 |
| 416.8 | 1.019 | 18.8 | 0.704 | 6.00 | 2.21 |
| 445.8 | 2.018 | 30.8 | 0.535 | 12.3 | 2.40 |
| 474.2 | 3.454 | 52.5 | 1.27 | 20.1* | 1.34 |
| 492.8 | 6.823 | 76.2* | 1.15 | 33.7 | 1.59 |

Decane-Water System

| Temperature (K) | Pressure (MPa) | $x_{decane}$ ($10^6$) | % Uncertainty | $x_{water}$ ($10^2$) | % Uncertainty |
|---|---|---|---|---|---|
| 295.5 | 0.173 | 0.0324 | 32.1 | 0.0568 | 19.2 |
| 323.5 | 0.150 | 0.0242 | 18.7 | 0.155 | 14.6 |
| 363.2 | 0.160 | 0.0549 | 19.3 | 0.324* | 8.42 |
| 402.9 | 0.367 | 0.469 | 10.2 | 1.35 | 6.11 |
| 440.3 | 0.967 | 2.14 | 2.49 | 4.78* | 1.56 |
| 477.3 | 2.350 | 11.8 | 2.19 | 9.14 | 2.85 |
| 513.8 | 4.762 | 61.6 | 1.70 | 18.3 | 1.51 |
| 542.3 | 7.857 | 195. | 1.35 | 34.9 | 3.34 |

1-Hexene-Water System

| Temperature (K) | Pressure (MPa) | $x_{1\text{-}hexene}$ ($10^5$) | % Uncertainty | $x_{water}$ ($10^2$) | % Uncertainty |
|---|---|---|---|---|---|
| 296.4 | 0.154 | 1.19 | 1.07 | 0.176 | 5.11 |
| 328.4 | 0.156 | 1.44 | 2.04 | 0.347 | 2.31 |
| 353.5 | 0.294 | 2.20 | 1.77 | - | - |
| 383.5 | 0.607 | 3.92 | 0.810 | 1.44 | 3.25 |
| 407.2 | 1.049 | 6.88 | 0.914 | 2.43 | 4.16 |
| 434.9 | 2.025 | 14.4* | 0.867 | 5.07 | 1.99 |
| 463.5 | 3.518 | 29.2 | 1.05 | 9.99 | 3.80 |
| 486.7 | 5.676 | 52.5 | 1.18 | 17.3 | 1.71 |

* Not used in the regression of the solubility parameters because it contained a weighted deviation of greater than 2.5.

**Table 2.** Derivative Data for Hydrocarbon Solubilities

| | Parameters in Equation 3 | | | $\Delta H$, kJ/mole | $\Delta C_p$, J/mole-K | $T_{min}$, |
|---|---|---|---|---|---|---|
| Solute | A | B, K | C, $K^2$ | at 298.15 K | at 298.15 K | K |
| Benzene | 9.852 | –1.041E+04 | 1.534E+06 | 0.96 | 287.0 | 295 |
| Decane | 27.099 | –2.644E+04 | 3.863E+06 | 4.41 | 722.5 | 292 |
| 1-Hexene | 14.758 | –1.573E+04 | 2.369E+06 | –1.38 | 443.1 | 301 |

**Table 3.** Derivative Data for Water Solubilities

| Hydrocarbon | Parameters in Equation 7<br>A | B, K | C, $K^2$ | $\Delta H$, kJ/mole at 298.15 K | $\Delta C_p$, J/mole-K at 298.15 K |
|---|---|---|---|---|---|
| Benzene | –93.000 | 1853.0 | 14.217 | 21.8 | 77.3 |
| Decane | –64.435 | –18.385 | 10.112 | 26.6 | 84.1 |
| 1-Hexene | –124.40 | 3483.0 | 18.661 | 23.1 | 77.5 |

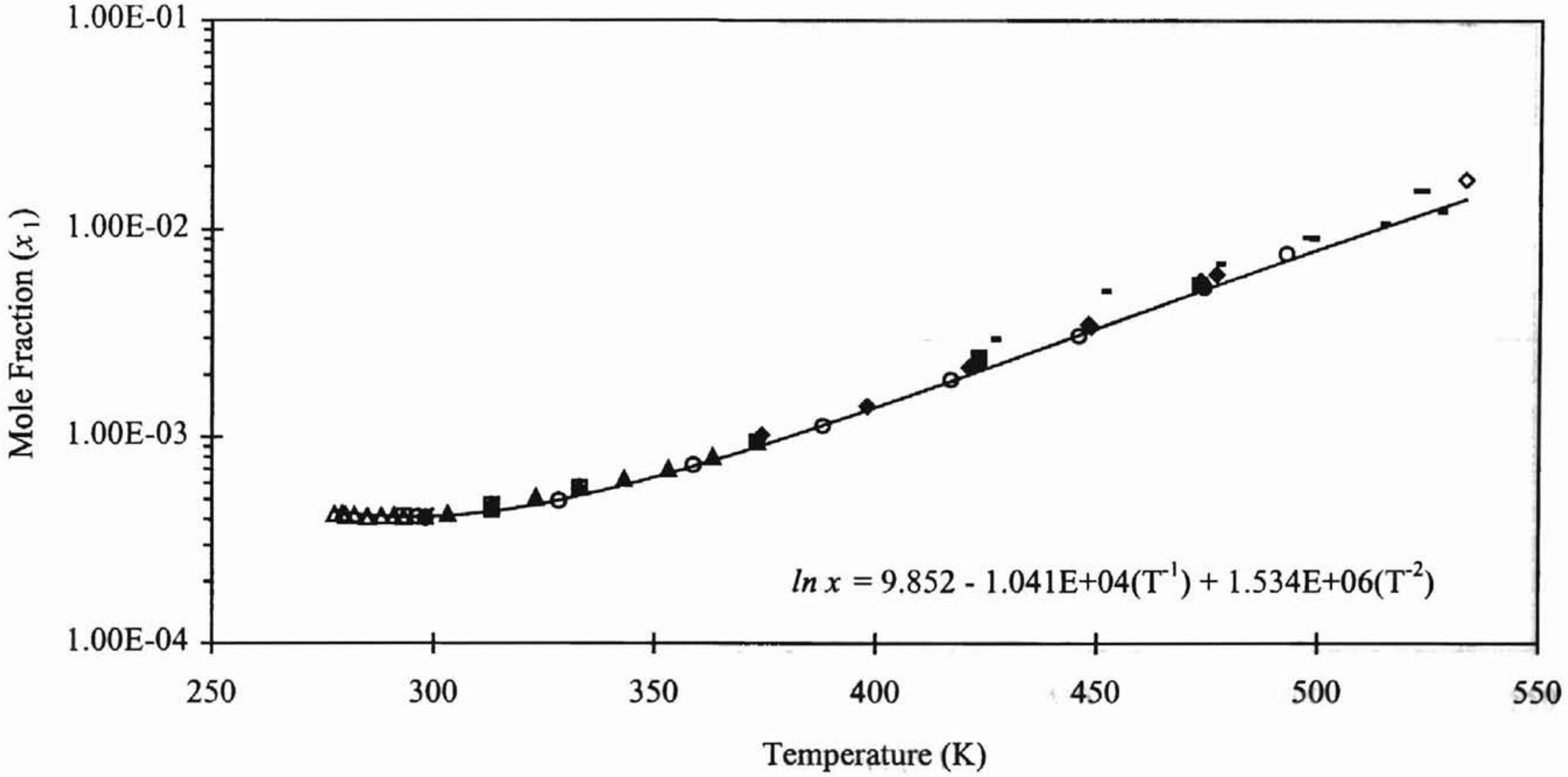

**Figure 2.** Solubility of Benzene in Water: ○ this work; — Chandler et al. (13); ▲ Chen and Wagner (16); ◆ Anderson and Prausnitz (1); ■ Tsonopoulos and Wilson (60); ● Banerjee et al. (4); □ Bittrich et al. (8); × May et al. (37); + Price (46); ∗Mackay and Shiu (35); △ Brown and Wasik (10); ◇ Connolly (18); – Guseva and Parnov (27).

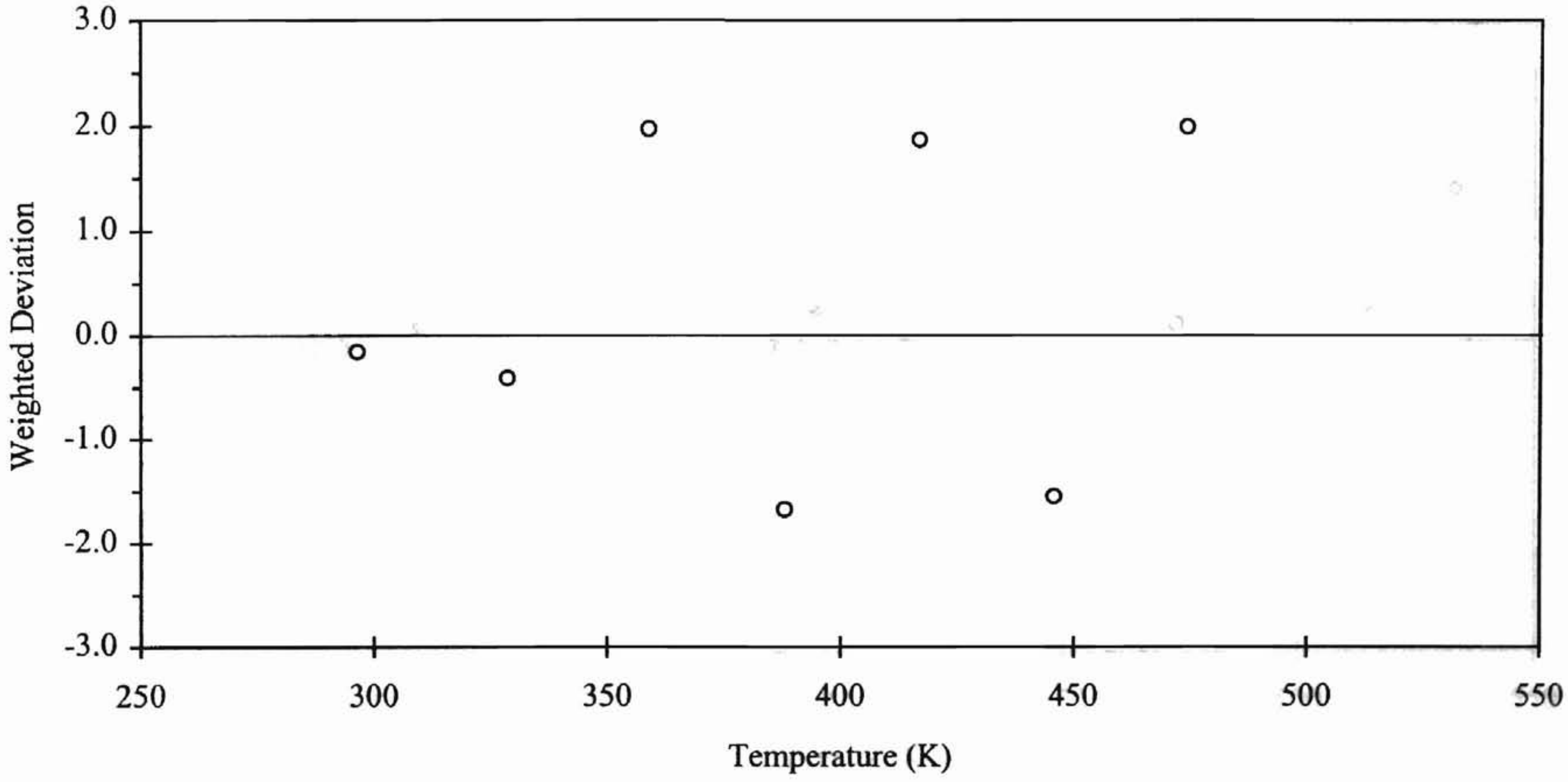

**Figure 3.** Weighted Deviation in the Solubility of Benzene in Water: ○, this work.

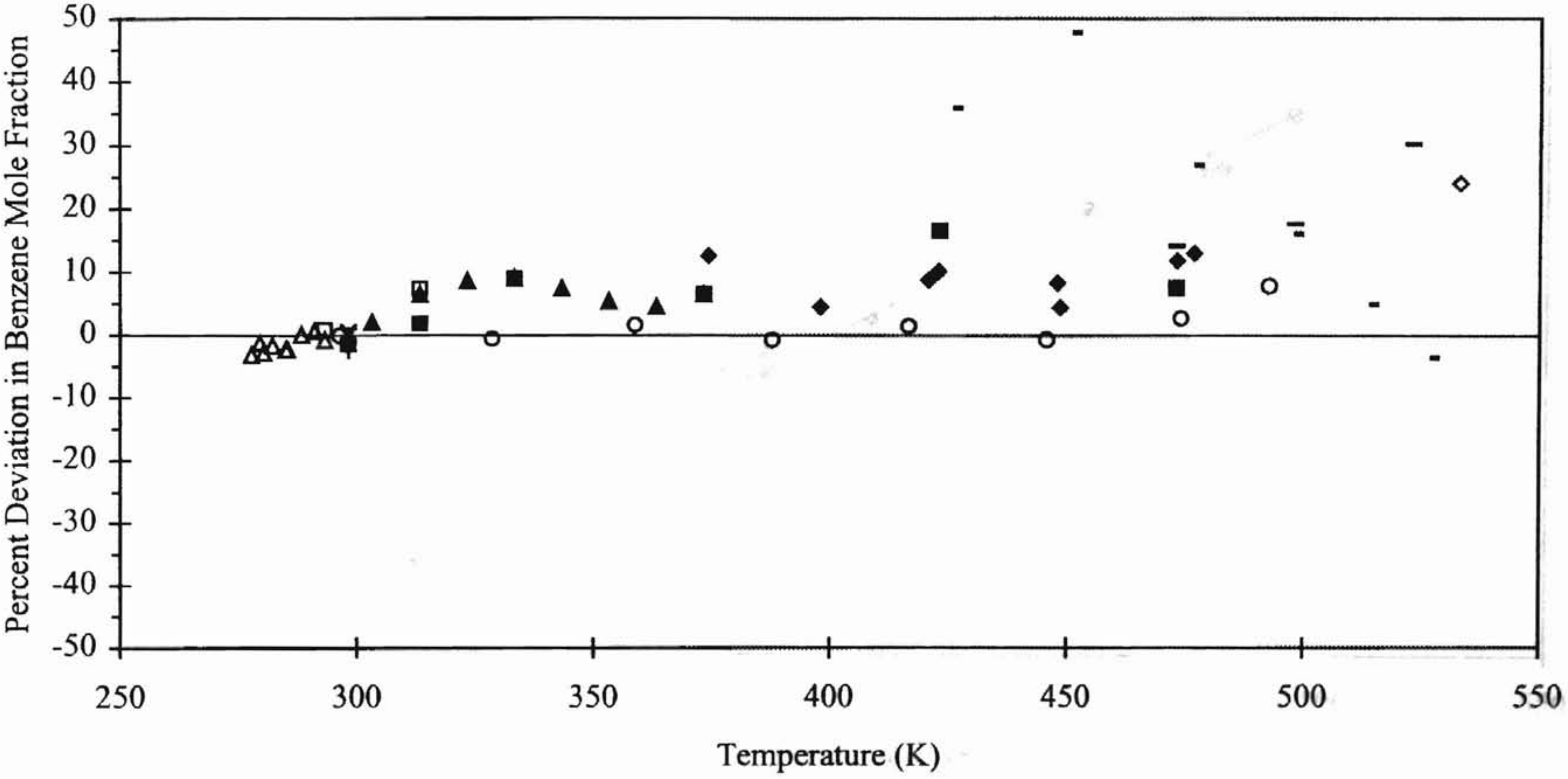

**Figure 4.** Comparison of Solubility Data for Benzene in Water: ○ this work; — Chandler et al. (13); ▲ Chen and Wagner (16); ◆ Anderson and Prausnitz (1); ■ Tsonopoulos and Wilson (60); ● Banerjee et al. (4); □ Bittrich et al. (8); × May et al. (37); + Price (46); ∗Mackay and Shiu (35); △ Brown and Wasik (10); ◇ Connolly (18); – Guseva and Parnov (27).

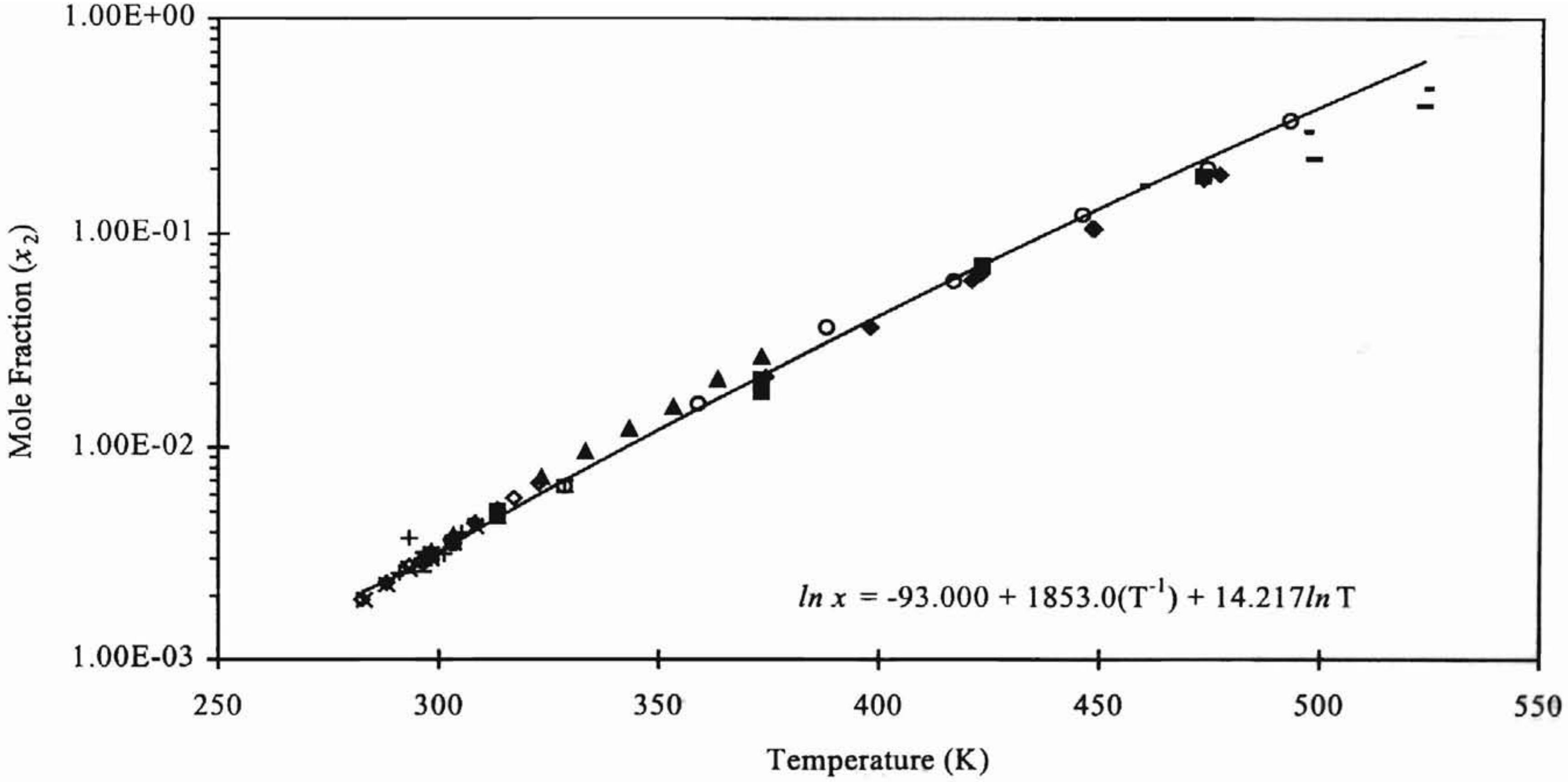

**Figure 5.** Solubility of Water in Benzene: ○ this work; — Chandler et al. (13); ▲ Chen and Wagner (16); ◆ Anderson and Prausnitz (1); ■ Tsonopoulos and Wilson (60); ● Singh and Sah (56); □ Kirchnerova and Cave (31); × Goldman (25); + Karlsson (29); ∗ Polak and Lu (45); △ Roddy and Coleman (50); ◇ Moule and Thurston (40); – Umano and Hayano (61).

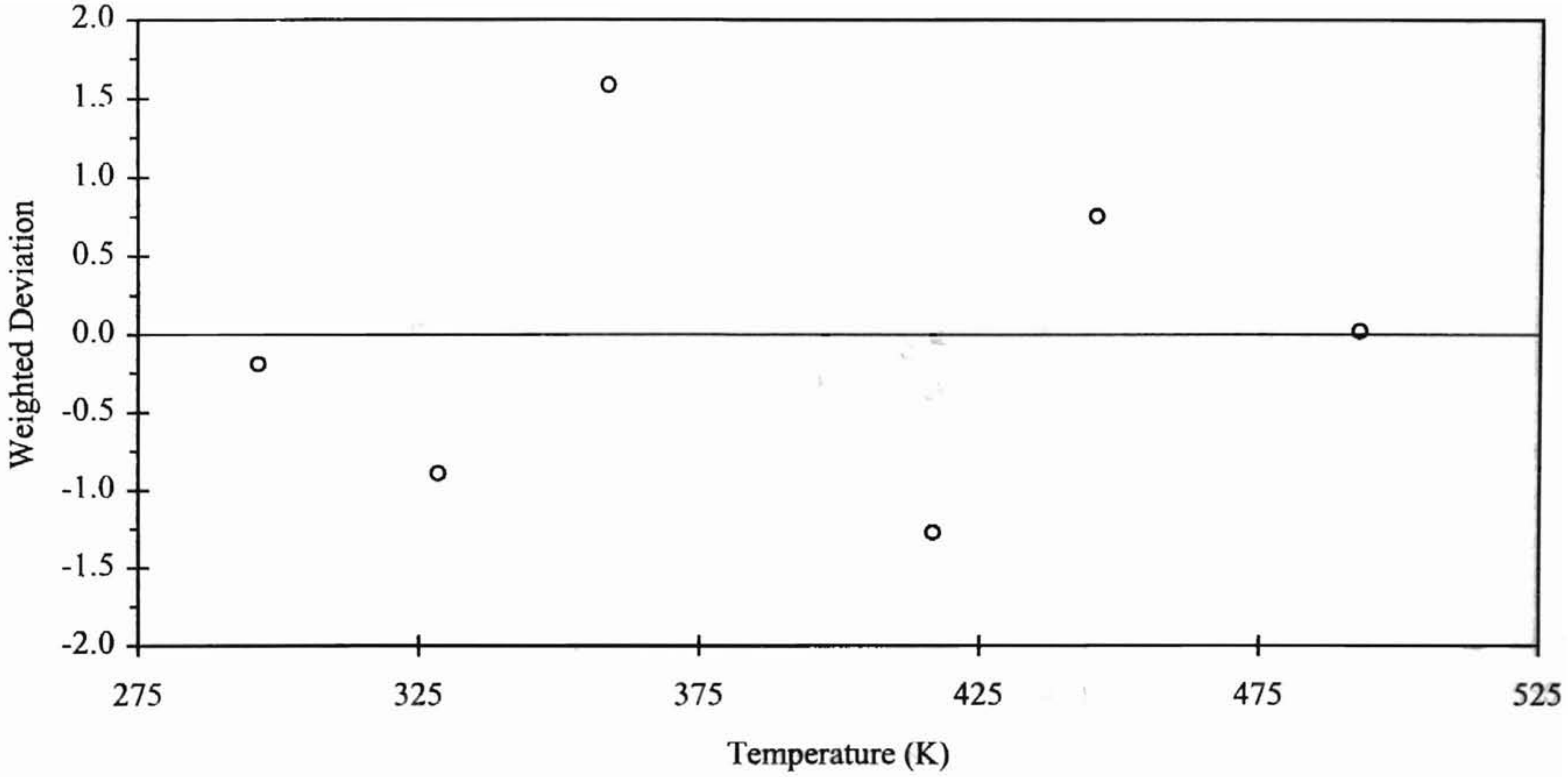

**Figure 6.** Weighted Deviation in the Solubility of Water in Benzene: ○, this work.

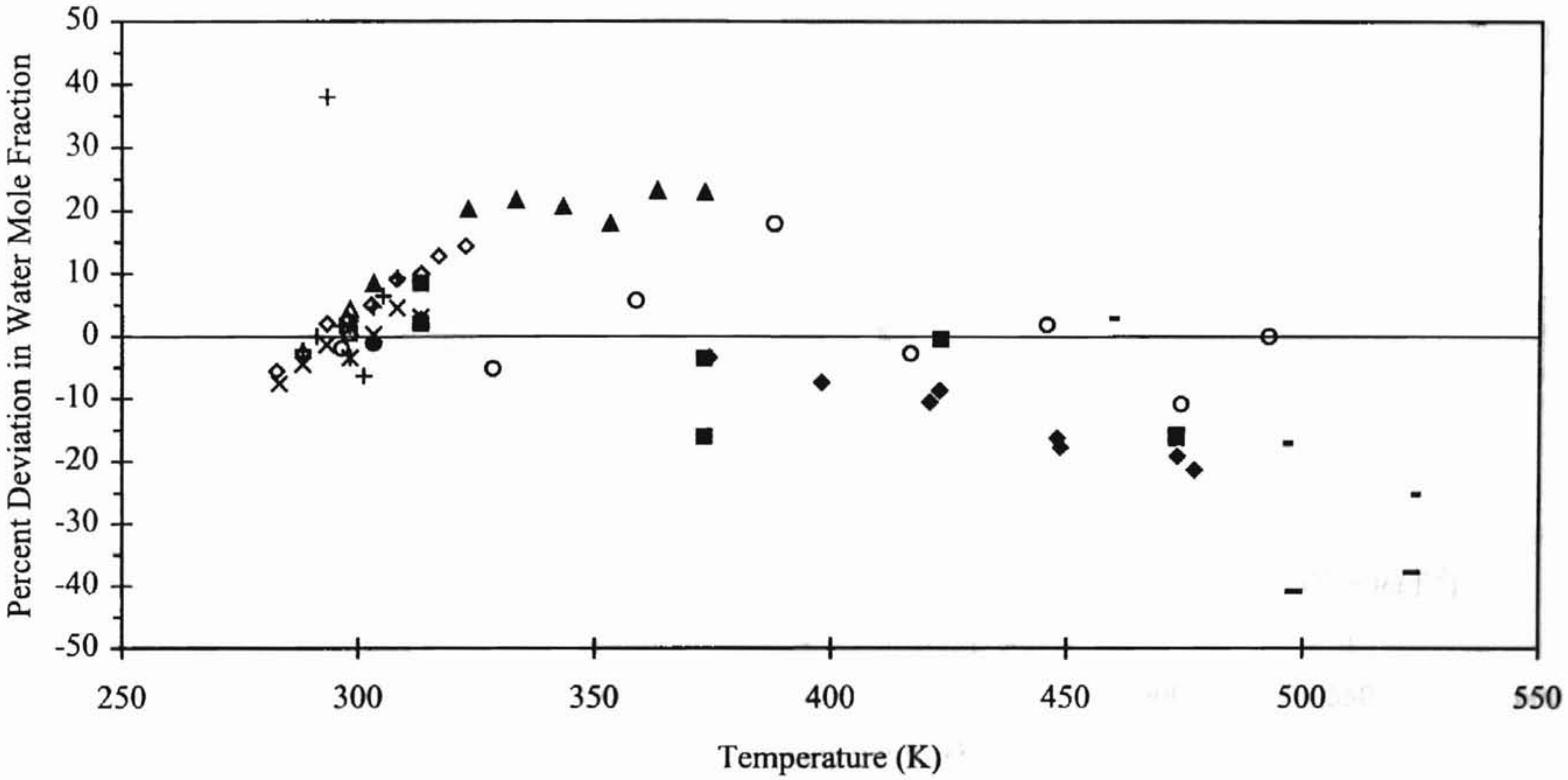

**Figure 7.** Comparison of Solubility Data for Water in Benzene: ○ this work; — Chandler et al. (13); ▲ Chen and Wagner (16); ◆ Anderson and Prausnitz (1); ■ Tsonopoulos and Wilson (60); ● Singh and Sah (56); □ Kirchnerova and Cave. (31); × Goldman (25); + Karlsson (29); ∗ Polak and Lu (45); △ Roddy and Coleman (50); ◇ Moule and Thurston (40); – Umano and Hayano (61).

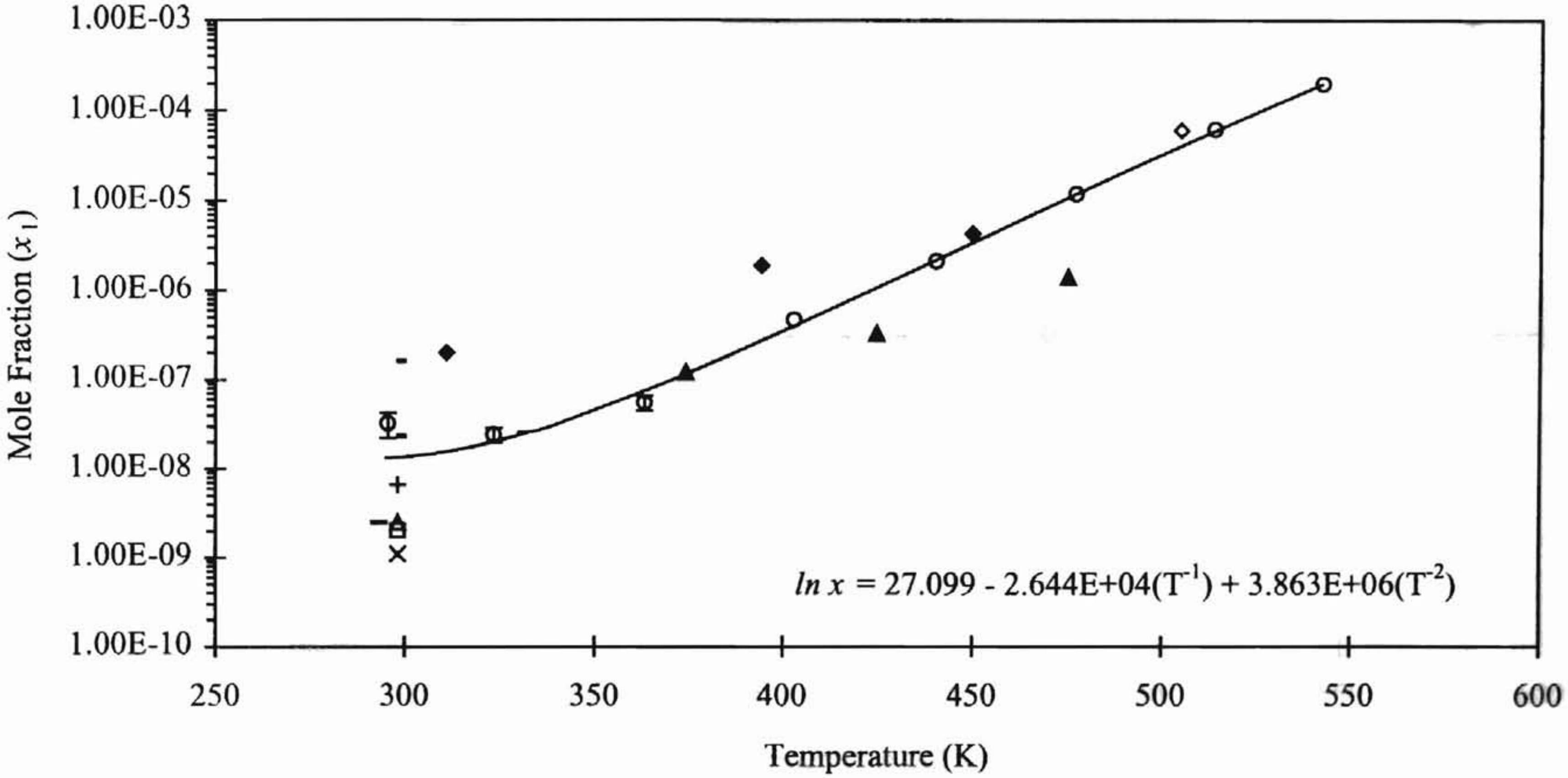

**Figure 8.** Solubility of Decane in Water: ○ this work; ▲ Economou et al. (20); ◆ Ng and Chen (43); — Becke and Quitzsch (5); – Mackay et al. (36); × Krasnoshchekova and Gubergrits (32); + McAuliffe (38); △ Franks (23); ◇ Guerrant (26); □ Baker (3).

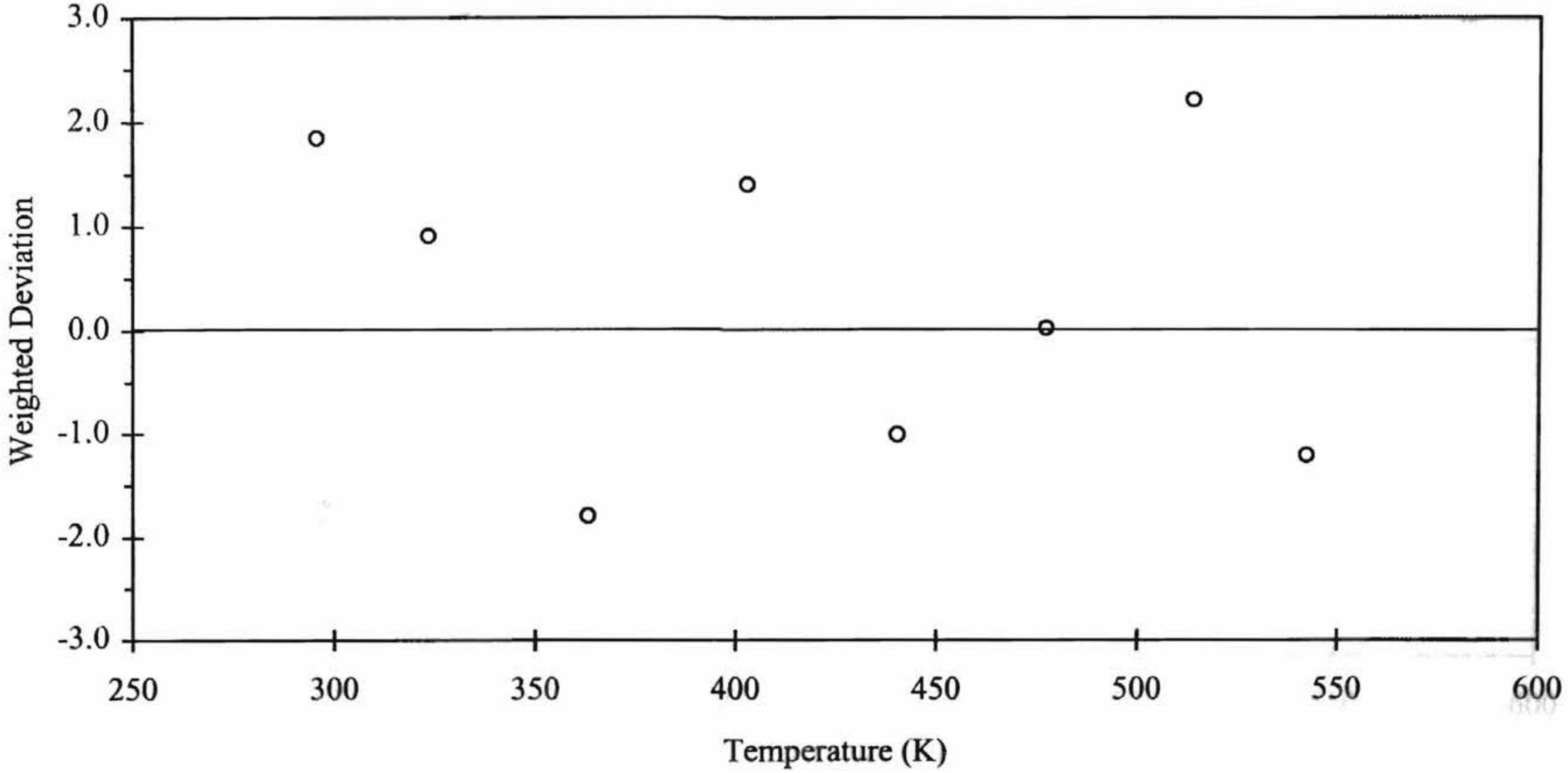

**Figure 9.** Weighted Deviation in the Solubility of Decane in Water: ○, this work.

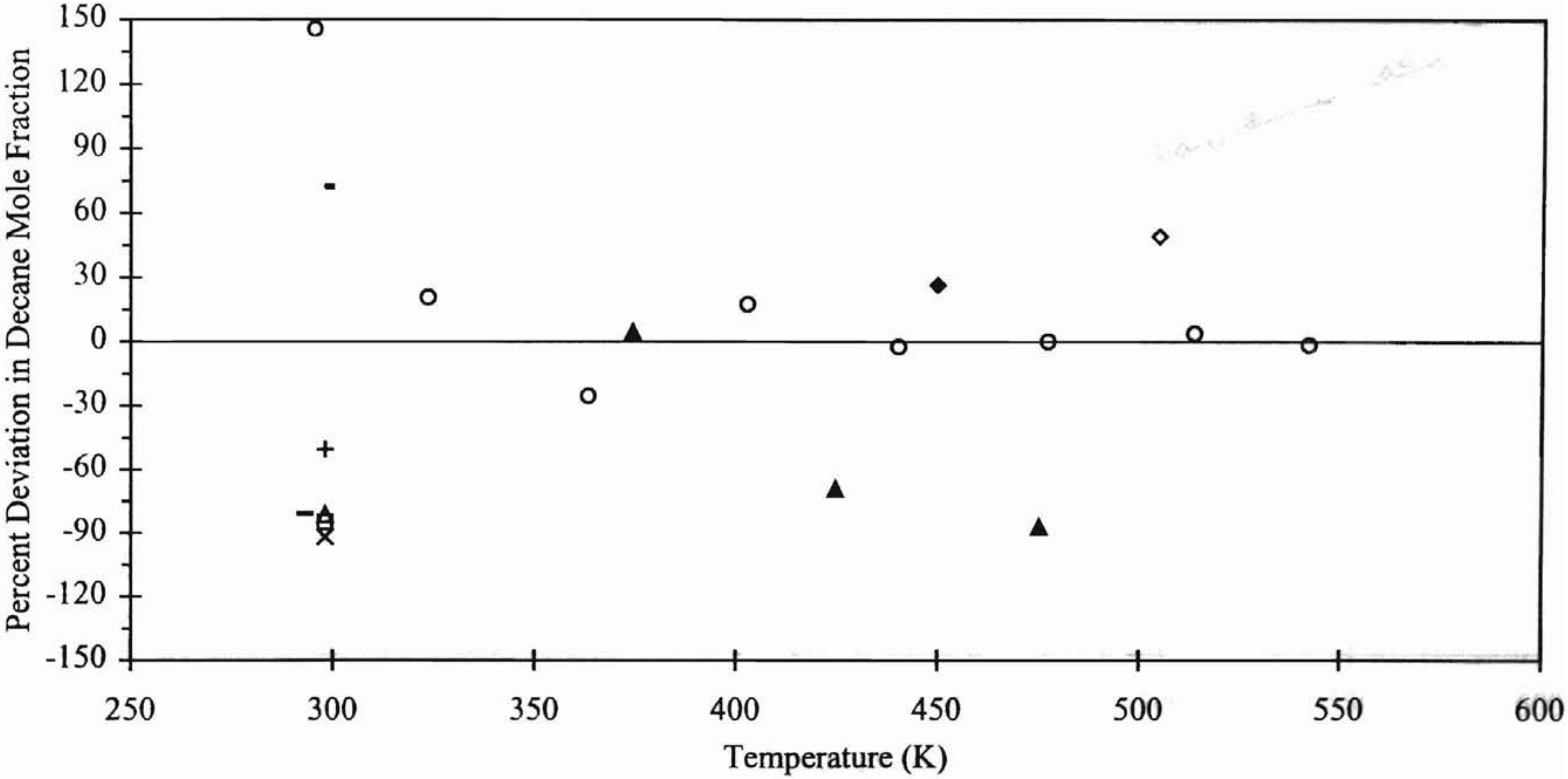

**Figure 10.** Comparison of Solubility Data for Decane in Water: ○ this work; ▲ Economou et al. (20); ◆ Ng and Chen (43); — Becke and Quitzsch (5); – Mackay et al. (36); × Krasnoshchekova and Gubergrits (32); + McAuliffe (38); △ Franks (23); ◇ Guerrant (26); □ Baker (3).

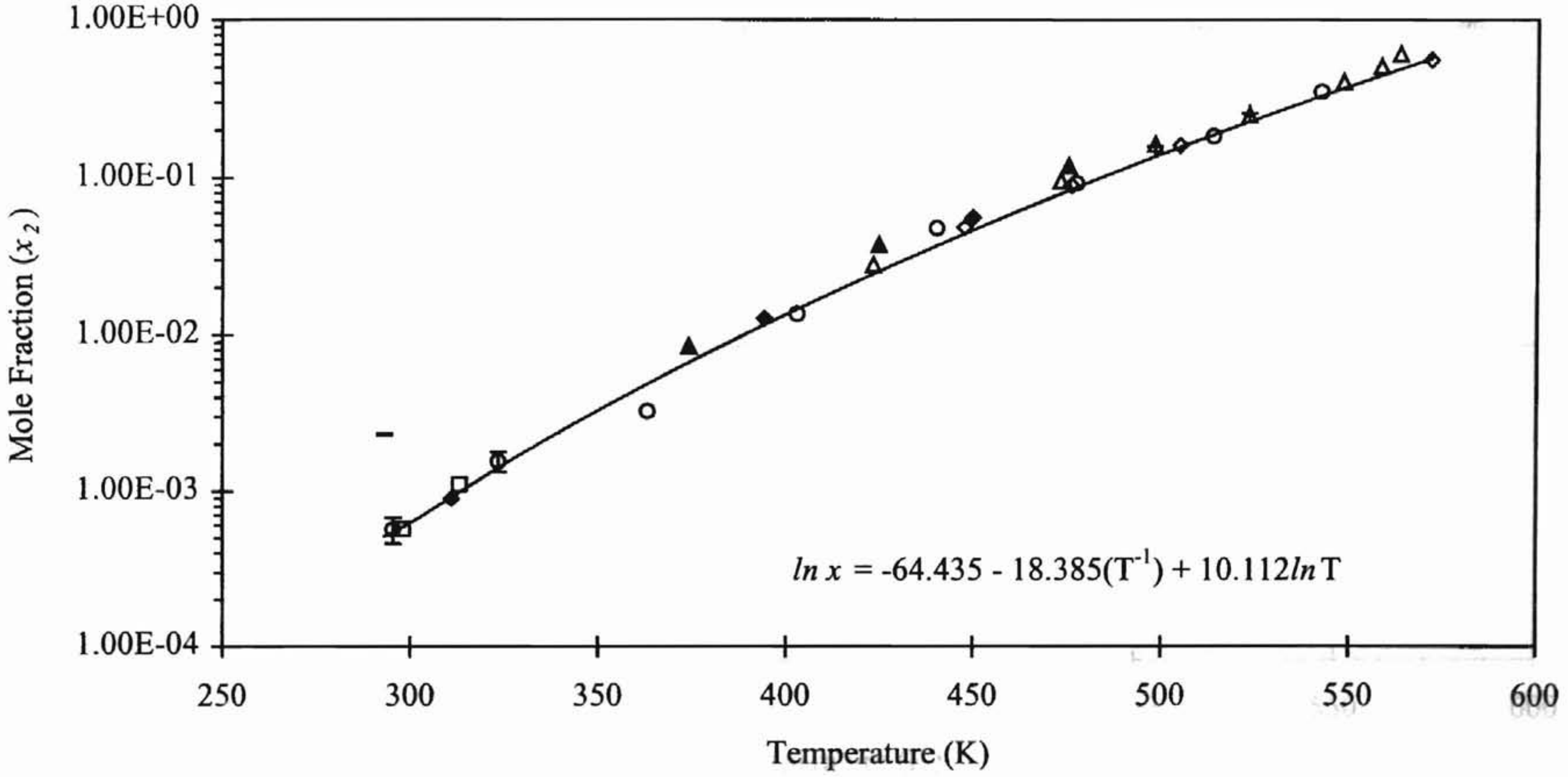

**Figure 11.** Solubility of Water in Decane: ○ this work; ▲ Economou et al. (20); ◆ Ng and Chen (43); — Becke and Quitzsch (5); + Skripka (57); △ Namiot et al. (41); ◇ Guerrant (26); □ Schatzberg (54).

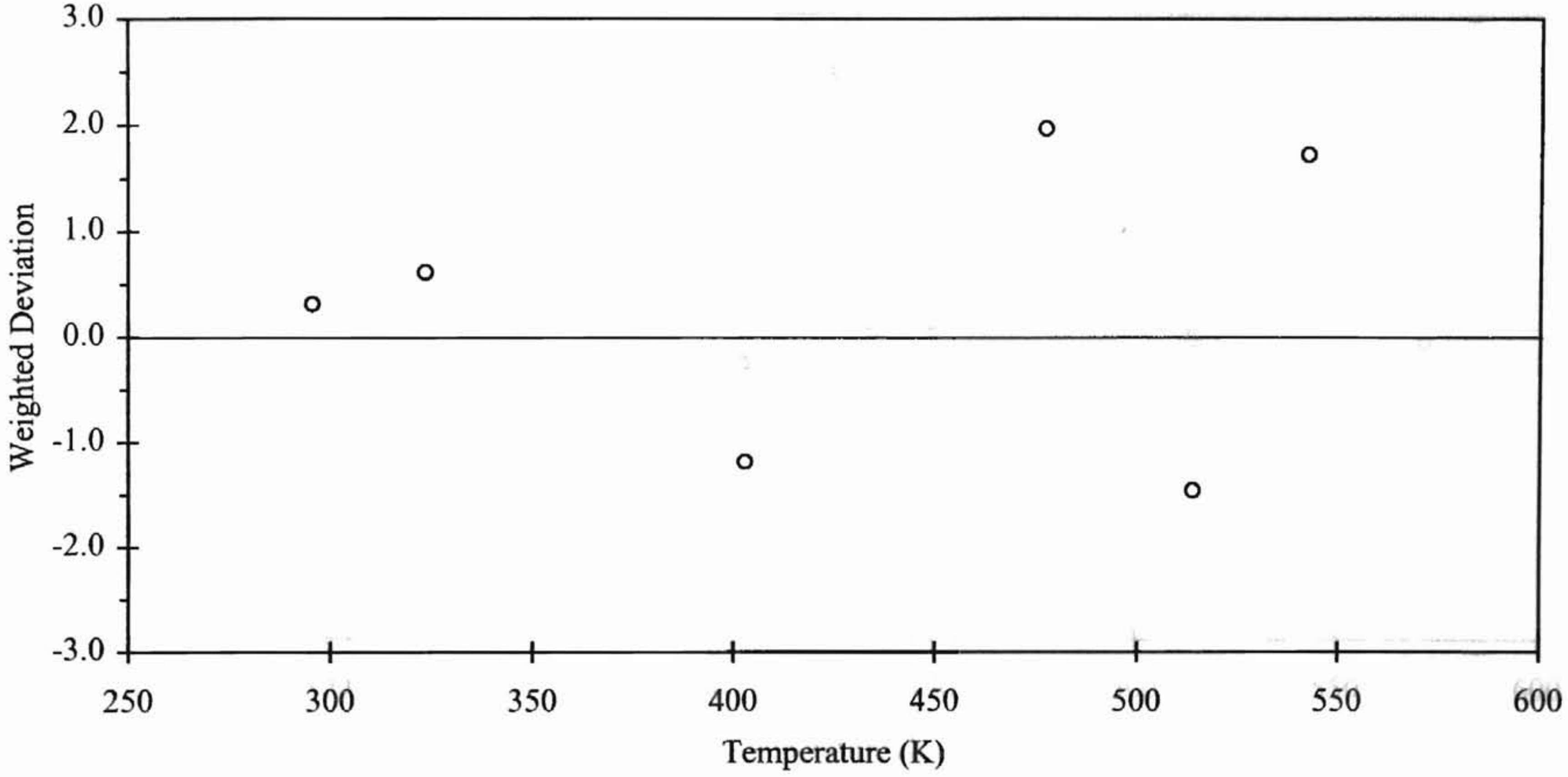

**Figure 12.** Weighted Deviation in the Solubility of Water in Decane: o, this work.

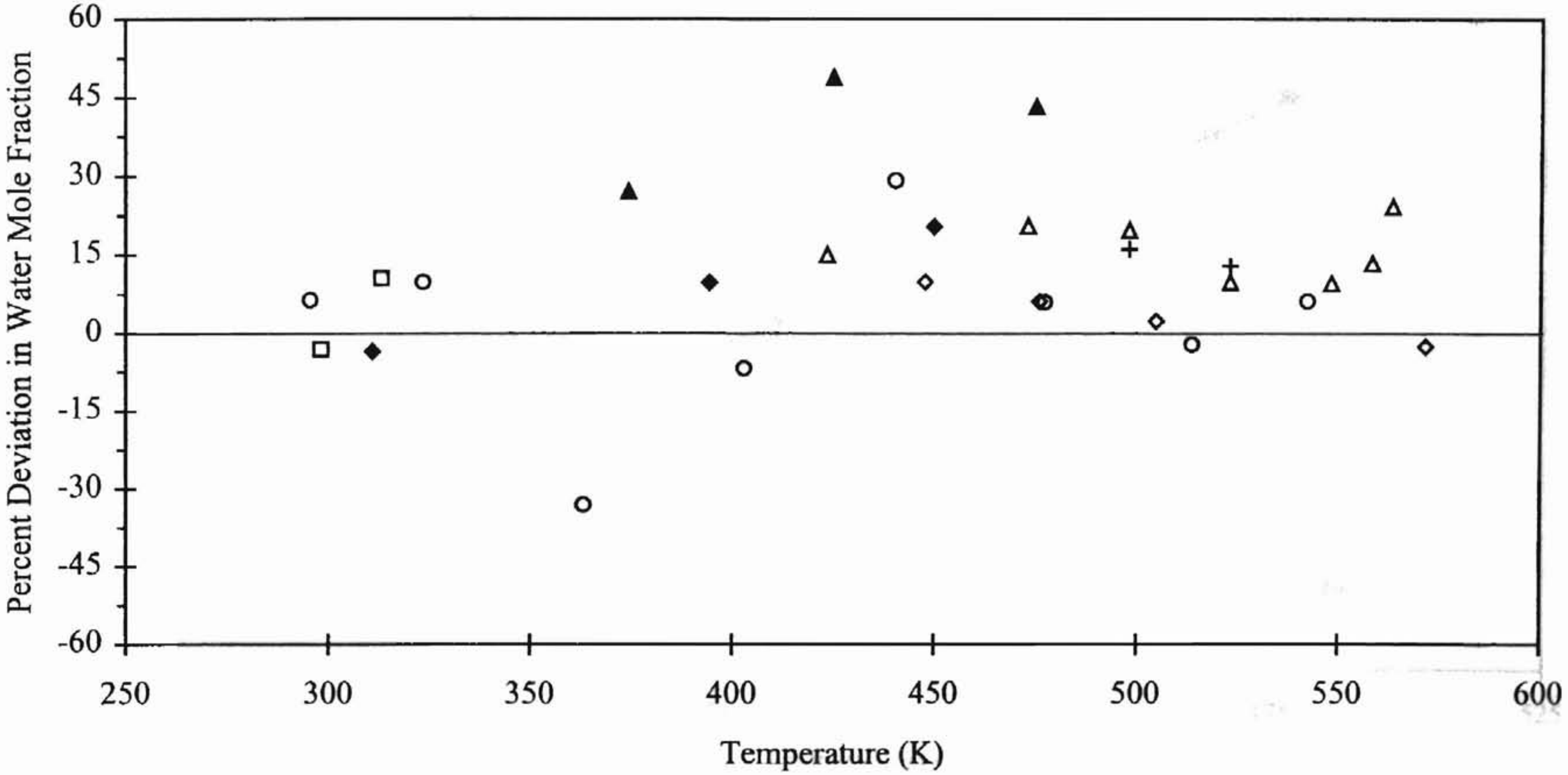

**Figure 13.** Comparison of Solubility Data for Water in Decane: ○ this work; ▲ Economou et al. (20); ◆ Ng and Chen (43); Mackay — Becke and Quitzsch (5); + Skripka (57); △ Namiot et al. (41); ◇ Guerrant (26); □ Schatzberg (54).

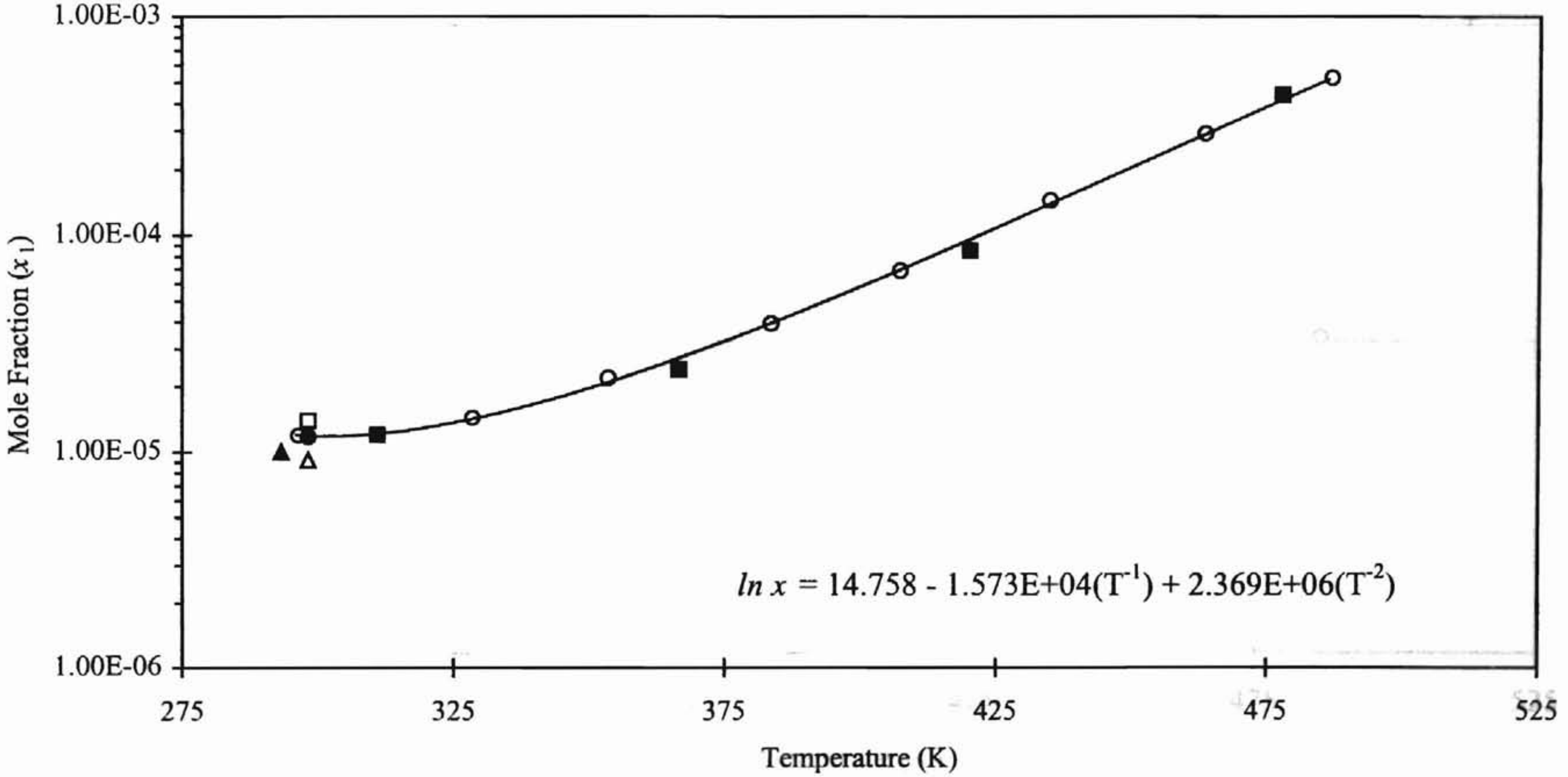

**Figure 14.** Solubility of 1-Hexene in Water: ○ this work; ■ Economou et al. (20); ▲ Budantseva et al. (11); ● Leinonen and Mackay (34); □ Natarajan and Venkatachalam (42); △ McAuliffe (39).

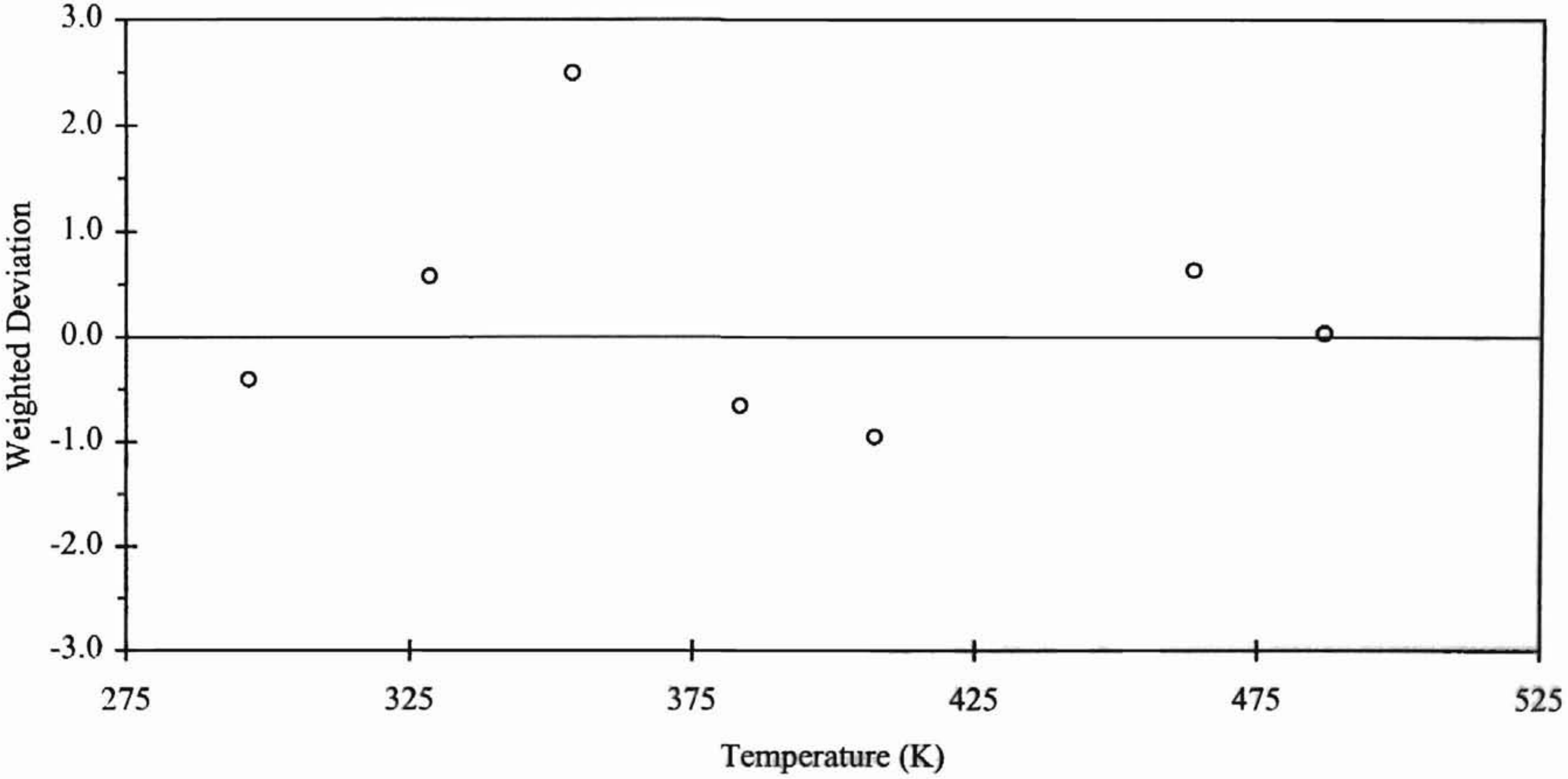

**Figure 15.** Weighted Deviation in the Solubility of 1-Hexene in Water: ○, this work.

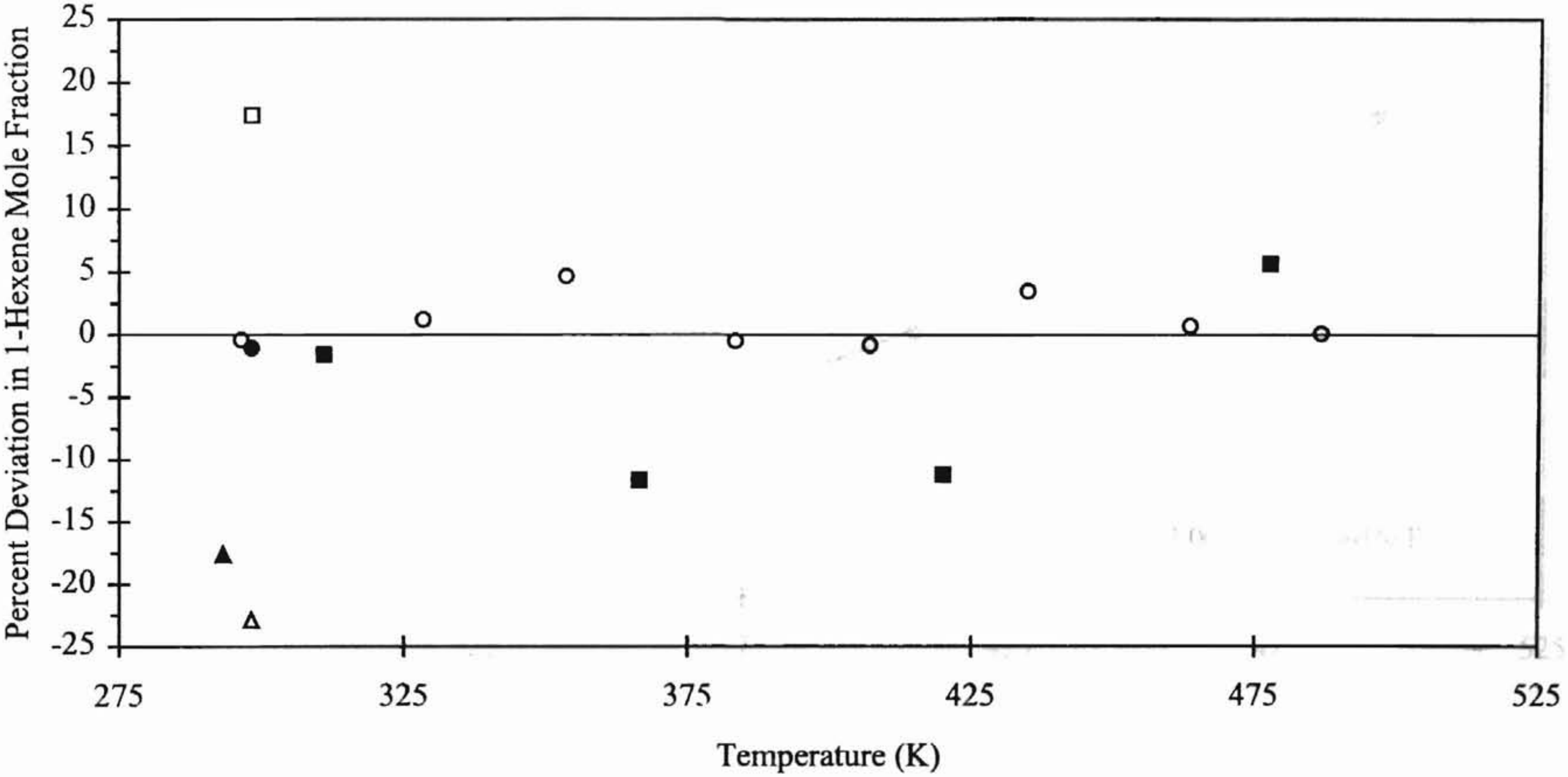

**Figure 16.** Comparison of Solubility Data for 1-Hexene in Water: ○ this work; ■ Economou et al. (20); ▲ Budantseva et al. (11); ● Leinonen and Mackay (34); □ Natarajan and Venkatachalam (42); △ McAuliffe (39).

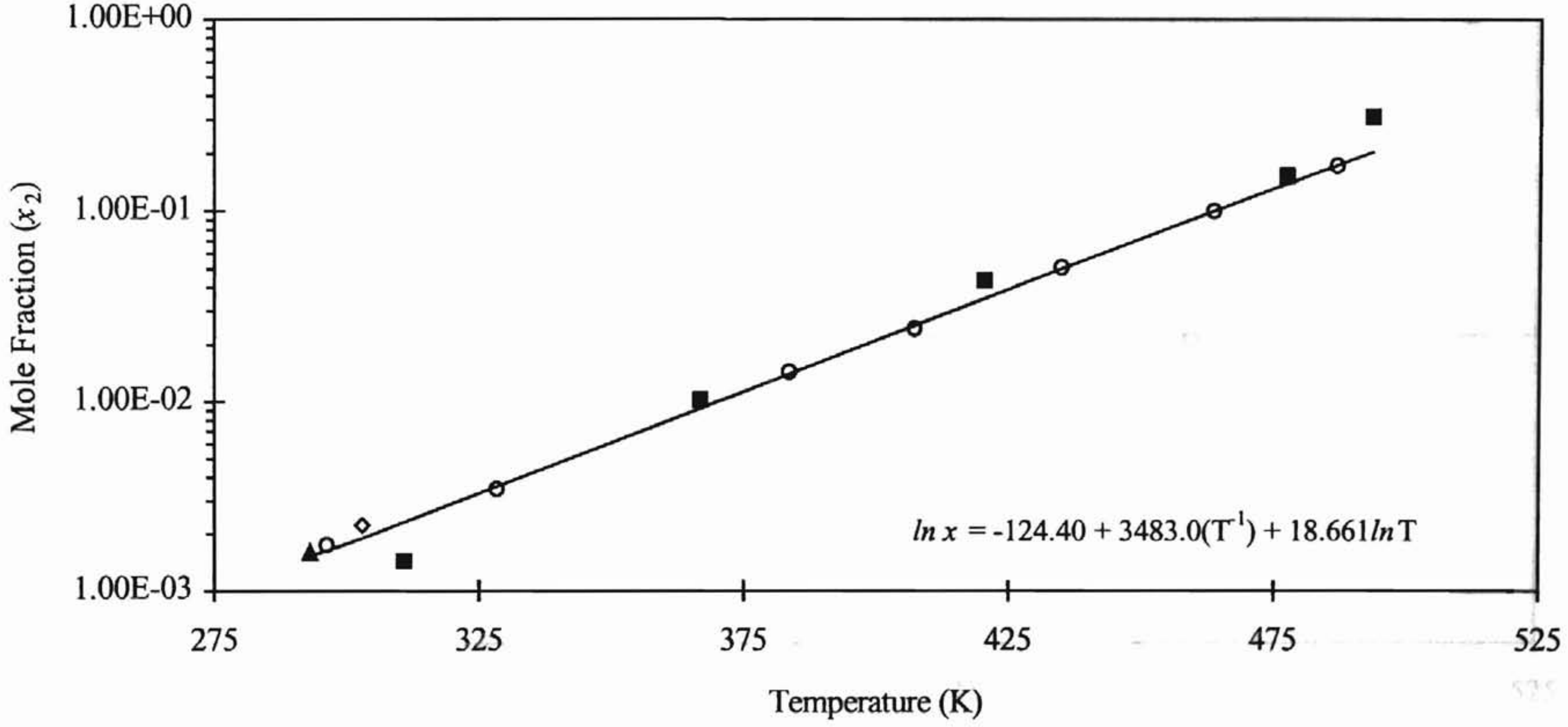

**Figure 17.** Solubility of Water in 1-Hexene: ○ this work; ■ Economou et al. (20); ▲ Budantseva et al. (11); ◇ Englin et al. (21).

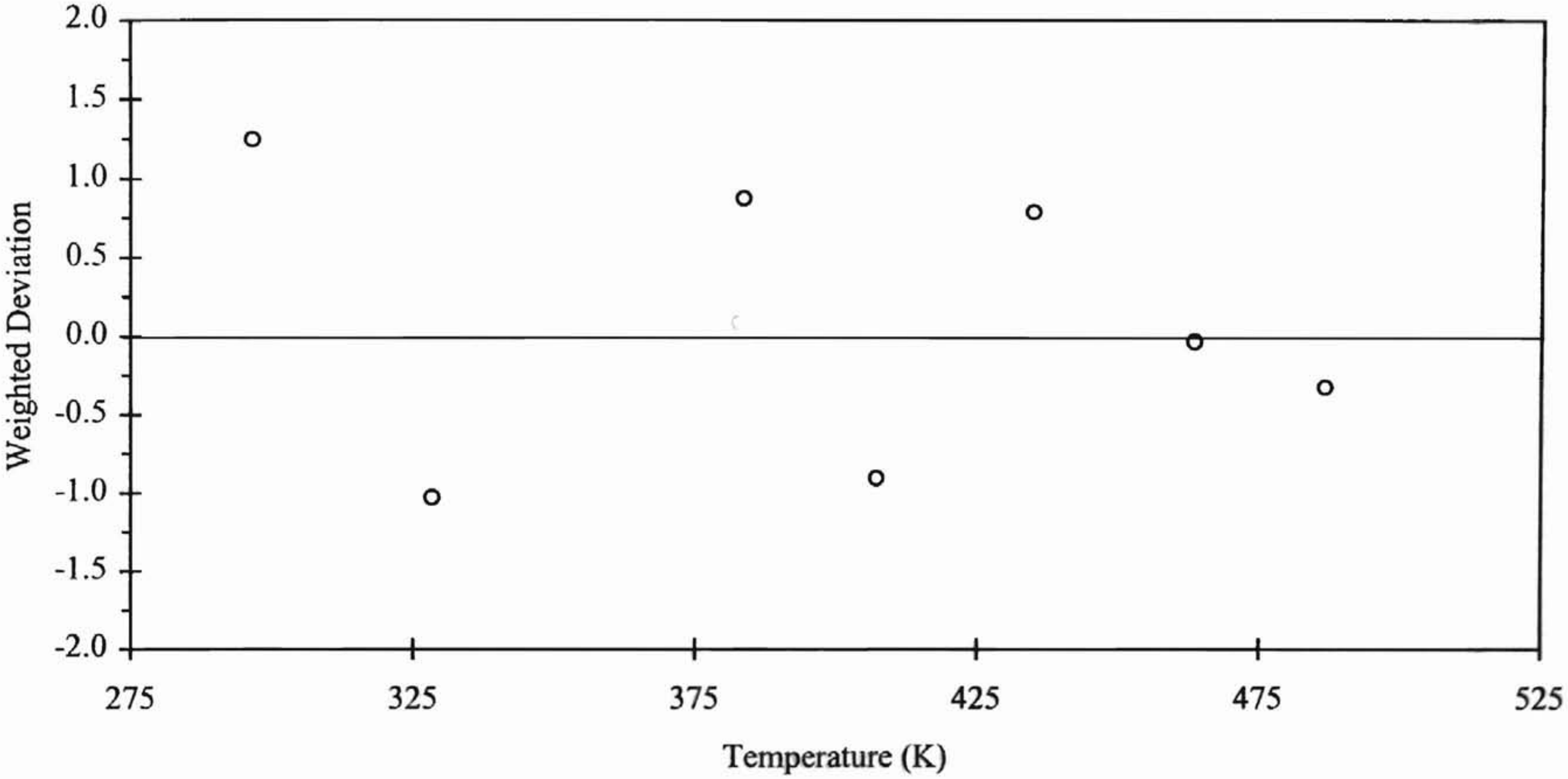

**Figure 18.** Weighted Deviation in the Solubility of Water in 1-Hexene: ○, this work.

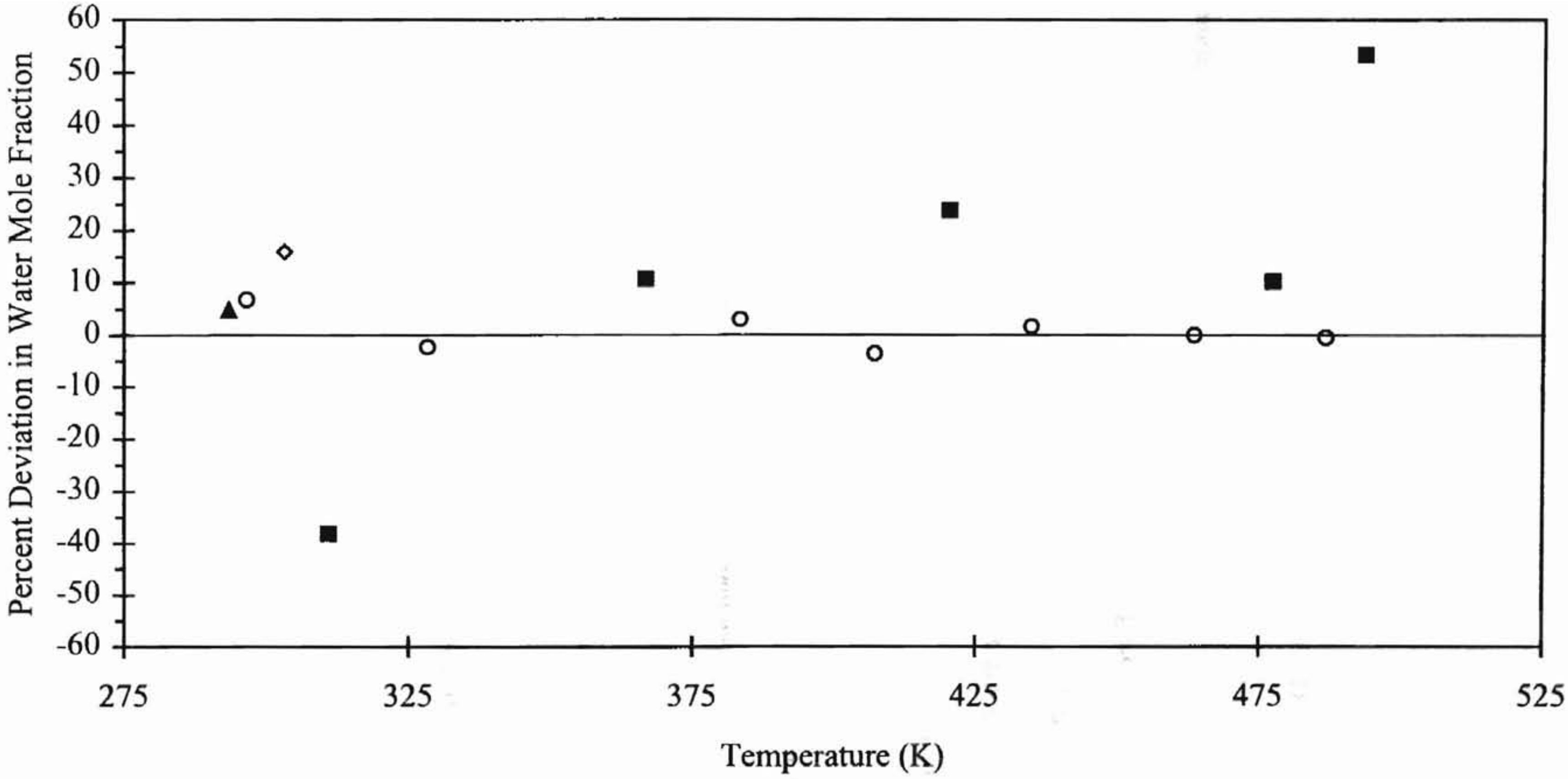

**Figure 19.** Comparison of Solubility Data for Water in 1-Hexene: ○ this work; ■ Economou et al. (20); ▲ Budantseva et al. (11); ◇ Englin et al. (21).

# CHAPTER VI

# CONCLUSIONS AND RECOMMENDATIONS

## Conclusions

1. A continuous flow apparatus has been designed and constructed to facilitate liquid-liquid equilibrium measurements at temperatures from ambient to 623 K and at pressures from ambient to 13.8 MPa. This is significant, since only a limited number of investigations in the literature report solubility data at both ambient and elevated conditions.

2. A standard operating procedure was developed, along with accurate sampling and analytical techniques, which produced consistent data.

3. Mutual solubilities were measured for three binary systems: benzene-water, decane-water, and 1-hexene-water. The measurements were made near the three-phase equilibrium curve from ambient temperature to near the three-phase critical end point of the mixture of interest. A comparison of the benzene-water data to well-documented literature data verified the accuracy of the data obtained with this apparatus and experimental procedure.

4. An error analysis was performed to determine the reliability of the apparatus and procedure. The error associated with the gas chromatograph analysis accounted for a majority of the total uncertainty. The maximum expected uncertainty was about 30% for

the very low decane solubility in water. For the majority of the experimental data, the expected uncertainty was less than 5%.

## Recommendations

A functional apparatus, the associated operating procedures, and sampling and analytical techniques have been developed for future liquid-liquid equilibrium studies at ambient and elevated temperatures and pressures. To continue to progress in this field of research, a few recommendations are given below:

1. Succeeding studies should focus on obtaining mutual solubility data for binary, ternary, and multicomponent systems that have not been completely investigated. The primary focus should be on obtaining liquid-liquid equilibrium data at elevated temperatures, since this is often the area that has not been studied.

2. To allow investigators to spend time on more challenging tasks, the analysis could be set up to accommodate an autosampler for GC analysis of the calibration mixtures. This automation would allow for multiple analyses of each mixture without requiring the investigator to spend the time to perform this tedious task.

3. A recycle stream would be an environmentally conscious addition to the apparatus. This would reduce the amount of waste generated and would help to keep chemical costs down.

4. The apparatus in its current configuration provides sufficient mixing for accurate mutual solubility measurements, but a more effective means of mixing would be for all the mixing to take place inside the oven at the experimental temperature. This would require the nearly 10 m of initial mixing, currently outside the oven, to be

relocated inside the oven. The relief valve (RV1) should remain outside the oven and be placed directly after the Whitey three-way valve (V1).

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* The references for Chapter V are independent of the literature cited here and are included at the end of that chapter

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# APPENDIXES

# APPENDIX A

# STANDARD OPERATING PROCEDURES

As part of this study, a set of operating procedures and sampling and analytical techniques has been developed to accompany the apparatus used in this study to obtain liquid-liquid equilibrium data. These procedures and techniques are described here.

## I. Start-Up

### *A. Load the Backpressure Regulator*

Before sampling at elevated temperatures and pressures, the hydrocarbon-water system must be raised to a pressure greater than the mixture vapor pressure. This is accomplished by applying a nitrogen blanket to the system, controlled by a backpressure regulator (BPR). To control the pressure, BPR must be "loaded" to the desired system pressure by the following steps:

1. Turn the Whitey three-way valve (V9) so the nitrogen gas flows to BPR.
2. Turn the setscrew on BPR labeled "load" counterclockwise to allow the nitrogen to fill the diaphragm of BPR.
3. To reach the desired pressure in BPR, increase the pressure from the nitrogen source. The pressure gauge (P4) will reflect the change in pressure.
4. When the desired control pressure is reached, isolate the diaphragm by turning the setscrew on BPR labeled "load" clockwise until resistance is met.

### *B. Isolate the Apparatus*

Before pressurizing the system, the apparatus must be isolated from the atmosphere. The following accomplishes this:

5. Close the Parker CPI needle valves (V6 and V7) and turn the Whitey three-way valve (V4) so nitrogen is not vented to the atmosphere.
6. Turn the Whitey three-way valve (V2) to direct the organic phase sample flow to the waste collection cell (C2).
7. Connect the water phase sample line to the Whitey three-way valve (V8) via a 0.318 cm-o.d.-tubing sleeve.
8. After tightening the Swagelok fittings on the connection, turn V8 so the sample tubing is opened to the system pressure. This acts as a shutoff valve for the water phase sample.

### *C. Pressurize the System*

The system may now be pressurized. The apparatus is designed so BPR is set at the desired experimental pressure. The nitrogen source regulator must be set at a slightly higher pressure so a small amount of nitrogen will flow past BPR to the atmosphere. This effectively controls the system pressure by allowing a constant flow of nitrogen to pressurize the apparatus while the excess nitrogen is vented to the atmosphere. The following steps should be taken to pressurize the system:

9. Turn V9 so the nitrogen flows to the system.
10. The system pressure may be adjusted by turning the regulator on the nitrogen source. The Sensotec 450D pressure readout (P1) will reflect the change in pressure.

11. If BPR has been set too high initially, it may need to be reset to a lower pressure in order for the system pressure to be accurately controlled.
12. To lower the pressure in BPR, turn the setscrew on BPR labeled "vent" counterclockwise. The pressure gauge (P4) will reflect the change in pressure.
13. When the desired system pressure has been reached, close the vent by turning the setscrew clockwise until resistance is met.

### *D. Prepare to Collect the Sample*

Once the desired pressure has been set, additional preparation steps should be followed:

14. Set the oven temperature to the desired temperature.
15. Once the desired temperature has been reached, turn on the duplex pump (DP1) and flush the system with at least one system volume (120 $cm^3$) of the hydrocarbon-water mixture. The pump should never be started against pressures in excess of 6.9 MPa (1000 psi) and should never be run dry.
16. Vent the 0.159 cm-o.d. stainless steel tubing (water phase sample) by opening V8 to the atmosphere. This may allow some water phase sample to exit from V8 so a waste bottle should be placed under this valve when venting to collect the small amount released.
17. Remove the water phase sample line from V8. This will allow the water phase to exit from the bottom of the phase separation cell and through the water phase sample tubing.
18. Adjust the Autoclave Engineering micrometering valve (MV1) inside the oven to control the hydrocarbon-water interface level in the phase separation cell. The

hydrocarbon-water interface should be kept near the level of the inlet, which is the center of the phase separation cell. If this is accomplished, the water phase outlet flow rate will be equal to the water feed rate. Never use MV1 as a shutoff valve; closing the valve beyond the zero position will damage the stem and/or the Teflon packing inside the valve.

### *E. Prepare the Sample Bottles*

Before collecting the samples, the sample bottles should be prepared in the following manner:

19. Number and weigh each empty sample bottle, including the cap and Teflon liner.
20. Add the solvent to the sample bottles. Ethanol is the solvent used in the organic phase samples. Decane or 2,2,4-trimethylpentane is the solvent used in the water phase samples.
21. Weigh the capped sample bottle with the solvent to determine the weight of the solvent.
22. Place the water phase sample bottle in an ice bath. The ice bath is used to minimize vaporization of the volatile hydrocarbon.
23. Uncap the organic phase sample bottle and place the bottle in the sampling cell (C1).
24. Close C1 with the bottle in it and the organic phase sample tubing inserted into the bottle.
25. Close the Parker CPI needle valve (V5) and turn the Whitey three-way valve (V3) so the nitrogen flows to C1. This will pressurize C1. The pressure differential between the system pressure and the pressure in C1 will cause nitrogen to flow from the rest of the apparatus, along with the nitrogen from the nitrogen source; thus, causing the

system pressure to drop when C1 is pressurized. Therefore, the flow of nitrogen into C1 should be controlled with V3 so the system pressure does not drop below the mixture vapor pressure when pressurizing C1.

## II. Sampling

### *F. Collect the Sample*

After placing the organic phase sample bottle in C1 and pressurizing it to the elevated system pressure, the sample may be collected by taking the following steps:

26. Turn V2 so the organic phase sample is directed to the sample bottle in C1.
27. Direct the water phase sample tube through the Teflon liner and cap and into the bottle in the ice bath. The bottle is capped to prevent any contact with the atmosphere.
28. Fill the bottles to the neck to reduce headspace and to keep mass transfer to the vapor phase at a minimum. The liquid level in the water phase bottle can be determined by sight. The liquid level in the organic phase bottle is determined from the organic phase flow rate, since it is collected in a sightless cell.
29. When the water phase sample bottle is full, remove the sample tubing from the bottle and cap it with the original cap and Teflon liner.
30. When the organic phase sample bottle is determined to be full, turn V2 to direct the organic phase sample flow to C2.
31. Turn V3 so C1 is closed off from the flow of nitrogen.
32. Open V5 so C1 depressurizes slowly. Venting too quickly could lead to vaporization of the sample.
33. Once C1 has been completely vented, open C1.

34. Remove the organic phase sample bottle and cap it with the original cap and Teflon liner.

## III. Shut Down and Preventive Maintenance

### *G. Shut down the Apparatus*

After sampling has been completed, the apparatus should be shut down and left in a state ready to begin sampling with minimal preparatory time.

35. Connect the water phase sample line to V8.
36. Pressurize this line by opening V8 to the system pressure. This prevents liquid from leaking out of the apparatus via the water phase sample line.
37. Turn V2 to direct the flow of the organic phase to either C1 at system pressure or C2 at system pressure.
38. Turn off DP1.

### *H. Preventive Maintenance*

As preventive maintenance, C2 should be emptied periodically to keep from overfilling it by following this procedure:

39. Make sure C1 is closed, then turn V2 to direct the organic phase sample flow to C1.
40. Turn the Whitey three-way valve (V4) so C2 is isolated from the flow of nitrogen.
41. Open the Parker CPI needle valve (V6) to vent C2.
42. Once C2 has been vented, open the Parker CPI needle valve (V7) to empty the contents of C2 into a waste bottle.
43. After emptying C2, close V7 and V6.

44. Turn V4 so the nitrogen flows to C2. This will pressurize C2. The pressure differential between the system pressure and the pressure in C2 will cause nitrogen to flow from the rest of the apparatus, along with the nitrogen from the nitrogen source; thus, causing the system pressure to drop when C2 is pressurized. Therefore, the flow of nitrogen into C2 should be controlled with V4 so the system pressure does not drop below the mixture vapor pressure when pressurizing C2.

## IV. Sample Analysis

### *I. Prepare to Analyze the Sample*

After the samples have been collected, the following procedure should be employed:

45. Weigh the organic phase and water phase sample bottles to determine the sample weight.
46. Shake the sample bottles vigorously. The organic phase is shaken to homogenize the hydrocarbon/water/ethanol mixture, while the water phase is shaken to extract the hydrocarbon from the water.
47. Refrigerate the water phase for several hours to allow the less dense extractant to separate from the water. The chilled environment helps to prevent the volatile hydrocarbon from vaporizing.

### *J. Analyze the Sample*

The samples are analyzed as follows:

48. The organic phase may be analyzed immediately after collection.
49. Inject 0.003 cm$^3$ (3 $\mu$L) of the homogenous organic phase into the gas chromatograph (GC) for analysis. The only peaks of interest in the GC analysis of the organic phase

are those of water and ethanol, since the calibration curve is prepared from the water-ethanol weight ratio as a function of the water-ethanol area ratio.

50. After the water phase sample has separated into two phases (extractant phase and water phase), inject 0.003 $cm^3$ (3 μL) of the extractant phase into the GC for analysis. The peaks of interest in the GC analysis of the water phase are those of the solute and solvent, since the calibration curve is prepared from the solute-to-solvent weight ratio as a function of the solute-to-solvent area ratio.
51. Rinse the syringe with the solution to be analyzed to prevent cross-contamination between sample bottles.

# APPENDIX B

# CALIBRATION TECHNIQUE AND DATA

The gas chromatograph (GC) is calibrated by a serial dilution technique. This entails diluting a fixed amount of the solute with increased proportions of the solvent through a series of dilutions. The weights of the solute and solvent are recorded to determine the solute-to-solvent weight ratio of each dilution. The mixtures are analyzed to obtain the corresponding solute-to-solvent area ratio. A calibration curve is then produced yielding the weight ratio as a function of the area ratio. A schematic diagram of the calibration technique is shown in Figure B-1.

## Procedure

Dilutions of the organic in either decane or 2,2,4-trimethylpentane are prepared to calibrate the GC for the water phase samples and dilutions of water in ethanol are prepared to calibrate the GC for the organic phase samples. All solutions are prepared gravimetrically in 16 $cm^3$ vials. First, the empty vial is weighed. Next, the solvent is added to the vial and the vial is reweighed to get the weight of the solvent. After this, the pure solute is added if the dilution is the first in the series of dilutions; otherwise, a portion of the previous dilution, the diluent, is added to the solvent in the vial. The vial is weighed again to get the weight of the solute. Immediately after preparing the dilution, it is analyzed by gas chromatography. The vial is placed in an ice bath to reduce

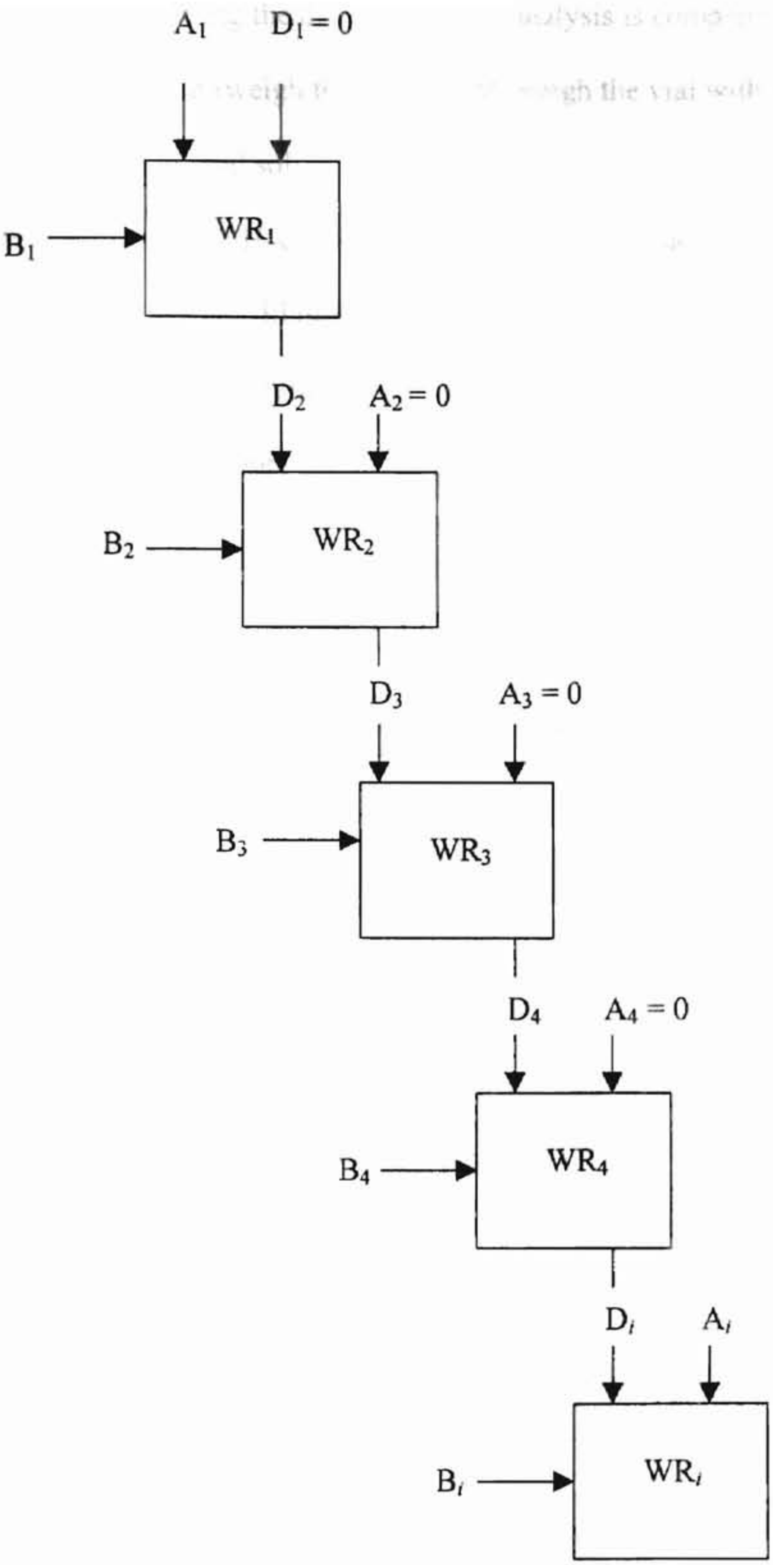

**Figure B-1.** Schematic Diagram of the Calibration Technique evaporation while analyzing the dilution. When analysis is complete, the next dilution is made in the same fashion (weigh the empty vial, weigh the vial with solvent, weigh the vial with solvent and diluted solute) and analyzed.

The same Hamilton 10 cm$^3$ syringe is used to make each serial dilution so it is rinsed with acetone between dilutions and allowed to dry in air. The syringe is then flushed with the solution to be transferred before making the next dilution. This eliminates cross-contamination. The vials are filled to the neck to reduce the effects of headspace evaporation.

### Material Balance

A material balance is used to determine the mass of the solute and the mass of the solvent in each calibration mixture. The weight ratio of the $i^{\text{th}}$ dilution, $WR_i$, is the weight of the solute in the mixture, $A_i$, divided by the weight of the solvent in the mixture, $B_i$:

$$WR_i = \frac{A_i}{B_i} \tag{B-1}$$

The dilution is made up of pure solute, $A_i$, and pure solvent, $B_i$, if it is the initial dilution in the series; otherwise, the solvent is mixed with the diluent, $D_i$. The diluent, $D_i$, is a fraction, $x$, of the previous mixture and consists of solute from the previous dilution, $A_{i-1}$, and solvent from the previous dilution, $B_{i-1}$:

$$D_i = x\left(A_{i-1} + B_{i-1}\right) \tag{B-2}$$

As the series of dilutions progress, the amount of solute in each dilution decreases; hence, serial dilution. Equation B-1, may be written as:

$$WR_i = \frac{A_i + x(A_{i-1})}{B_i + x(B_{i-1})} \tag{B-3}$$

Equation B-2 is rearranged to express it in terms of $A_{i-1}$:

$$\frac{D_i}{x(A_{i-1})} = 1 + \frac{x(B_{i-1})}{x(A_{i-1})} \tag{B-4}$$

but, from Equation B-1:

$$\frac{D_i}{x(A_{i-1})} = 1 + \frac{1}{WR_{i-1}} \tag{B-5}$$

so,

$$\frac{D_i}{x(A_{i-1})} = \frac{1 + WR_{i-1}}{WR_{i-1}} \tag{B-6}$$

In terms of $A_{i-1}$, Equation B-6 is:

$$x(A_{i-1}) = D_i\left(\frac{WR_{i-1}}{1 + WR_{i-1}}\right) \tag{B-7}$$

Equation B-2 is rearranged to express it in terms of $B_{i-1}$:

$$\frac{D_i}{x(B_{i-1})} = \frac{x(A_{i-1})}{x(B_{i-1})} + 1 \tag{B-8}$$

but, from Equation B-1:

$$\frac{D_i}{x(B_{i-1})} = WR_{i-1} + 1 \tag{B-9}$$

In terms of $B_{i-1}$, Equation B-9 is:

$$x(B_{i-1}) = D_i\left(\frac{1}{1 + WR_{i-1}}\right) \tag{B-10}$$

Combining Equations B-3, B-7, and B-10 results in a general equation for the calibration weight ratio:

$$WR_i = \frac{A_i + D_i\left(\frac{WR_{i-1}}{1+WR_{i-1}}\right)}{B_i + D_i\left(\frac{1}{1+WR_{i-1}}\right)} \tag{B-11}$$

This expression is rearranged:

$$WR_i = \frac{\left\{\frac{(A_i)(1+WR_{i-1})+(D_i)(WR_{i-1})}{1+WR_{i-1}}\right\}}{\left\{\frac{(B_i)(1+WR_{i-1})+D_i}{1+WR_{i-1}}\right\}} \tag{B-12}$$

or,

$$WR_i = \frac{(A_i)(1+WR_{i-1})+(D_i)(WR_{i-1})}{(B_i)(1+WR_{i-1})+D_i} \tag{B-13}$$

where, $WR_i$ is the solute-to-solvent weight ratio, $A_i$ is the weight of the pure solute, $B_i$ is the weight of the pure solvent, $WR_{i-1}$ is the solute-to-solvent weight ratio of the previous dilution, and $D_i$ is the weight of the diluent from the previous dilution added to the $i^{th}$ dilution.

The calibration data are listed at the end of the appendix in Table B-1. The uncertainty in the weight ratio was determined by an analysis of propagated error, which is described in Appendix C. This uncertainty was used as the weighting of each data point in the nonlinear weighted-least-squares regression of the calibration data.

**Sample Calculation (Benzene-Decane)**

1st Mixture

$A_1$ = 2.6180 grams $B_1$ = 8.6591 grams $WR_0$ = 0.0000 $D_1$= 0.0000

$$WR_1 = \frac{A_1}{B_1} = \frac{2.6180}{8.6591} = 0.302$$

2nd Mixture

$A_2$ = 0.0000 grams $B_2$ = 5.4221 grams $WR_1$ = 0.3023 $D_2$ = 5.5531

$$WR_2 = \frac{(0.0000)(1+0.3023)+(5.5531)(0.3023)}{(5.4221)(1+0.3023)+5.5531} = \frac{1.6787}{12.6143} = 0.1331$$

3rd Mixture

$A_3$ = 0.0000 grams $B_3$ = 5.4063 grams $WR_2$ = 0.1331 $D_3$ = 5.4198

$$WR_3 = \frac{(0.0000)(1+0.1331)+(5.4198)(0.1331)}{(5.4063)(1+0.1331)+5.4198} = \frac{0.7214}{11.5457} = 0.0625$$

4th Mixture

$A_4$ = 0.0000 grams $B_4$ = 5.4058 grams $WR_3$ = 0.0625 $D_4$ = 5.4691

$$WR_4 = \frac{(0.0000)(1+0.0625)+(5.4691)(0.0625)}{(5.4058)(1+0.0625)+5.4691} = \frac{0.3418}{11.2128} = 0.0305$$

5th Mixture

$A_5$ = 0.0000 grams $B_5$ = 5.4173 grams $WR_4$ = 0.0305 $D_5$ = 5.3574

$$WR_5 = \frac{(0.0000)(1+0.0305)+(5.3574)(0.0305)}{(5.4173)(1+0.0305)+5.3574} = \frac{0.1634}{10.9399} = 0.0149$$

6th Mixture

$A_6 = 0.0000$ grams $B_6 = 5.4232$ grams $WR_5 = 0.0149$ $D_6 = 5.2467$

$$WR_6 = \frac{(0.0000)(1+0.0149)+(5.2467)(0.0149)}{(5.4232)(1+0.0149)+5.2467} = \frac{0.0782}{10.7507} = 0.0073$$

7th Mixture

$A_7 = 0.0000$ grams $B_7 = 5.4115$ grams $WR_6 = 0.0073$ $D_7 = 5.2500$

$$WR_7 = \frac{(0.0000)(1+0.0073)+(5.2500)(0.0073)}{(5.4115)(1+0.0073)+5.2500} = \frac{0.0383}{10.7010} = 0.0036$$

8th Mixture

$A_8 = 0.0000$ grams $B_8 = 5.7647$ grams $WR_7 = 0.0036$ $D_8 = 4.9804$

$$WR_8 = \frac{(0.0000)(1+0.0036)+(4.9804)(0.0036)}{(5.7647)(1+0.0036)+4.9804} = \frac{0.0179}{10.7659} = 0.0017$$

**Table B-1.** Calibration Data

Benzene-Decane Calibration

| Area Ratio | Weight Ratio | Uncertainty in the Weight Ratio |
|---|---|---|
| 0.2003 | 0.3023 | 0.00274 |
| 0.0502 | 0.0625 | 0.00027 |
| 0.0253 | 0.0305 | 0.00014 |
| 0.0126 | 0.0149 | 0.00005 |
| 0.0062 | 0.0073 | 0.00003 |
| 0.0030 | 0.0036 | 0.00003 |
| 0.0014 | 0.0017 | 0.00002 |

Decane-2,2,4-Trimethylpentane Calibration

| Area Ratio | Weight Ratio | Uncertainty in the Weight Ratio |
|---|---|---|
| 0.0601 | 0.0341 | 0.00017 |
| 0.0203 | 0.0113 | 0.00008 |
| 0.0102 | 0.0056 | 0.00006 |
| 0.0051 | 0.0028 | 0.00004 |
| 0.0026 | 0.0014 | 0.00003 |
| 0.0013 | 0.0007 | 0.00003 |
| 0.0006 | 0.0004 | 0.00003 |
| 0.0003 | 0.0002 | 0.00003 |
| 0.0002 | 0.0001 | 0.00002 |

1-Hexene-Decane Calibration

| Area Ratio | Weight Ratio | Uncertainty in the Weight Ratio |
|---|---|---|
| 0.1703 | 0.1882 | 0.00115 |
| 0.0809 | 0.0849 | 0.00020 |
| 0.0397 | 0.0406 | 0.00019 |
| 0.0197 | 0.0200 | 0.00005 |
| 0.0098 | 0.0099 | 0.00003 |
| 0.0049 | 0.0049 | 0.00003 |
| 0.0024 | 0.0025 | 0.00002 |
| 0.0012 | 0.0012 | 0.00002 |

| Water-Ethanol Calibration | | |
|---|---|---|
| Area Ratio | Weight Ratio | Uncertainty in the Weight Ratio |
| 0.2131 | 0.2990 | 0.00215 |
| 0.1060 | 0.1335 | 0.00145 |
| 0.0527 | 0.0631 | 0.00147 |
| 0.0273 | 0.0307 | 0.00039 |
| 0.0130 | 0.0152 | 0.00012 |
| 0.0065 | 0.0075 | 0.00023 |
| 0.0033 | 0.0037 | 0.00016 |
| 0.0017 | 0.0019 | 0.00009 |

# APPENDIX C

# PROPAGATED CALIBRATION ERROR

In the calibration of the gas chromatograph, the solute-to-solvent weight ratio is measured and given as a function of the solute-to-solvent gas chromatograph area ratio. Thus, the weight ratio is a function of the weight measurements and the area ratio. The weight ratio, as a function of the weight measurements, is shown in the governing material balance equation:

$$WR_i = \frac{(A_i)(1+WR_{i-1})+(D_i)(WR_{i-1})}{(B_i)(1+WR_{i-1})+D_i} \tag{C-1}$$

where, $WR_i$ is the solute-to-solvent weight ratio, $A_i$ is the weight of the pure solute, $B_i$ is the weight of the pure solvent, $WR_{i-1}$ is the solute-to-solvent weight ratio of the previous dilution, and $D_i$ is the weight of the diluent from the previous dilution added to the $i^{th}$ dilution. The dependence of the weight ratio on the area ratio is described by the calibrating equation:

$$WR_i = \alpha AR_i^2 + \beta AR_i + \gamma \tag{C-2}$$

where, $WR_i$ is the solute-to-solvent weight ratio, $AR_i$ is the solute-to-solvent area ratio, and $\alpha$, $\beta$, and $\gamma$ are the regressed parameters.

The propagated uncertainty in the weight ratio can be expressed in terms of variances below:

$$\sigma_{WR_i}^2 = \left(\frac{\partial WR_i}{\partial A_i}\right)^2 \sigma_{A_i}^2 + \left(\frac{\partial WR_i}{\partial B_i}\right)^2 \sigma_{B_i}^2 + \left(\frac{\partial WR_i}{\partial WR_{i-1}}\right)^2 \sigma_{WR_{i-1}}^2 \tag{C-3}$$

$$+\left(\frac{\partial WR_i}{\partial D_i}\right)^2 \sigma_{D_i}^2 + \left(\frac{\partial WR_i}{\partial AR_i}\right)^2 \sigma_{AR_i}^2$$

This may be expressed in terms of fractional uncertainty:

$$\left(\frac{\sigma_{WR_i}}{WR_i}\right)^2 = \left(\frac{\partial WR_i}{\partial A_i}\right)^2\left(\frac{\sigma_{A_i}}{WR_i}\right)^2 + \left(\frac{\partial WR_i}{\partial B_i}\right)^2\left(\frac{\sigma_{B_i}}{WR_i}\right)^2 + \left(\frac{\partial WR_i}{\partial WR_{i-1}}\right)^2\left(\frac{\sigma_{WR_{i-1}}}{WR_i}\right)^2 \tag{C-4}$$

$$+\left(\frac{\partial WR_i}{\partial D_i}\right)^2\left(\frac{\sigma_{D_i}}{WR_i}\right)^2 + \left(\frac{\partial WR_i}{\partial AR_i}\right)^2\left(\frac{\sigma_{AR_i}}{WR_i}\right)^2$$

The final term in Equation C-4 accounts for the fact that, even if the weight ratios were exact, the value calculated from the calibration relation would be uncertain due to the uncertainty of the area ratio at which the calibration relation was read. The last term in the relation is independent of any previous measurements; therefore, the uncertainty associated with the area ratio is not propagated.

**Uncertainty Associated with the Weight of Pure Solute**

The partial derivative of $WR_i$ with respect to $A_i$ is given below:

$$\left(\frac{\partial WR_i}{\partial A_i}\right)^2 = \left(\frac{1+WR_{i-1}}{(B_i)(1+WR_{i-1})+D_i}\right)^2 \tag{C-5}$$

This equation is divided by $WR_i^2$ (from Equation C-1) to find the fractional uncertainty associated with the weight of pure solute added to the $i^{\text{th}}$ dilution. Thus, the first term in Equation C-4 becomes:

$$\left(\frac{\partial WR_i}{\partial A_i}\right)^2\left(\frac{\sigma_{A_i}}{WR_i}\right)^2 = \left\{\frac{1+WR_{i-1}}{(A_i)(1+WR_{i-1})+(D_i)(WR_{i-1})}\right\}^2 \sigma_{A_i}^2 \tag{C-6}$$

### Uncertainty Associated with the Weight of Pure Solvent

The partial derivative of WR$_i$ with respect to B$_i$ is given as:

$$\left(\frac{\partial WR_i}{\partial B_i}\right)^2 = \left\{-\frac{[(A_i)(1+WR_{i-1})+(D_i)(WR_{i-1})](1+WR_{i-1})}{[(B_i)(1+WR_{i-1})+D_i]^2}\right\}^2 \tag{C-7}$$

Dividing this equation by WR$_i^2$ to get the fractional uncertainty associated with the weight of pure solvent added to the $i^{\text{th}}$ dilution results in the second term of Equation C-4:

$$\left(\frac{\partial WR_i}{\partial B_i}\right)^2\left(\frac{\sigma_{B_i}}{WR_i}\right)^2 = \left\{\frac{1+WR_{i-1}}{(B_i)(1+WR_{i-1})+D_i}\right\}^2 \sigma_{B_i}^2 \tag{C-8}$$

### Uncertainty Associated with the Weight Ratio of the Diluent

The partial derivative of WR$_i$ with respect to WR$_{i-1}$ is:

$$\left(\frac{\partial WR_i}{\partial WR_{i-1}}\right)^2 = \left\{\frac{(A_i+D_i)[(B_i)(1+WR_{i-1})+D_i]-[(A_i)(1+WR_{i-1})+(D_i)(WR_{i-1})](B_i)}{[(B_i)(1+WR_{i-1})+D_i]^2}\right\}^2 \tag{C-9}$$

To find the fractional uncertainty associated with the weight ratio of the $i$-1$^{\text{th}}$ dilution, the third term in Equation C-4, this equation is divided by WR$_i^2$:

$$\left(\frac{\partial WR_i}{\partial WR_{i-1}}\right)^2\left(\frac{\sigma_{WR_{i-1}}}{WR_i}\right)^2 = \left\{\frac{A_i+D_i}{(A_i)(1+WR_{i-1})+(D_i)(WR_{i-1})}-\frac{B_i}{(B_i)(1+WR_{i-1})+D_i}\right\}^2 \sigma_{WR_{i-1}}^2 \tag{C-10}$$

### Uncertainty Associated with the Weight of Diluent

The partial derivative of WR$_i$ with respect to D$_i$ is:

$$\left(\frac{\partial WR_i}{\partial D_i}\right)^2 = \left\{\frac{(WR_{i-1})[(B_i)(1+WR_{i-1})+D_i]-[(A_i)(1+WR_{i-1})+(D_i)(WR_{i-1})]}{[(B_i)(1+WR_{i-1})+D_i]^2}\right\}^2 \tag{C-11}$$

The fractional uncertainty associated with the weight of the $i$-1th dilution added to the $i$th dilution, the fourth term of Equation C-4, is determined by dividing this equation by $WR_i^2$:

$$\left(\frac{\partial WR_i}{\partial D_i}\right)^2\left(\frac{\sigma_{D_i}}{WR_i}\right)^2 = \left\{\frac{WR_{i-1}}{(A_{i.})(1+WR_{i-1})+(D_i)(WR_{i-1})} - \frac{1}{(B_i)(1+WR_{i-1})+D_i}\right\}^2 \sigma_{D_i}^2 \qquad \text{(C-12)}$$

## Uncertainty Associated with the Gas Chromatograph Area Ratio

The partial derivative of the calibration equation, C-2, is given by taking the partial derivative of $WR_i$ with respect to $AR_i$, as shown here:

$$\frac{\partial WR_i}{\partial AR_i} = 2\alpha AR_i + \beta \qquad \text{(C-13)}$$

This expression is divided by $WR_i$ to determine the fractional uncertainty associated with the gas chromatograph area ratio, the final term in Equation C-4:

$$\left(\frac{\partial WR_i}{\partial AR_i}\right)^2\left(\frac{\sigma_{AR_i}}{WR_i}\right)^2 = \left\{\frac{2\alpha AR_i + \beta}{WR_i}\right\}^2 \sigma_{AR_i}^2 \qquad \text{(C-14)}$$

## Total Fractional Uncertainty

Combining equations C-6, C-8, C-10, C-12 and C-14 gives the total propagated fractional uncertainty in the weight ratio:

$$\begin{aligned}\left(\frac{\sigma_{WR_i}}{WR_i}\right)^2 &= \left\{\frac{1+WR_{i-1}}{(A_i)(1+WR_{i-1})+(D_i)(WR_{i-1})}\right\}^2 \sigma_{A_i}^2 \qquad \text{(C-15)}\\ &+ \left\{\frac{1+WR_{i-1}}{(B_i)(1+WR_{i-1})+D_i}\right\}^2 \sigma_{B_i}^2\\ &+ \left\{\frac{A_i+D_i}{(A_i)(1+WR_{i-1})+(D_i)(WR_{i-1})} - \frac{B_i}{(B_i)(1+WR_{i-1})+D_i}\right\}^2 \sigma_{WR_{i-1}}^2\end{aligned}$$

$$+\left\{\frac{WR_{i-1}}{(A_i)(1+WR_{i-1})+(D_i)(WR_{i-1})}-\frac{1}{(B_i)(1+WR_{i-1})+D_i}\right\}^2\sigma_{D_i}^2$$

$$+\left\{\frac{2\alpha AR_i+\beta}{WR_i}\right\}^2\sigma_{AR_i}^2$$

This uncertainty expression was used to weight the calibration data in the weighted-least-squares regression for the calibration equation, Equation C-2. (Values of α, β, and γ were initially estimated from unweighted regression and used in Equation C-15. An iterative approach was used to determine the final values of the calibration constants and the weighting of the calibration data). The variance in the weight measurements, $\sigma_{A_i}$, $\sigma_{B_i}$, and $\sigma_{D_i}$, was determined from repeated measurements and the variance in the area ratio, $\sigma_{AR_i}$, was determined from multiple analyses. The uncertainty associated with the area ratio, the last term in Equation C-15, is independent of any previous measurements and is, thus, not propagated. Therefore, this term was not included when determining the variance in the weight ratio of the *i*-1th dilution, $\sigma_{WR_{i-1}}$.

The total uncertainty is largely dependent upon the uncertainty associated with the gas chromatograph area ratio, the last term in Equation C-15. For the initial calibration dilutions, all other terms are negligible. For the final dilutions, or the mixtures lowest in concentration, the uncertainty associated with the gas chromatograph area ratio is approximately one-half the total uncertainty.

## Sample Calculation (Benzene-Decane)

*Dilution #1*

$A_1 = 2.6180$ grams  $B_1 = 8.6591$ grams  $WR_0 = 0.0000$  $D_1 = 0.0000$ grams

$\sigma_{A_1} = 0.0002$  $\sigma_{B_1} = 0.0002$  $\sigma_{WR_0} = 0.0000$  $\sigma_{D_1} = 0.0000$

$WR_1 = 0.3023$  $AR_1 = 0.2003$  $\sigma_{AR_1} = 1.48E-03$

$\alpha = 1.7145$  $\beta = 1.1620$  $\gamma = 3.67E-06$

$$\left(\frac{\sigma_{WR_1}}{WR_1}\right)^2 = \left\{\frac{1}{(2.6180)(1)}\right\}^2 (0.0002)^2$$

$$+\left\{\frac{1}{(8.6591)(1)}\right\}^2 (0.0002)^2$$

$$+\left\{\frac{2.6180}{(2.6180)(1)} - \frac{8.6591}{(8.6591)(1)}\right\}^2 (0.0000)^2$$

$$+\left\{\frac{0.0000}{(2.6180)(1)} - \frac{1}{(8.6591)(1)}\right\}^2 (0.0000)^2$$

$$+\left\{\frac{(2)(1.7145)(0.2003)+1.1620}{0.3023}\right\}^2 (1.48E-03)^2$$

$$\left(\frac{\sigma_{WR_1}}{WR_1}\right)^2 = 5.836E\text{-}09 + 5.335E\text{-}10 + 0.000 + 0.000 + 8.193E\text{-}05$$

$$= 8.194E\text{-}05$$

or,

$$\sigma_{WR_1} = (9.052E-03)(WR_1)$$

$$= (9.052E-03)(0.3023)$$

$$= 2.736E\text{-}03$$

This is the total uncertainty for the first dilution in the calibration. This value is used to weight the first point in the weighted-least-squares regression of the calibration curve.

*Dilution #2*

$A_2 = 0.0000$ grams $\quad B_2 = 5.4221$ grams $\quad WR_1 = 0.3023 \quad D_2 = 5.5531$ grams

$\sigma_{A_2} = 0.0002 \quad \sigma_{B_2} = 0.0002 \quad \sigma_{WR_1} = 2.559E-05 \quad \sigma_{D_2} = 0.0002$

$WR_2 = 0.1331 \quad AR_2 = 0.0963 \quad \sigma_{AR_1} = 6.25E-04$

$\alpha = 1.7145 \quad \beta = 1.1620 \quad \gamma = 3.67E-06$

$$\left(\frac{\sigma_{WR_2}}{WR_2}\right)^2 = \left\{\frac{1+0.3023}{(5.5531)(0.3023)}\right\}^2 (0.0002)^2$$

$$+\left\{\frac{1+0.3023}{(5.4221)(1+0.3023)+5.5531}\right\}^2 (0.0002)^2$$

$$+\left\{\frac{5.5531}{(5.5531)(0.3023)} - \frac{5.4221}{(5.4221)(1+0.3023)+5.5531}\right\}^2 (2.559E-05)^2$$

$$+\left\{\frac{0.3023}{(5.5531)(0.3023)} - \frac{1}{(5.4221)(1+0.3023)+5.5531}\right\}^2 (0.0002)^2$$

$$+\left\{\frac{(2)(1.7145)(0.0963)+1.1620}{0.1331}\right\}^2 (6.25E-04)^2$$

$$\left(\frac{\sigma_{WR_1}}{WR_1}\right)^2 = 2.407E\text{-}08 + 4.263E\text{-}10 + 5.425E\text{-}09 + 4.065E\text{-}10 + 4.910E\text{-}05$$

$$= 4.913E\text{-}05$$

or,

$$\sigma_{WR_1} = (7.009E-03)(WR_1)$$

$$= (7.009E-03)(0.1331)$$

$$= 9.329E\text{-}04$$

This is the total uncertainty for the second dilution in the calibration. This value is used to weight the second point in the weighted-least-squares regression of the calibration curve.

# APPENDIX D

# SOLUBILITY CALCULATION

The mutual solubilities are expressed as the mole fraction of solute in the sample. Since the weight of the solute in the sample is not known, the solute-to-solvent weight ratio (WR) and the solvent-to-sample weight ratio (SSR) are used, along with the molecular weights (MW) of the two species of interest, to calculate the mole fraction. The resulting expression for the mole fraction of a binary system is:

$$x_1 = \frac{[(WR)(SSR)]/MW_1}{\left\{[(WR)(SSR)]/MW_1\right\} + \left\{1/MW_2\right\}} \qquad \text{(D-1)}$$

The solute-to-solvent weight ratio is given in the calibration equation as a function of the solute-to-solvent area ratio, which is determined by gas chromatography. The solvent-to-sample weight ratio is a ratio of the weight of the solvent added (ethanol in the organic phase and decane, or 2,2,4-trimethylpentane, in the water phase) to the weight of the sample collected.

Each solubility measurement reported is an average of nine to twelve measurements. At each temperature studied, three samples were collected of each phase. Each phase was analyzed three to four times. An example calculation is shown below.

## Sample Calculation (Benzene-Water)

Temperature = 296.4 K $MW_{Benzene} = 78.114$
Pressure = 0.139 MPa $MW_{Water} = 18.015$

Water Phase:

| Bottle # | Solvent-to-Sample Weight Ratio (SSR) | Solute-to-Solvent Area Ratio | Weight Ratio From Eqn. 1 (WR) | Mole Fraction Benzene ($x_1$) |
|---|---|---|---|---|
| W-1 | 0.3802 | 0.00414 | 0.00484 | 4.242E-04 |
| W-1 | 0.3802 | 0.00413 | 0.00483 | 4.232E-04 |
| W-1 | 0.3802 | 0.00412 | 0.00482 | 4.222E-04 |
| W-2 | 0.4013 | 0.00374 | 0.00438 | 4.051E-04 |
| W-2 | 0.4013 | 0.00371 | 0.00434 | 4.018E-04 |
| W-2 | 0.4013 | 0.00371 | 0.00434 | 4.018E-04 |
| W-3 | 0.8458 | 0.00178 | 0.00208 | 4.059E-04 |
| W-3 | 0.8458 | 0.00180 | 0.00210 | 4.104E-04 |
| W-3 | 0.8458 | 0.00178 | 0.00208 | 4.059E-04 |

Mole Fraction of Benzene = 4.100E-04

Organic Phase:

| Bottle # | Solvent-to-Sample Weight Ratio (SSR) | Solute-to-Solvent Area Ratio | Weight Ratio From Eqn. 1 (WR) | Mole Fraction Water ($x_2$) |
|---|---|---|---|---|
| O-1 | 1.0340 | 0.00053 | 0.00060 | 2.688E-03 |
| O-1 | 1.0340 | 0.00058 | 0.00066 | 2.931E-03 |
| O-1 | 1.0340 | 0.00059 | 0.00067 | 2.992E-03 |
| O-1 | 1.0340 | 0.00059 | 0.00067 | 3.000E-03 |
| O-2 | 1.4964 | 0.00048 | 0.00053 | 3.431E-03 |
| O-2 | 1.4964 | 0.00042 | 0.00047 | 3.060E-03 |
| O-2 | 1.4964 | 0.00040 | 0.00042 | 2.730E-03 |
| O-2 | 1.4964 | 0.00042 | 0.00045 | 2.906E-03 |
| O-3 | 0.8713 | 0.00064 | 0.00074 | 2.792E-03 |
| O-3 | 0.8713 | 0.00061 | 0.00070 | 2.651E-03 |
| O-3 | 0.8713 | 0.00061 | 0.00070 | 2.653E-03 |

Mole Fraction of Water = 2.894E-03

# APPENDIX E

# ORGANIC PHASE SAMPLE ANALYSIS CORRECTION

Ethanol, used as the cosolvent to homogenize the organic phase samples, is hydroscopic and contains a small amount of water (less than 0.015% by GC analysis). If this water is not accounted for, the measured water solubilities may be in error by as much as 15%. Thus, a correction for the water introduced to the sample by the ethanol is made in the sample analysis, as described below.

The total weight of an ethanol aliquot, $W_e$, is the sum of the weight of the water fraction of the ethanol, $W_{w,e}$, plus the weight of the ethanol fraction, $W_{e,e}$:

$$W_e = W_{w,e} + W_{e,e} \tag{E-1}$$

The total weight of the sample, $W_s$, from the experiment is the sum of the weight of the water in the sample, $W_{w,s}$, plus the weight of the hydrocarbon in the sample, $W_{h,s}$:

$$W_s = W_{w,s} + W_{h,s} \tag{E-2}$$

Before beginning the mass balance, several terms are defined:

$ER_{w\text{-}e} = W_{w,e}/W_{e,e}$; weight ratio of the water fraction of the ethanol, $W_{w,e}$, to the ethanol fraction of the ethanol, $W_{e,e}$

$ER_w = W_{w,e}/W_e$; mass fraction of water in the ethanol

$WR_{s\text{-}s} = W_s/W_e$; weight ratio of the sample, $W_s$, to the solvent, $W_e$

$WR_{w\text{-}h} = W_{w,s}/W_{h,s}$; weight ratio of the water in the sample, $W_{w,s}$ to the hydrocarbon in the sample, $W_{h,s}$

$MF_w = W_{w,s}/W_s$; mass fraction of water in the sample

**Material Balance**

The total weight of the ethanol in a given analysis mixture (sample mixed with ethanol) is given as:

$$W_e = W_{w,e} + \frac{W_{w,e}}{ER_{w-e}} \tag{E-3}$$

$$= W_{w,e}\left(\frac{1 + ER_{w-e}}{ER_{w-e}}\right) \tag{E-4}$$

$$= \frac{W_{w,e}}{ER_w} \tag{E-5}$$

$$= W_{ee}ER_{w-e} + W_{e,e} \tag{E-6}$$

$$= W_{e,e}\left(1 + ER_{w-e}\right) \tag{E-7}$$

The total weight of the sample is expressed as:

$$W_s = W_{w,s} + \frac{W_{w,s}}{WR_{w-h}} \tag{E-8}$$

$$= W_{w,s}\left(\frac{1 + WR_{w-h}}{WR_{w-h}}\right) \tag{E-9}$$

$$= \frac{W_{w,s}}{MF_w} \tag{E-10}$$

$$= W_{h,s}WR_{w-h} + W_{h.s} \tag{E-11}$$

$$= W_{h,s}\left(1 + WR_{w-h}\right) \tag{E-12}$$

The equation used in the calibration of the GC is:

$$WR_{w-e} = \alpha AR_{w-e}^2 + \beta AR_{w-e} + \gamma \tag{E-13}$$

where, $WR_{w-e}$ is the weight ratio of the total amount of water to the total amount of ethanol, $AR_{w-e}$ is the area ratio of the total amount of water to the total amount of ethanol, and α, β and γ are the calibration parameters.

Thus, a sample analyzed by GC is handled in the following manner:

$$WR_{w-e} = \alpha AR_s^2 + \beta AR_s + \gamma \tag{E-14}$$

where, $AR_s$ is the area ratio of the total amount of water to the total amount of ethanol in the sample. By mass balance, this becomes:

$$\frac{MF_w(W_s) + W_e(ER_w)}{W_e(1-ER_w)} = \frac{WR_{s-s}(MF_w)}{1-ER_w} + \frac{ER_w}{1-ER_w} \tag{E-15}$$

$$= \frac{WR_{s-s}(MF_w) + ER_w}{1-ER_w} \tag{E-16}$$

$$= \alpha AR_s^2 + \beta AR_s + \gamma \tag{E-17}$$

so,

$$MF_w = \frac{(\alpha AR_s^2 + \beta AR_s + \gamma)(1-ER_w) - ER_w}{WR_{s-s}} \tag{E-18}$$

The measurable variables in Equation E-18 are $AR_s$ and $WR_{s-s}$, while the calibration parameters, α, β and γ, are regressed from the plot of the calibration data. The mass fraction of water in the ethanol, $ER_w$, is determined from the calibration and a GC analysis of the hydroscopic ethanol source.

The calibration is performed by analyzing a series of distilled water and ethanol mixtures. Equation E-18 applies to the calibration in the following form:

$$\frac{WR_{s-s}MF_w + ER_w}{1 - ER_w} = \alpha AR_s^2 + \beta AR_s + \gamma \tag{E-19}$$

but, in the calibration

$$WR_{s-s} = \frac{W_w}{W_e} \tag{E-20}$$

and

$$MF_w = 1 \tag{E-21}$$

so,

$$\frac{WR_{s-s} + ER_w}{1 - ER_w} = \alpha AR_c^2 + \beta AR_c + \gamma \tag{E-22}$$

where, $AR_c$ is the area ratio of the total amount of water to the total amount of ethanol in the calibration mixture.

The mass fraction of water in the ethanol, $ER_w$, is unknown and is determined from a GC analysis of the ethanol source. The area ratio of this ethanol blank is applied to Equation E-22 and the mass fraction of water in the ethanol, $ER_w$, is solved for. As it is applied in this case, $W_w$, the total weight of water from an additional source, is zero. So,

$$\frac{ER_w}{1 - ER_w} = \alpha AR_e^2 + \beta AR_e + \gamma \tag{E-23}$$

where, $AR_e$ is the water-to-ethanol area ratio from the ethanol blank. Solving for $ER_w$, this becomes:

$$ER_w = \frac{\alpha AR_e^2 + \beta AR_e + \gamma}{1 + \alpha AR_e^2 + \beta AR_e + \gamma} \tag{E-24}$$

To account for the water introduced to the sample from the ethanol source, Equations E-20 and E-24 are combined to get the corrected mass fraction of water in the sample:

$$MF_w = \frac{\left(\alpha AR_s^2 + \beta AR_s + \gamma\right) - \left(\alpha AR_e^2 + \beta AR_e + \gamma\right)}{WR_{s-s}\left(1 + \alpha AR_e^2 + \beta AR_e + \gamma\right)} \qquad \text{(E-25)}$$

# APPENDIX F

# EXPERIMENTAL ERROR ANALYSIS

The expected uncertainties in the solubility data presented in this study are estimated by error propagation. In general, where R is a function of the measured variables $x_1, x_2 \ldots x_n$, the expected variance ($\sigma_R^2$) is given by Equation F-1 *(19)*.

$$\sigma_R^2 = \sum_{i=1}^{n}\left[\left(\frac{\partial R}{\partial x_i}\right)^2 \sigma_{x_i}^2\right] \tag{F-1}$$

The mole fraction of a component in a binary mixture is expressed by Equation F-2.

$$x_1 = \frac{n_1}{n_1 + n_2} \tag{F-2}$$

The number of moles of component 1 is $n_1$, the number of moles of component 2 is $n_2$, and $x_1$ is the mole fraction of component 1. Component 1 is considered to be the solute. If $n_1$ and $n_2$ are replaced in terms of the weight ratio of solute to solvent, WR, the weight ratio of solvent to sample, SSR, and the molecular weight of component 1, $MW_1$, and of component 2, $MW_2$, the result is the mole fraction of the solute, $x_1$:

$$x_1 = \frac{\left[\dfrac{WR\,(SSR)}{MW_1}\right]}{\left[\dfrac{WR\,(SSR)}{MW_1} + \dfrac{1}{MW_2}\right]} \tag{F-3}$$

Liquid-liquid mutual solubilities at equilibrium increase with temperature; thus, the mole fraction is a function of temperature, T, as well. The uncertainty in $x_1$ can be expressed in terms of variances as:

$$\sigma_{x_1}^2 = \left(\frac{\partial x_1}{\partial SSR}\right)^2 \sigma_{SSR}^2 + \left(\frac{\partial x_1}{\partial WR}\right)^2 \sigma_{WR}^2 + \left(\frac{\partial x_1}{\partial T}\right)^2 \sigma_T^2 \qquad \text{(F-4)}$$

but,

$$\mathrm{WR} = f(\mathrm{AR})$$

therefore,

$$\sigma_{WR}^2 = \left(\frac{\partial WR}{\partial AR}\right)^2 \sigma_{AR}^2 \qquad \text{(F-5)}$$

where, AR is the gas chromatograph area ratio of solute-to-solvent. The expression, thus, becomes:

$$\sigma_{x_1}^2 = \left(\frac{\partial x_1}{\partial SSR}\right)^2 \sigma_{SSR}^2 + \left(\frac{\partial x_1}{\partial WR}\right)^2 \left(\frac{\partial WR}{\partial AR}\right)^2 \sigma_{AR}^2 + \left(\frac{\partial x_1}{\partial T}\right)^2 \sigma_T^2 \qquad \text{(F-6)}$$

This may be expressed in terms of fractional uncertainty:

$$\left(\frac{\sigma_{x_1}}{x_1}\right)^2 = \left(\frac{\partial x_1}{\partial SSR}\right)^2 \left(\frac{\sigma_{SSR}}{x_1}\right)^2 + \left(\frac{\partial x_1}{\partial WR}\right)^2 \left(\frac{\partial WR}{\partial AR}\right)^2 \left(\frac{\sigma_{AR}}{x_1}\right)^2 + \left(\frac{\partial x_1}{\partial T}\right)^2 \left(\frac{\sigma_T}{x_1}\right)^2 \qquad \text{(F-7)}$$

**Uncertainty Associated with the Solvent-to-Sample Weight Ratio**

The partial derivative of $x_1$ with respect to SSR is given below:

$$\frac{\partial x_1}{\partial SSR} = \frac{\left(\frac{WR}{MW_1}\right)\left(\frac{(WR)(SSR)}{MW_1} + \frac{1}{MW_2}\right) - \left(\frac{(WR)(SSR)}{MW_1}\right)\left(\frac{WR}{MW_1}\right)}{\left[\frac{(WR)(SSR)}{MW_1} + \frac{1}{MW_2}\right]^2} \qquad \text{(F-8)}$$

Combining terms, this becomes:

$$\frac{\partial x_1}{\partial SSR} = \frac{\frac{(WR)^2(SSR)}{(MW_1)^2} + \frac{WR}{(MW_1)(MW_2)} - \frac{(WR)^2(SSR)}{(MW_1)^2}}{\left[\frac{(WR)(SSR)}{MW_1} + \frac{1}{MW_2}\right]^2} \tag{F-9}$$

After canceling terms, the partial derivative is:

$$\left(\frac{\partial x_1}{\partial SSR}\right)^2 = \left\{\frac{\frac{WR}{(MW_1)(MW_2)}}{\left[\frac{(WR)(SSR)}{MW_1} + \frac{1}{MW_2}\right]^2}\right\}^2 \tag{F-10}$$

Dividing this equation by $x_1^2$ to get the fractional uncertainty associated with the solvent-to-sample weight ratio in relative terms results in:

$$\left(\frac{\partial x_1}{\partial SSR}\right)^2\left(\frac{1}{x_1}\right)^2 = \left\{\frac{1}{\left[\frac{(WR)(SSR)}{MW_1} + \frac{1}{MW_2}\right](MW_2)(SSR)}\right\}^2 \tag{F-11}$$

but, from Equation F-3,

$$\left[\frac{(WR)(SSR)}{MW_1} + \frac{1}{MW_2}\right] = \frac{(WR)(SSR)}{(MW_1)(x_1)} \tag{F-12}$$

so,

$$\left(\frac{\partial x_1}{\partial SSR}\right)^2\left(\frac{1}{x_1}\right)^2 = \left\{\frac{1}{\left[\frac{(WR)(SSR)}{(MW_1)(x_1)}\right](MW_2)(SSR)}\right\}^2 \tag{F-13}$$

and, thus, the fractional uncertainty associated with the solvent-to-sample weight ratio becomes:

$$\left(\frac{\partial x_1}{\partial SSR}\right)^2\left(\frac{\sigma_{SSR}}{x_1}\right)^2=\left\{\frac{(MW_1)(x_1)}{(MW_2)(WR)(SSR)^2}\right\}^2\sigma_{SSR}^2 \tag{F-14}$$

To find the variance in the solvent-to-sample weight ratio, the ratio is given by the weight of the solvent divided by the weight of the sample, as shown in Equation F-15.

$$SSR=\left(\frac{m_{sol}}{m_{sam}}\right) \tag{F-15}$$

SSR is the solvent-to-sample weight ratio, $m_{sol}$ is the average solvent mass, and $m_{sam}$ is the average sample mass. The propagated uncertainty in the solvent-to-sample ratio, expressed in terms of variances, is a function of the solvent mass and the sample mass:

$$\sigma_{SSR}^2=\left(\frac{\partial SSR}{\partial m_{sol}}\right)^2\sigma_{m_{sol}}^2+\left(\frac{\partial SSR}{\partial m_{sam}}\right)^2\sigma_{m_{sam}}^2 \tag{F-16}$$

The partial differentials are:

$$\frac{\partial SSR}{\partial m_{sol}}=\left(\frac{1}{m_{sam}}\right) \tag{F-17}$$

and

$$\frac{\partial SSR}{\partial m_{sam}}=\left(-\frac{m_{sol}}{m_{sam}^2}\right) \tag{F-18}$$

The variance associated with the solvent-to-sample weight ratio, after combining terms, is thus,

$$\sigma_{SSR}^2=\left(\frac{1}{m_{sam}}\right)^2\sigma_{m_{sol}}^2+\left(\frac{m_{sol}}{m_{sam}^2}\right)^2\sigma_{m_{sam}}^2 \tag{F-19}$$

Combining Equations F-14 and F-19, the propagated fractional uncertainty associated with the solvent-to-sample weight ratio, which is the first term in Equation F-7, is:

$$\left(\frac{\partial x_1}{\partial SSR}\right)^2\left(\frac{\sigma_{SSR}}{x_1}\right)^2=\left\{\frac{(MW_1)(x_1)}{(MW_2)(WR)(SSR)^2}\right\}^2\left\{\left(\frac{1}{m_{sam}}\right)^2\sigma_{m_{sol}}^2+\left(\frac{m_{sol}}{m_{sam}^2}\right)^2\sigma_{m_{sam}}^2\right\} \qquad \text{(F-20)}$$

**Uncertainty Associated with the Weight Ratio**

The partial derivative of $x_1$ with respect to WR is given below:

$$\frac{\partial x_1}{\partial WR}=\frac{\left(\frac{SSR}{MW_1}\right)\left(\frac{(WR)(SSR)}{MW_1}+\frac{1}{MW_2}\right)-\left(\frac{(WR)(SSR)}{MW_1}\right)\left(\frac{SSR}{MW_1}\right)}{\left[\frac{(WR)(SSR)}{MW_1}+\frac{1}{MW_2}\right]^2} \qquad \text{(F-21)}$$

Combining terms, this becomes:

$$\frac{\partial x_1}{\partial WR}=\frac{\frac{(WR)(SSR)^2}{(MW_1)^2}+\frac{SSR}{(MW_1)(MW_2)}-\frac{(WR)(SSR)^2}{(MW_1)^2}}{\left[\frac{(WR)(SSR)}{MW_1}+\frac{1}{MW_2}\right]^2} \qquad \text{(F-22)}$$

After canceling terms, the partial derivative is:

$$\left(\frac{\partial x_1}{\partial WR}\right)^2=\left\{\frac{\frac{SSR}{(MW_1)(MW_2)}}{\left[\frac{(WR)(SSR)}{MW_1}+\frac{1}{MW_2}\right]^2}\right\}^2 \qquad \text{(F-23)}$$

Dividing this equation by $x_1^2$ to get the fractional uncertainty associated with the weight ratio results in:

$$\left(\frac{\partial x_1}{\partial WR}\right)^2\left(\frac{1}{x_1}\right)^2=\left\{\frac{1}{\left[\frac{(WR)(SSR)}{MW_1}+\frac{1}{MW_2}\right](MW_2)(WR)}\right\}^2 \qquad \text{(F-24)}$$

but, from Equation F-3,

$$\left[\frac{(WR)(SSR)}{MW_1}+\frac{1}{MW_2}\right]=\frac{(WR)(SSR)}{(MW_1)(x_1)} \tag{F-12}$$

so,

$$\left(\frac{\partial x_1}{\partial WR}\right)^2\left(\frac{1}{x_1}\right)^2=\left\{\frac{1}{\left[\frac{(WR)(SSR)}{(MW_1)(x_1)}\right](MW_2)(WR)}\right\}^2 \tag{F-25}$$

thus, the fractional uncertainty associated with the weight ratio becomes:

$$\left(\frac{\partial x_1}{\partial WR}\right)^2\left(\frac{\sigma_{WR}}{x_1}\right)^2=\left\{\frac{(MW_1)(x_1)}{(MW_2)(WR)^2(SSR)}\right\}^2\sigma_{WR}^2 \tag{F-26}$$

The weight ratio is a function of the area ratio; thus, the variance in the weight ratio is a function of the variance in the gas chromatograph area ratio, as seen in Equation F-5.

$$\sigma_{WR}^2=\left(\frac{\partial WR}{\partial AR}\right)^2\sigma_{AR}^2$$

The derivative of the weight ratio with respect to the area ratio can be estimated from the slope of the calibration curve. The calibration curve is expressed as a second order polynomial:

$$\mathrm{WR}=\alpha\mathrm{AR}^2+\beta\mathrm{AR}+\gamma \tag{F-27}$$

where, WR is the weight ratio, AR is the area ratio and $\alpha$, $\beta$, and $\gamma$ are the regressed calibration parameters. The slope of the calibration curve is shown in Equation F-28.

$$\frac{\partial WR}{\partial AR}=2\alpha AR+\beta \tag{F-28}$$

Thus, combining Equations F-26, F-5 and F-28, the propagated fractional uncertainty associated with the weight ratio, which is the second term in Equation F-7, is:

$$\left(\frac{\partial x_1}{\partial WR}\right)^2\left(\frac{\partial WR}{\partial AR}\right)^2\left(\frac{\sigma_{AR}}{x_1}\right)^2 = \left\{\frac{(MW_1)(x_1)}{(MW_2)(WR)^2(SSR)}\right\}^2 \{2\alpha AR + \beta\}^2 \sigma_{AR}^2 \qquad \text{(F-29)}$$

The variance in the area ratio was determined from repeated measurements.

## Uncertainty Associated with the Temperature

The uncertainty associated with the temperature is a result of thermometer imprecision and fluctuation in the oven temperature control. The deviation in the mole fraction with respect to temperature is determined by finding the slope of the solubility curve. The variance in the temperature was estimated to be ±0.3K. Using non-linear regression, the solubility curves are fit to an equation of the form:

$$x = A + BT + CT^2 + DT^3 + ET^4 + FT^5 \qquad \text{(F-30)}$$

Thus, the slope of the solubility curve is:

$$\frac{\partial x_1}{\partial T} = B + 2CT + 3DT^2 + 4ET^3 + 5FT^4 \qquad \text{(F-31)}$$

This expression is divided by $x_1{}^2$ to express it in terms of fractional uncertainty:

$$\left(\frac{\partial x_1}{\partial T}\right)^2\left(\frac{1}{x_1}\right)^2 = \left(B + 2CT + 3DT^2 + 4ET^3 + 5FT^4\right)^2\left(\frac{1}{x_1}\right)^2 \qquad \text{(F-32)}$$

Shown in terms of variance, the fractional uncertainty associated with the temperature, which is the final term in Equation F-7, is:

$$\left(\frac{\partial x_1}{\partial T}\right)^2\left(\frac{\sigma_T}{x_1}\right)^2 = \left(B + 2CT + 3DT^2 + 4ET^3 + 5FT^4\right)^2\left(\frac{\sigma_T}{x_1}\right)^2 \qquad \text{(F-33)}$$

## Total Fractional Uncertainty

Combining Equations F-20, F-29, and F-33, the total fractional uncertainty is:

$$
\begin{aligned}
\left(\frac{\sigma_{x_1}}{x_1}\right)^2 = {} & \left\{\frac{(MW_1)(x_1)}{(MW_2)(WR)(SSR^2)}\right\}^2 \left\{\left(\frac{1}{m_{sam}}\right)^2 \sigma_{m_{sol}}^2 + \left(\frac{m_{sol}}{m_{sam}^2}\right)^2 \sigma_{m_{sam}}^2\right\} \\
& + \left\{\frac{(MW_1)(x_1)}{(MW_2)(WR)^2(SSR)}\right\}^2 \{2\alpha AR + \beta\}^2 \sigma_{AR}^2 \\
& + \left(B + 2CT + 3DT^2 + 4ET^3 + 5FT^4\right)^2 \left(\frac{\sigma_T}{x_1}\right)^2
\end{aligned}
\qquad \text{(F-34)}
$$

The first term represents the uncertainty associated with the solvent-to-sample weight ratio, the second term represents the uncertainty associated with the solute-to-solvent weight ratio, and the final term represents the uncertainty associated with the temperature.

The uncertainty estimates used to calculate the uncertainty in the measured mole fractions were determined by repeated measurements. The uncertainties in the solvent mass, $\sigma_{m_{sol}}$, and sample mass, $\sigma_{m_{sam}}$, are the standard deviation of twenty measurements of an empty, capped vial. The uncertainty in the temperature, $\sigma_T$, is the standard deviation of ten ice point measurements of distilled water. The uncertainty in the area ratio, $\sigma_{AR}$, is the standard deviation in the GC analyses. The uncertainties in the solvent mass (0.0002), sample mass (0.0002), and temperature (0.3) are constant throughout the entire study. The uncertainties in the area ratio are shown at the end of the appendix in Table F-1.

**Sample Calculation (Benzene-Water)**

$$\left(\frac{\sigma_{x_1}}{x_1}\right)^2 = \left\{\frac{(MW_1)(x_1)}{(MW_2)(WR)(SSR^2)}\right\}^2 \left\{\left(\frac{1}{m_{sam}}\right)^2 \sigma^2_{m_{sol}} + \left(\frac{m_{sol}}{m^2_{sam}}\right)^2 \sigma^2_{m_{sam}}\right\}$$

$$+ \left\{\frac{(MW_1)(x_1)}{(MW_2)(WR)^2(SSR)}\right\}^2 \{2\alpha AR + \beta\}^2 \sigma^2_{AR}$$

$$+ \left(B + 2CT + 3DT^2 + 4ET^3 + 5FT^4\right)^2 \left(\frac{\sigma_T}{x_1}\right)^2$$

The values given below are for the solubility of benzene in water at 296.4 K. The uncertainty estimates are expressed as standard deviations.

$\sigma_{m_{sol}} = 0.0002$ grams $\qquad$ $\sigma_{m_{sam}} = 0.0002$ grams

$\sigma_{AR} = 1.743E-05$ $\qquad$ $\sigma_T = 0.3$ K

$x_1 = 4.100E-04$ $\qquad$ T = 296.4 K

$MW_1$ = 78.114 grams/mole $\qquad$ $MW_2$ = 18.015 grams/mole

WR = 0.0046 $\qquad$ SSR = 0.4013 $\qquad$ AR = 0.00374

$m_{sol}$ = 7.2426 grams $\qquad$ $m_{sam}$ = 18.0482 grams

B = 8.095*E*-03 $\qquad$ C = -4.429*E*-05 $\qquad$ D = 1.206*E*-07

E = -1.639*E*-10 $\qquad$ F = 8.912*E*-14

$\alpha$ = 1.7145 $\qquad$ $\beta$ = 1.1620

According to Equation F-34 the total fractional propagated uncertainty in the solubility measurements is:

$$\left(\frac{\sigma_{x_1}}{x_1}\right)^2 = \left\{\frac{(78.114)(4.100E-04)}{(18.015)(0.0046)(0.4013)^2}\right\}^2 \left\{\left(\frac{1}{18.0482}\right)^2 (0.0002)^2 + \left(\frac{7.2426}{(18.0482)^2}\right)(0.0002)^2\right\}$$

$$+ \left\{\frac{(78.114)(4.100E-04)}{(18.015)(0.0046)^2(0.4013)}\right\}^2 \{(2)(1.7145)(0.00374)+1.1620\}^2 (1.743E-05)^2$$

$$+ \{(8.095E-03)-(2)(4.429E-05)(296.4)+(3)(1.206E-07)(296.4)^2$$

$$-(4)(1.639E-10)(296.4)^3+(5)(8.912E-14)(296.4)^4\}^2 \left(\frac{0.3}{4.100E-04}\right)^2$$

$$= 5.829E\text{-}09 + 1.838E\text{-}05 + 2.837E\text{-}05 \qquad \equiv \qquad (\sigma_{SSR})^2 + (\sigma_{WR})^2 + (\sigma_T)^2$$

$$= 4.676E\text{-}05$$

or,

$$\sigma_{x_1} = (0.0068)(x_1)$$

$$= (0.0068)(4.100E-04)$$

$$= 2.798E\text{-}06$$

The percentage of uncertainty in the mole fraction of benzene at 296.4 K is determined by dividing the uncertainty by the mole fraction, as shown below:

% uncertainty = (2.798*E*-06 / 4.100*E*-04 = 0.68%)

The percentage of uncertainty associated with each term is determined by dividing the individual fractional uncertainty by the total fractional uncertainty, as shown below:

% uncertainty associated with SSR = (5.829*E*-09 / 4.676*E*-05 < 1%)

% uncertainty associated with WR = (1.838*E*-05 / 4.676*E*-05 = 39%)

% uncertainty associated with T = (2.837*E*-05 / 4.676*E*-05 = 61%)

The uncertainty associated with the solvent-to-sample weight ratio is negligible. For the hydrocarbon solubility in water measurements, the uncertainty associated with the weight ratio is roughly proportional to the uncertainty associated with the temperature. For the water solubility in hydrocarbon measurements, the uncertainty associated with the weight ratio accounts for approximately 75% of the total uncertainty.

**Table F-1.** Uncertainty Estimates for the Area Ratio

| Benzene-Water System | | |
|---|---|---|
| Temperature (K) | Benzene Solubility Area Ratio Uncertainty ($10^5$) | Water Solubility Area Ratio Uncertainty ($10^5$) |
| 296.4 | 1.120 | 1.743 |
| 328.5 | 3.045 | 7.644 |
| 358.8 | 0.7613 | 8.908 |
| 388.0 | 1.555 | 23.25 |
| 416.8 | 3.291 | 28.76 |
| 445.8 | 6.278 | 61.10 |
| 474.2 | 24.31 | 54.61 |
| 492.8 | 33.05 | 73.47 |

| Decane-Water System | | |
|---|---|---|
| Temperature (K) | Decane Solubility Area Ratio Uncertainty ($10^5$) | Water Solubility Area Ratio Uncertainty ($10^5$) |
| 295.5 | 1.054 | 61.56 |
| 323.5 | 1.005 | 3.205 |
| 363.2 | 1.529 | 2.669 |
| 402.9 | 0.5783 | 8.769 |
| 440.3 | 3.425 | 9.662 |
| 477.3 | 18.97 | 25.15 |
| 513.8 | 16.30 | 26.06 |
| 542.3 | 161.3 | 101.2 |

| 1-Hexene-Water System | | |
|---|---|---|
| Temperature (K) | 1-Hexene Solubility Area Ratio Uncertainty ($10^5$) | Water Solubility Area Ratio Uncertainty ($10^5$) |
| 296.4 | 0.5265 | 1.624 |
| 328.4 | 1.475 | 0.5033 |
| 353.5 | 1.083 | - |
| 383.5 | 0.8278 | 8.556 |
| 407.2 | 1.902 | 23.13 |
| 434.9 | 3.571 | 19.18 |
| 463.5 | 9.415 | 10.23 |
| 486.7 | 23.64 | 70.33 |

# VITA

Douglas Wade Ratzlaff

Candidate for the Degree of

Master of Science

Thesis: HYDROCARBON-WATER SOLUBILITIES AT ELEVATED TEMPERATURES NEAR THE THREE-PHASE EQUILIBRIUM PRESSURE

Major Field: Chemical Engineering

Biographical:

Personal Data: Born in Enid, Oklahoma, November 15, 1972.

Education: Graduated from Kremlin-Hillsdale High School, Kremlin, Oklahoma in May, 1991; Received Bachelor of Arts degree in Chemistry from Tabor College, Hillsboro, Kansas in May, 1995; Completed the requirements for the Master of Science degree in Chemical Engineering at Oklahoma State University in December, 1999.

Experience: Field Chemist, Plains Environmental Services, Salina, Kansas, June, 1995 to June, 1996; Engineering Intern, Ultramar Diamond Shamrock, Ardmore, Oklahoma, June, 1998 to August, 1998; Teaching Assistant, School of Chemical Engineering, Oklahoma State University, Stillwater, Oklahoma, August, 1996 to May, 1998; Research Assistant, School of Chemical Engineering, Oklahoma State University, Stillwater, Oklahoma, August, 1998 to August, 1999; Black & Veatch Pritchard, Inc., Overland Park, Kansas, August, 1999 to present.