Copyright by

Yichen Xin

The Report Committee for Yichen Xin
Certifies that this is the approved version of the following report:

## Experiment Design and Improvement for PGE 427 Properties of Petroleum Fluids

## APPROVED BY SUPERVISING COMMITTEE:

Supervisor:

> David DiCarlo

Ryosuke Okuno

# Experiment Design and Improvement for PGE 427 Properties of Petroleum Fluids 

by

Yichen Xin

## Report

Presented to the Faculty of the Graduate School of
The University of Texas at Austin
in Partial Fulfillment
of the Requirements
for the Degree of

Master of Science in Engineering

## The University of Texas at Austin

December 2017

## Dedication

To my mother, father, and my wife.


#### Abstract

Experiment Design and Improvement for PGE 427 Properties of Petroleum Fluids

Yichen Xin, M.S.E.<br>The University of Texas at Austin, 2017

Supervisor: David DiCarlo

PGE 427 Properties of Petroleum Fluids is an undergraduate core course focused on the physical properties of organic chemicals (a.k.a. Fluids). However the corresponding lab course is duplicated from PGE 421 Physical and Chemical Behavior of Fluids II (a.k.a. Pchem). Thus the lab materials are sometimes irrelevant and inappropriate. Also the Pchem course has not been updated for decades, some lab materials are outdated. The purpose of this project is to filter the existing labs, remove the irrelevant contents, update the obsolete labs, and design several new labs which relate to the Fluids course. The report primarily focus on the new lab designs and documents the updated labs as well. Two new labs has been developed. They are Freezing Point Depression, and Viscosity Measurement. The report includes background information, objectives, design principals, safety management and Lab Manual for each lab.


## Table of Contents

List of Tables ..... X
List of Figures ..... xi
Chapter 1: Introduction .....  1
Chapter 2: Newly Designed Lab - Freezing Point Depression ..... 3
2.1 Introduction ..... 3
2.2 Apparatus and Materials .....  3
2.3 Results and DISCUSSION .....  3
2.4 Lab Mandal .....  4
Objectives ..... 4
Background .....  4
Materials .....  6
Apparatus .....  6
Procedure .....  7
Results .....  9
Discussion ..... 10
Chapter 3: Newly Designed Lab - Capillary Viscometer ..... 11
3.1 Introduction ..... 11
3.2 Apparatus and Materials ..... 11
3.3 Results and DISCUSSION ..... 11
3.4 Lab Mandal ..... 12
Objectives ..... 12
Background ..... 12
Materials ..... 14
Apparatus ..... 14
Procedure ..... 15
Results ..... 17
Discussion ..... 17
Chapter 4: Updated Old Labs ..... 18
4.1 Mixing Properties ..... 18
4.1.1 Addition ..... 18
Obtaining partial molar volume by graphic method (For example, IPA + Water) ..... 18
Derivation ..... 19
4.2 Thermochemistry: Measuring Heat of Reaction. ..... 21
4.2.1 Modification ..... 21
Analysis ..... 21
A. Calorimeter constant ..... 23
B. Heats of mixing and heats of reaction. ..... 24
4.3 Ternary Phase Behavior ..... 25
4.3.1 Addition ..... 25
Calculate the volume fraction of each component in each phase 25
Plot the binodal curve ..... 26
Draw the tie lines ..... 26
4.4 Treating Emulsions ..... 28
4.4.1 Addition ..... 28
Solution ..... 28
4.5 Surface/ Interfacial Tension and Contact Angle ..... 31
4.5.1 Reduction ..... 31
4.5.2 Modification ..... 31
4.6 Compatibility of Oilfield Brines ..... 33
4.6.1 Modification ..... 33
4.6.2 Addition ..... 34
Scale Identification and Calculation ..... 34
Appendix A: Mixing Properties Lab Manual ..... 37
ObJEctives ..... 37
Background ..... 37
Procedure ..... 39
Results ..... 42
DISCUSSION ..... 43
Appendix B: Thermochemistry: Measuring Heat of Reaction ..... 44
Objectives ..... 44
Background ..... 44
Analysis ..... 46
Procedure ..... 48
Results ..... 52
DISCUSSION ..... 53
Appendix C: Ternary Phase Behavior ..... 55
ObJECTIVES ..... 55
BACKGROUND ..... 55
Apparatus and Materials ..... 56
Procedure ..... 57
Results ..... 61
DISCUSSION. ..... 64
Appendix D: Treating Emulsion ..... 65
ObJEctives ..... 65
Background ..... 65
Apparatus and Materials ..... 66
Procedure ..... 66
Results ..... 68
DISCUSSION ..... 69
Appendix E: Surface/ Interfacial Tension and Contact Angle ..... 71
ObJECTIVES ..... 71
Background for Surface/ Interfacial Tension ..... 71
Background for Contact Angle ..... 73
Apparatus and Materials for Surface Tension ..... 75
Apparatus and Materials for Contact Angle ..... 75
Procedure ..... 75
Results ..... 80
DISCUSSION ..... 81
Appendix F: Compatibility of Oilfield Brines ..... 83
ObJectives ..... 83
Background ..... 83
Apparatus and Materials ..... 84
Procedure ..... 84
Results: ..... 85
DISCUSSION: ..... 85
References ..... 87

## List of Tables

Table 3.1: Fluid and viscometer information......................................................... 14
Table 4.1: Pipette 1 results..................................................................................... 28
Table 4.2: Pipette 2 results.................................................................................... 29
Table 4.3: Pipette 3 results..................................................................................... 29
Table 4.4: Pipette 4 results..................................................................................... 30

## List of Figures

Figure 2.1: Freezing Point Depression Apparatus .....  7
Figure 3.1: Cannon-Fenske Viscometer Setup ..... 15
Figure 4.1: Molar Volume Diagram ..... 18
Figure 4.2: Molar Volume Diagram with tangent line ..... 19
Figure 4.3: Molar Volume Diagram with tangent line and symbol ..... 19
Figure C.1: Density Table ..... 59
Figure C.2: Refractive Index of IPA curve ..... 61
Figure E.1: Condition of drop at breaking point. ..... 72
Figure E.2: Contact angle between a solid, a vapor and a liquid ..... 73
Figure E.3: Expanded view of three-phase contact zone. ..... 74

## Chapter 1: Introduction

PGE 427. Properties of Petroleum Fluids is known as the Fluid course. Course contents include principles of organic chemistry, phase behavior of multicomponent mixtures, properties of hydrocarbon gases and liquids and oil field waters, overview of laboratory phase behavior measurements, and material balance calculations. Three lecture hours and three laboratory hours a week for one semester. PGE 421K. Physical and Chemical Behavior of Fluids II is known as the Pchem course. Course contents include applications of thermodynamics and physical chemistry to petroleum and geosystems engineering. Three lecture hours and three laboratory hours a week for one semester. Based on the course descriptions, Fluid course and Pchem course have similar contents but different focused area. Fluid course is more fundamental and the corresponding lab should be focused on basic fluid property measurement. However, the Fluid lab materials are duplicated from Pchem lab without adjustment and modification. Thus, the lab materials are sometimes irrelevant and inappropriate. Also, the Pchem course has not been updated for decades, some lab materials are outdated.

This report includes two new labs:

1. Determination of the Molar Mass of an Unknown Substance by Freezing Point Depression
2. Determination of Kinematic Viscosity of Fluid

Six old labs:

1. Mixing Properties
2. Thermochemistry: Measuring Heat of Reaction
3. Ternary Phase Behavior
4. Treating Emulsions
5. Surface/ Interfacial Tension and Contact Angle
6. Compatibility of Oilfield Brines

For the new labs, this report includes introduction, background information, apparatus and materials, safety management, and results and discussion. For the old labs, changes made are documented. Lab manual is also included for each lab.

## Chapter 2: Newly Designed Lab - Freezing Point Depression

### 2.1 InTRODUCTION

It is important in fluid characterization to determine the average molecular weight of C7+ in a reservoir fluid. For fluid characterization, we can preliminarily determine the molar mass for the oil sample without specifying the composition. Freezing point depression is a common method used to determine the molar mass of an unknown substance. The method consists of measuring the freezing point of a pure solvent and then measuring it again with a known mass of fluid sample dissolved in the solvent. This depression depends on the moles of dissolved substance. Thus, it can be used to determine the moles of a substance - combining this with the easily measured mass of a substance gives the molecular mass.

### 2.2 Apparatus and Materials

The freezing point measurement for educational purpose is restricted to ice bath. Thus, the solvent we selected is cyclohexane. The melting point of cyclohexane at room pressure is $7{ }^{\circ} \mathrm{C}$ which is slightly above the temperature of ice bath $0^{\circ} \mathrm{C}$. The solutes we selected are naphthalene and 1,4-dichlorobenzene. These are the effective ingredients of the moth ball. Standard gloves, goggles, long pants, and closed shoes are required when using the chemicals. To avoid headache, dizziness, and nausea, ventilation is highly recommended.

### 2.3 ReSUlTS AND DISCUSSION

The results section required students to report the measured freezing points, calculated freezing point depression constants, and calculated molar mass of the unknown substance (1,4-dichlorobenzene). The discussion section demanded students to compare the calculated molar mass with literature value and analyze the experiment accuracy.

Finally a comprehensive calculation problem is asked to simulate a real-life problem. Students need to use all the knowledge learned in the lab to solve the problem.

### 2.4 Lab Manual

Determination of the Molar Mass of an Unknown Substance by Freezing Point Depression

## Objectives

- Determine unknown substance's molar mass
- Measure the freezing point of a solvent using an ice bath
- Practice in calculating the freezing point depression constant, Kf


## Background

Freezing point depression
Freezing point depression is a common method used to determine the molar mass of an unknown substance. This is important for fluid characterization in determining the average molecular weight of the heptane plus fraction in a reservoir fluid. For fluid characterization, we can preliminarily determine the molar mass for the oil sample without specifying the composition.

The method consists of measuring the freezing point of a pure solvent and then measuring it again with a known mass of oil dissolved in the solvent. When oil is dissolved in the solvent, the solvent is slightly diluted in the liquid phase. This causes the Gibbs free energy of the liquid solvent to decrease. In contrast, when the solvent is frozen, it becomes pure as the solute does not fit into the crystal lattice. Thus, the Gibbs free energy of the solid remains the same. The net effect is that the liquid phase of the solvent is preferred to temperatures below the original freezing point. Or in other words, the freezing point decreases with increasing solvent in the solute.

This depression depends on the moles of dissolved substance. Thus, it can be used to determine the moles of a substance - combining this with the easily measured mass of a substance gives the molecular mass.

In the first part of the lab we will determine the freezing point of liquid (Tf), the freezing point depression constant (Kf) for the solvent cyclohexane under atmospheric pressure. In the second part of the lab we will determine the molar mass of an unknown organic solid. To calculate the molar mass, the measured freezing point change ( $\Delta \mathrm{Tf}$ ), the experimentally-determined freezing point depression constant (Kf) will be used.

Freezing point depression is one of four important colligative properties of ideal solutions (freezing point depression, boiling point elevation, vapor pressure decrease, and osmotic pressure increase) in which the change in the solvent properties is dependent on the concentration, not the identity, of the solute particles.

When determining changes in freezing point (or boiling point), solute concentration is measured in molality. Molality is moles of solute per kilogram of solvent. The concentration unit $\mathrm{mol} / \mathrm{kg}$ is temperature independent, unlike the $\mathrm{mol} / \mathrm{L}$ concentration unit, because volume changes with temperature but mass does not

$$
\begin{equation*}
T_{f, \text { solution }}-T_{f, \text { solvent }}=-K_{f} \frac{n_{\text {solute }}}{m_{\text {solvent }}} \tag{2.1}
\end{equation*}
$$

From Equation (2.1) if we plot the change in freezing point between solution and solvent against the molality, the slope of the best fitting straight line is -Kf. Thus, the freezing point depression constant for a specific solvent can be determined under the specific pressure. Also, if we know the mass of an unknown constant, the solvent properties, and the change in freezing point, we can calculate the moles of solute and determined the molar mass.

$$
\begin{equation*}
n_{\text {solute }}=\frac{\Delta T_{f} * m_{\text {solvent }}}{-K_{f}} \tag{2.2}
\end{equation*}
$$

Freezing point and melting point
If the liquid temperature is higher than its surroundings, the liquid will release heat and the temperature will fall. When the liquid's temperature reaches its freezing point, the liquid's temperature will not fall as it continues to release heat to the surroundings. Instead, the liquid will begin to freeze. The parts closest to the cold surroundings start to turn to solid. This freezing process releases a quantity of heat energy that is equal in magnitude but opposite in sign to the heat of fusion, $\Delta$ Hfusion, of the substance. $\Delta$ Hfusion is defined as the heat absorbed by a solid in the process of melting. When the liquid freezes to form the solid phase, it must release the same amount of heat: $\Delta$ Hfreezing $=-\Delta$ Hfusion. The temperature of the system (the freezing liquid) remains at the freezing point until all the liquid has frozen. Once the liquid has completely frozen, only then will the temperature start to fall again.

## Materials

1. Cyclohexane is highly flammable and no flames are permitted in the lab.
2. Naphthalene and the organic unknowns are irritants and should not be inhaled or allowed to touch the skin.
3. Always wear goggles.

## Apparatus

Experiment setup includes thermometer, split stopper, clamp, test tube, beaker, ice water, and stirrer.


Figure 2.1: Freezing Point Depression Apparatus

## Procedure

Part A: Determination of Kf for Cyclohexane
a. Pure cyclohexane:

1. Clean the test tube and dry thoroughly. Rinse the clean test tubes with $1-2 \mathrm{~mL}$ cyclohexane to remove impurities; dispose rinse liquid properly.
2. Pipet 20 mL of cyclohexane in the test tube.
3. Seal the test tube with the split stopper and adjust the apparatus so that 1 ) the thermometer does not touch the side of the test tube, and 2) all the solution in the tube is immersed below the surface of the ice bath.
4. Turn on the magnetic stirrer.
5. Record the time and temperature data. Start timing when the temperature gets 15. Record the temperature every 5 seconds.
6. The change in temperature will gradually become smaller when the temperature is close to freezing point. Take the reading every 10 seconds instead. Stop recording if the temperature does not change (within $0.1^{\circ} \mathrm{C}$ ) for 5 times (50 seconds).
7. Place the test tube in an empty beaker and unfreeze it with room temperature.
b. Naphthalene solutions of known concentrations:
8. Weigh 0.0897 g naphthalene. Make sure all the solid is transferred into the test tube. DO NOT weigh out the naphthalene before using it. Older mothballs consisted primarily of naphthalene and as we know it is volatile.
9. Add to your 20 mL of cyclohexane. Use the magnetic stirrer to completely mix the solution before ice bath.
10. Repeat steps 3-6 from "A. Pure cyclohexane" to take the temperature and time data.
11. Weigh 0.1395 g naphthalene. Repeat steps 2-3 to take the temperature and time data.
c. Determine the freezing points and the freezing point depression constant Kf
12. Determine the freezing point of the pure solvent and of the two solutions of known molality.
13. Calculate the molalities of two solutions using solute mole and solvent mass.
14. Plot freezing point difference $\Delta \mathrm{Tf}$ against molality for the pure solvent $(\Delta \mathrm{Tf}=$ 0 for the pure solvent $)$ and two solutions $((\Delta \mathrm{Tf}=\mathrm{Tfsolution}-\mathrm{Tfsolvent}<0)$.
15. Fit the best straight line to your three points and determine the Kf.
16. Compare your experimentally-determined value with the literature value of $20.2^{\circ} \mathrm{C} / \mathrm{mol} / \mathrm{kg}$.

## Part B: Molar Mass of an Unknown Organic Solid

1. Clean the test tube and dry thoroughly. Rinse the clean test tubes with $1-2 \mathrm{~mL}$ cyclohexane to remove impurities; dispose rinse liquid properly.
2. Pipet 20 mL of cyclohexane in the test tube.
3. Weigh 0.1145 g unknown material. Make sure all the solid is transferred into the test tube.
4. Add to your 20 mL of cyclohexane. Use the magnetic stirrer to completely mix the solution before ice bath.
5. Turn on the magnetic stirrer.
6. Record the time and temperature data. Start timing when the temperature gets 15. Record the temperature every 5 seconds.
7. The change in temperature will gradually become smaller when the temperature is close to freezing point. Take the reading every 10 seconds instead. Stop recording if the temperature does not change (within $0.1^{\circ} \mathrm{C}$ ) for 5 times (50 seconds).
8. Use your experimentally-determined Kf , freezing point difference $\Delta \mathrm{Tf}$, and solvent mass to calculate the number of moles and then the molar mass of your unknown solid.

## Results

For Part A:

1. Three graphs of freezing point determinations (temperature vs. time).
2. One graph of Kf determination with trend line and equation (freezing point difference vs. molality).
3. For each solvent/solution create a table include:
a. Solute mole
b. Solvent mass
c. Calculated molality
d. Tf
e. $\quad \Delta \mathrm{Tf} \quad * *$ Solution freezing point minus pure solvent freezing point

## For Part B:

1. One graph of freezing point determinations (temperature vs. time).
2. Create a table include:
a. Tf
b. $\quad \Delta \mathrm{Tf} \quad * *$ Solution freezing point minus pure solvent freezing point
c. Solvent mass
d. Calculated solute mole
e. Calculated molar mass

## Discussion

1. Compare your experimentally-determined Kf with literature value and discuss what may cause the difference.
2. Based on the calculated molar mass which one of the following may be the unknown organic solid? Discuss your reason.
a. Ortho-dichlorobenzene
b. Para-dichlorobenzene
c. Meta-dibromobenzene
3. A lab technician is required to measure the molar weight of an unknown crude oil. He received 20 g of the sample. After the freezing point depression experiment using 200cc of benzene as solvent, the freezing point decreased $5^{\circ} \mathrm{C}$. Help him calculate the molar weight.

## Chapter 3: Newly Designed Lab - Capillary Viscometer

### 3.1 InTRODUCTION

In Petroleum Engineering, the viscosity is one of the most important fluid properties. This is because the production rate is almost inversely dependent on the viscosity. The relationship can be presented by the most important equation in the Petroleum Engineering, the Darcy's equation: $q=-\frac{k}{\mu} \nabla p$. Students are required to measure the kinematic viscosity of a given fluid by using the glass capillary viscometer. As the most commonly used viscometer, the principle is based on the time of flow for a given volume of liquid through a precision capillary. In a glass capillary viscometer, the radius of tube, the pressure difference between the two ends, and the length of the tube are constants during the experiment. The kinematic viscosity is proportional to the time of flow and the governing equation: $\kappa=\alpha \Delta t$.

### 3.2 Apparatus and Materials

It takes two hours to finish the calibration and measurement for one fluid. Thus, the only apparatus using in this experiment is the size 150 Cannon-Fenske Viscometer. The measurement range is 7.0 to 35 cSt . We selected Standard 20 as the standard fluid and Ethylene glycol as the unknown fluid, and hexane and IPA as the cleansers. Standard lab protection is required.

### 3.3 RESULTS AND DISCUSSION

The result section required students to report the viscometer constant and the measured fluid viscosity. Since the experiment is straightforward, most effort should be put into the understanding of governing equations and assumptions. The discussion section demanded students to dervie the expression of the viscometer constant. Several questions
were asked to make sure students understand the most important quasi-steady-state assumption when using the Hagen-Poiseuille equation.

### 3.4 Lab Manual

Determination of kinematic viscosity of fluid

## Objectives

- Practice to use Glass Capillary Viscometer
- Calibrate the viscometer using standard fluid
- Determine the kinematic viscosity of given fluid within the calibration range


## Background

The internal property of a fluid for its resistance to flow is known as viscosity. In 1844 Hagen-Poiseuille did their work concerning the interpretation that liquid flow through tubes and they proposed an equation for viscosity of liquids. This equation is called Poiseuille's equation.

$$
\begin{equation*}
\mu=\frac{\pi R^{4} \Delta P}{8 L Q} \tag{3.1}
\end{equation*}
$$

Where $\mu$ is the dynamic viscosity, $\Delta \mathrm{P}$ is the pressure difference between the two ends, L is the length of the tube, R is the radius of the tube, and Q is the volumetric flow rate. In the honor of Hagen-Poiseuille, the unit of viscosity is called the Poise (P). The official SI unit for absolute viscosity is $\mathrm{kg} / \mathrm{m} \mathrm{s}$ (or Pascal-seconds).

In Petroleum Engineering, the viscosity is one of the most important fluid properties. This is because the production rate is almost inversely dependent on the viscosity. Light oils tend to have low viscosities which makes them preferential for high production rates and longer well spacing. These oils tend to be volatile, and thus their PVT behavior is more complicated, but we are willing to deal with complications to get higher
rates. In contrast heavy oils have simpler PVT behavior (a simple black oil model often suffices), but have a high viscosity thus the production rate per well is much lower. Remember, in the case of petroleum engineering, the main deal is getting out as much of the resource as fast as possible, and viscosity is one of the controlling parameters (along with pressure gradient and permeability of the reservoir) for rate.

Viscosity can be measured using a viscometer. The different types of viscometer are as follows:

1. Glass capillary viscometer
2. Falling sphere viscometer
3. Falling piston viscometer
4. Oscillating piston viscometer
5. Vibrational viscometers
6. Rotational viscometers
7. Bubble viscometer
8. Rectangular-slit viscometer

In this experiment, we will only use the glass capillary viscometer. These devices are also known as U-tube viscometer, Ostwald viscometer, and Cannon-Fenske viscometer. The glass capillary viscometer is the most commonly used viscometer, which consists of a U-shaped glass tube held vertically. A constant temperature bath is necessary for accurate measurements.

The principle of the glass capillary viscometer is based on the time of flow for a given volume of liquid through a precision capillary. In a glass capillary viscometer, the radius of tube, the pressure difference between the two ends, and the length of the tube are constants during the experiment. Equation (3.1) can then be simplified to:

$$
\begin{equation*}
\kappa=\alpha \Delta t \tag{2}
\end{equation*}
$$

where is the kinematic viscosity, $\Delta \mathrm{t}$ is the amount of time it takes for a certain volume of fluid to move through the tube, and $\alpha$ is a constant determined by the viscometer's properties (capillary radius, length, and liquid volume).

The simplest method for using this viscometer is to determine the parameter $\alpha$ using a standard fluid. Once $\alpha$ is determined for the viscometer, the viscometer can be used to measure viscosities of other fluids.

## Materials

Standard 20; Ethylene glycol; Hexane (Standard 20 cleanser); IPA (Ethylene glycol cleanser).

| Standard Fluid | Sample Fluid | Viscosity Range (cSt) | Viscometer Size |
| :--- | :--- | :--- | :--- |
| Standard 20 | Ethylene glycol | $7.0-35$ | 150 |

Table 3.1: Fluid and viscometer information

## Apparatus

Cannon-Fenske Viscometer, size 150; Pipette; Stop watch; Stand and titration clamp; Oven; Beaker; Graduated cylinder.


Figure 3.1: Cannon-Fenske Viscometer Setup

## Procedure

Part A: Calibration of the Glass Capillary Viscometer

1. Clean and dry the viscometer.
2. Cool it down to the room temperature.
3. Weigh the graduated cylinder.
4. Weigh the 10 ml of Standard Fluid with graduated cylinder.
5. Calculate the density of Standard Fluid and compare with given value ( 0.973 $\mathrm{g} / \mathrm{ml}$ ).
6. Transfer the 10 ml of Standard Fluid to the viscometer from Arm A.
7. Use the pipet bulb to pull the liquid up through the viscometer and pass both Mark 1 and Mark 2.
8. Stop when the Bulk B2 is filled with fluid and there is extra fluid in the Bulk B1.
9. Record the fluid level in Bulk B1 (e.g. $1 / 2$ of Bulk B1).
10. Prepare a stopwatch.
11. Remove the pipet bulb and watch the fluid drops.
12. Start the stopwatch when the fluid level hits the Mark 1.
13. Stop the stopwatch when the fluid level hits the Mark 2.
14. Calculate the time difference $\Delta \mathrm{t}$.
15. Determine the viscometer constant $\alpha$ using dynamic viscosity, fluid density and time difference.
16. Repeat 3 times to get the average value.

Part B: Determination of kinematic viscosity

1. Clean the viscometer with hexane and dry it in the oven.
2. Cool it down to the room temperature.
3. Rinse the viscometer with 2-3 ml of ethylene glycol.
4. Discard the fluid by using pipet bulb to pull the fluid level above Bulk B1 and transferring it from Arm B.
5. Transfer 10 ml of ethylene glycol in the viscometer from Arm A.
6. Use the pipet bulb to pull the liquid up through the viscometer and pass both Mark 1 and Mark 2.
7. Stop when the Bulk B2 is filled with fluid and there is extra fluid in the Bulk B1.
8. The desired fluid level is the same as the recorded level from Part A.
9. Prepare a stopwatch.
10. Remove the pipet bulb and watch the fluid drops.
11. Start the stopwatch when the fluid level hits the Mark 1.
12. Stop the stopwatch when the fluid level hits the Mark 2.
13. Calculate the time difference $\Delta \mathrm{t}$.
14. Determine the kinematic viscosity $\kappa$ of the sample fluid.
15. Repeat 3 times to get the average value.

## Results

1. Average viscometer constant $\alpha$ calculated by using standard fluid.
2. Time difference in Part B for each trial.
3. Kinematic viscosity for each trail.
4. Average kinematic viscosity for the sample fluid ethylene glycol.

## Discussion

1. Derive the Equation (3.2) from Equation (3.1) by using that the pressure difference is given by the differences of heights between Mark 1 and Bulk A. Obtain the parameter $\alpha$ in terms of the viscometer dimensions.
2. Compare your results with literature values and discuss the consistency or deviation. Kinematic viscosity of Ethylene glycol at $20^{\circ} \mathrm{C}$ is 17.8 cSt .
3. Why are Bulk A and Bulk B wider than the rest of the tube?
4. Notice that the head (pressure) changes during the transit of fluid from Bulk B2. Why is this OK?
5. What is an important assumption for this case? (Hint. The state of the whole process.)

## Chapter 4: Updated Old Labs

### 4.1 Mixing Properties

Most of the naturally occurring materials are mixture. Properties of mixtures and how they deviate from ideality play an important role in subsurface engineering. In this lab, students are required to observe and record the total volume of non-ideal mixing, and obtain the partial molar volume for each material by graphic method.

### 4.1.1 Addition

The lab materials are well organized. However, the method of determining partial molar volume is not mentioned in the manual. A supporting document has been generated to help the students fully understand the graphic method of determining partial molar volume.

## Obtaining partial molar volume by graphic method (For example, IPA + Water)

Step 1: Plot Molar Volume vs. Mole Fraction of IPA


Figure 4.1: Molar Volume Diagram

Step 2: At specific mole fraction, draw tangent line on the curve and find the intercepts on the y -axis for both $\mathrm{XIPA}=0$ and $\mathrm{XIPA}=1$.


Figure 4.2: Molar Volume Diagram with tangent line

Red line is the tangent line of the molar volume cure at specific mole fraction. (XIPA=0.2)

The $y$ intercept at XIPA $=1$ is the partial molar volume of IPA (VIPA) at this mole fraction.

The $y$ intercept at XIPA $=0$ is the partial molar volume of Water (VWater) at this mole fraction.

## Derivation



Figure 4.3: Molar Volume Diagram with tangent line and symbol

Definition:
$V=x_{1} V_{1}+x_{2} V_{2}$
$d V=x_{1} d V_{1}+x_{2} d V_{2}+d x_{1} V_{1}+d x_{2} V_{2}$
Gibbs-Dunhern : $x_{1} d V_{1}+x_{2} d V_{2}=0$
For binary system : $d x_{1}=-d x_{2}$
$\left\{\begin{array}{l}V_{1}=V+x_{2} \frac{d V}{d x_{1}} \\ V_{2}=V-x_{1} \frac{d V}{d x_{1}}\end{array}\right.$

On the graph with tangent line, let Intercept at $x_{1}=1$ as $I_{1}$ and Intercept at $x_{1}=0$ as $I_{2}$ Consider the slope of the tangent line
$\left\{\begin{array}{l}\frac{d V}{d x_{1}}=\frac{V-I_{2}}{x_{1}-0} \\ \frac{d V}{d x_{1}}=\frac{I_{1}-I_{2}}{1-0}\end{array}\right.$
solve
$\left\{\begin{array}{l}I_{1}=V+x_{2} \frac{d V}{d x_{1}} \\ I_{2}=V-x_{1} \frac{d V}{d x_{1}}\end{array}\right.$

Thus
$\left\{\begin{array}{l}I_{1}=V_{1} \\ I_{2}=V_{2}\end{array}\right.$

### 4.2 Thermochemistry: Measuring Heat of Reaction

The lab investigates the energy changes in the form of heat that accompany chemical reactions; this area of physical chemistry is known as thermochemistry. In this lab, students are required to measure the calorimeter constant, and calculate the heat of mixing for each chemical reaction.

### 4.2.1 Modification

The whole analysis section has been rewritten due to vague notations and incorrect equations. Correct subscripts and notations are added to all the equations. Full derivation has been supplemented. To clarify the concept of interpreting heat of mixing as heat of reaction, assumptions and hits are also provided.

## Analysis

We will use cumulative (or batch) mass and energy balances here. The reaction container is closed after the reactants are placed within it. Thus, the cumulative balance for total moles n within the system (control volume is the reaction container) reduces to:

$$
\begin{equation*}
0=\left.n\right|_{t_{2}}-\left.n\right|_{t_{1}} \tag{4.2.1}
\end{equation*}
$$

Where t 1 is the time before the two components are added to the container, and t 2 is the time at which the experiment is halted (typically, when the temperature becomes constant). The energy balance reduces to:

$$
\begin{equation*}
\left.(n H)\right|_{t_{2}}-\left.(n H)\right|_{t_{1}}=Q \tag{4.2.2}
\end{equation*}
$$

Where we have neglected all forms of energy except internal and enthalpy. The term H represents the molar enthalpy of the mixture. The term Q represents the cumulative heat transferred to or from the system between time t 1 and t 2 ; note the absence of the "dot" since we are working with a cumulative balance. The work term is absent since there are no moving parts.

For a binary mixture obtained by mixing n 1 moles of pure component 1 at initial temperature Tini with n 2 moles of pure component 2 at Tini, these two temperatures are not necessarily the same, the initial enthalpy of the system is:

$$
\left.(n H)\right|_{t_{1}}=n_{1} H_{1}\left(T_{i n i}\right)+n_{2} H_{2}\left(T_{i n i}\right)
$$

And the final enthalpy is:

$$
\left.(n H)\right|_{t_{2}}=\left(n_{1}+n_{2}\right) H\left(T_{f i n}\right)
$$

The Equation (4.2.2) can be written as:

$$
\begin{equation*}
H\left(T_{f i n}\right)-x_{1} H_{1}\left(T_{i n i}\right)-x_{2} H_{2}\left(T_{i n i}\right)=\frac{Q}{n} \tag{4.2.3}
\end{equation*}
$$

Where $n=n_{1}+n_{2}$. The left side of Equation (4.3.3) appears to be the definition of the enthalpy of mixing:

$$
\Delta H_{m i x i n g} \equiv H^{E}=H-\left(x_{1} H_{1}+x_{2} H_{2}\right)
$$

But it is not, because in general the final temperature of the contents of the container T 2 will be different than the initial temperature. The enthalpy of mixing (also known as the excess enthalpy) is defined for a constant temperature and pressure, thus in the definition equation you don't see enthalpy as a function of temperature. To obtain the correct form of enthalpy of mixing, we add and subtract the enthalpies of the components at temperature T2 (i.e. at time t2) to the left side of Equation (4.2.3):

$$
H\left(T_{f i n}\right)-x_{1} H_{1}\left(T_{i n i}\right)-x_{2} H_{2}\left(T_{i n i}\right)+\left[x_{1} H_{1}\left(T_{f i n}\right)-x_{1} H_{1}\left(T_{f i n}\right)\right]+\left[x_{2} H_{2}\left(T_{f i n}\right)-x_{2} H_{2}\left(T_{f i n}\right)\right]=\frac{Q}{n}
$$

Notice the equation does not change, the purpose is to match the definition. After gathering the enthalpies at time t 2 on the left side, we obtain:

$$
H\left(T_{f i n}\right)-x_{1} H_{1}\left(T_{f i n}\right)-x_{2} H_{2}\left(T_{f i n}\right)=\frac{Q}{n}+x_{1} H_{1}\left(T_{i n i}\right)-x_{1} H_{1}\left(T_{f i n}\right)+x_{2} H_{2}\left(T_{i n i}\right)-x_{2} H_{2}\left(T_{f i n}\right)
$$

Finally:

$$
\begin{equation*}
\Delta H_{\text {mixing }}=\frac{Q}{n}+x_{1}\left(H_{1}\left(T_{i n i}\right)-H_{1}\left(T_{f i n}\right)\right)+x_{2}\left(H_{2}\left(T_{i n i}\right)-H_{2}\left(T_{\text {fin }}\right)\right) \tag{4.2.4}
\end{equation*}
$$

In the ideal case of a perfectly insulated container, the cumulative heat transfer Q is zero. For real containers, even well insulated ones, Q is nonzero, because the temperature of the container itself changes from initial Tini to final Tfin.

## A. Calorimeter constant

For the case of part A of Procedure, water is the only component in the system, and Eq. (3) becomes:

$$
\begin{equation*}
\left(n_{1}+n_{2}\right) H\left(T_{m i x}\right)-n_{1} H_{1}\left(T_{\text {cold }}\right)-n_{2} H_{1}\left(T_{\text {hot }}\right)=Q \tag{4.2.5}
\end{equation*}
$$

Where Q is the heat transferred to raise the calorimeter itself to T 2 . Since there is no phase change, each of the enthalpies can be replaced by a term involving a heat capacity such as:

$$
\begin{equation*}
H=C_{p}\left(T-T_{r e f}\right) \tag{4.2.6}
\end{equation*}
$$

Where Tref is an arbitrary reference temperature. Also, the increase in temperature of the calorimeter itself corresponds to an increase in its enthalpy given by:

$$
\begin{equation*}
Q=-\Delta H_{c a l}=-m_{c a l} C_{v, c a l}\left(T_{m i x}-T_{\text {cold }}\right) \tag{4.2.7}
\end{equation*}
$$

The mass of the calorimeter cup and its heat capacity do not change for any of the experiments, and so we lump them together as the "calorimeter constant". $A_{c a l} \equiv m_{c a l} C_{v, c a l}$

Putting Equation (4.2.6) and (4.2.7) into (4.2.5) yields an expression with which we can calibrate the calorimeter constant:

$$
\begin{equation*}
A_{\text {cal }}=\frac{\left(n_{1}+n_{2}\right) T_{\text {mix }}-n_{1} T_{\text {cold }}-n_{2} T_{\text {hot }}}{T_{\text {cold }}-T_{\text {mix }}} C_{p} \tag{4.2.8}
\end{equation*}
$$

Estimate the calorimeter constant from the data of part A of Procedure. Take Cp, the specific heat of water to be $1 \mathrm{Btu} / \mathrm{lb} /{ }^{\circ} \mathrm{F}=1 \mathrm{cal} / \mathrm{g} /{ }^{\circ} \mathrm{C}$. The units on Acal should be cal $/{ }^{\circ} \mathrm{C}$.

## B. Heats of mixing and heats of reaction

No phase changes occur in these experiments, and it is reasonable to take the heat capacity of each solution (or component) as a constant over the range of temperatures involved. Thus, we can substitute equations such as (6) into (4) to evaluate the enthalpy changes on the right side of the balance, e.g.

$$
\begin{equation*}
\Delta H_{m i x i n g} n=Q+n_{1} C_{p, 1}\left(T_{i n i}-T_{f i n}\right)+n_{2} C_{p, 2}\left(T_{i n i}-T_{f i n}\right) \tag{4.2.9}
\end{equation*}
$$

The heat of mixing due to nonideality of the solution is often small and thus difficult to measure. On the other hand, the heat of reaction is often large and thus more convenient to measure. The cumulative energy balance Equation (4.2.4) is written in essentially the same way whether the process causing the temperature change is a chemical reaction or nonideal partial molar enthalpies. That is, only the initial and final temperatures are needed to account for the changes in energy. Thus, the calorimeter can measure the heat of reaction if we simply interpret $\Delta$ Hmixing as $\Delta \mathrm{Hrxn}$. Heats of reaction are normally reported per mole of reactants.

Hint $1: \mathrm{n}$ is not necessarily in the unit of mol. n is the amount of substance. It can be in mole or mass or volume, depends on the equation.

Hint 2: Even in the same equation, n can be in different units. In Equation (4.2.9), n 1 and n 2 at the right hand side have the same unit, however n at the left side has a different unit.

### 4.3 Ternary Phase Behavior

Liquid-liquid phase behavior is important for many subsurface applications: emulsion breaking, enhanced oil recovery, and contaminant removal. Many of these processes can be understood in terms of three-component phase behavior. In this lab, students are required to generate the binodal curve and tie lines of the IPA-Hexane-Water mixture.

### 4.3.1 Addition

A supporting document has been generated to guide the students to calculate the volume fraction of each component in each phase, plot the ternary diagram from the experiment data, and find the tie line by using Density method and RI method.

Calculate the volume fraction of each component in each phase
Notation
Brine: $i=1$; Hexane: $\mathrm{i}=2$; IPA: $\mathrm{i}=3$
S1: Inorganic denser phase (Brine + IPA); S2: Organic lighter phase (Hexane + IPA)

One important assumption is ideal mixing. For IPA/Hexane titrated with Brine, $\mathrm{S} 1=0, \mathrm{~S} 2=1$ since the organic phase is saturated.

In this case, since there is only one phase:
$\mathrm{C} 1=\mathrm{V} 1 / \mathrm{VT}$
$\mathrm{C} 2=\mathrm{V} 2 / \mathrm{VT}$
$\mathrm{C} 3=\mathrm{V} 3 / \mathrm{VT}$
Similarly, for IPA/Brine titrated with Hexane, $\mathrm{S} 1=1, \mathrm{~S} 2=0$, the inorganic phase is saturated.

$$
\mathrm{C} 1=\mathrm{V} 1 / \mathrm{VT}
$$

$\mathrm{C} 2=\mathrm{V} 2 / \mathrm{VT}$
$\mathrm{C} 3=\mathrm{V} 3 / \mathrm{VT}$

## Plot the binodal curve

You need to calculate the volumetric fraction and plot them by TRIPLOT 4.1.2: mypage.iu.edu/~tthomps/programs/

You need all the data from Part A to plot on one graph. Link these points and get the saturation line (binodal curve) by hand.

## Draw the tie lines

Assume lower phase only contains brine and IPA, and higher phase only contains hexane and IPA.
a. Density Method

First we measure the mass and volume of the solution and calculate the density of solution. Average density of solution can be calculated after several trails. Then, use the given table to obtain volumetric fraction of IPA (C31). Finally, we will use the volumetric IPA\% (C31) for this specific solution and determine the tie line. This step will be discussed in RI method.
b. RI Method

Similarly, by obtaining the RI of the solution, we can get the volumetric IPA\% (C31) on the calibration curve.

For a,b,c,
$\mathrm{Ci}=\mathrm{Vi} / \mathrm{VT}$
For d, e
S1 = Vmeasured/VT (denser phase)
S2 $=1-\mathrm{S} 1$ (lighter phase)

For f,g,h
We get h from the RI method. f and g can be read from the ternary diagram you generated in Part A.

For i,j,k
$\left\{\begin{array}{l}C_{i}=C_{i 1} S_{1}+C_{i 2} S_{2} \\ S_{1}+S_{2}=1\end{array}\right.$
$\left\{\begin{array}{l}S_{2}=\frac{C_{3}-C_{31}}{C_{32}-C_{31}}=\frac{C_{1}-C_{11}}{C_{12}-C_{11}} \\ S_{1}=\frac{C_{1}-C_{12}}{C_{11}-C_{12}}=\frac{C_{2}-C_{22}}{C_{21}-C_{22}}\end{array}\right.$
Using equation 2 and 3 , we can get $\mathrm{i}, \mathrm{j}, \mathrm{k}$ based on the previous results.
Ci 1 is the final lower phase composition and Ci 2 is the final upper phase composition. Locate Ci1 and Ci2 on the ternary diagram and link it. You should find out the overall composition is on the tie line.

### 4.4 Treating Emulsions

In many surface facilities the co-production of oil and water yields emulsions. Breaking these emulsions so the oil can be sold, and the water disposed can be a severe problem. Emulsions have also been employed as a clever means of transporting heavy (high viscosity) crude oil. The idea of injecting emulsions for enhanced recovery of viscous crudes is being publicly tested and researched. For this lab, students are required to observe the mixing of two immiscible fluids with and without surfactant, observe and record the mixing of immiscible fluids with four surfactants that have different EO numbers, and predict the influence of EO numbers on the surfactant efficiency.

### 4.4.1 Addition

This lab is well organized and up-to-date. The only changes made are format updating and results adding.

## Solution

Pipette 1, EO\# = 5.0

| Time <br> $[\mathrm{min}]$ | \# Phases | Vol Upper <br> $[\mathrm{ml}]$ | Vol Emulsion <br> $[\mathrm{ml}]$ | Vol Lower <br> $[\mathrm{ml}]$ |
| :--- | :--- | :--- | :--- | :--- |
| 0 | 1 | 0.0 | 10.2 | 0.0 |
| 10 | 2 | 0.1 | 10.1 | 0.0 |
| 20 | 2 | 0.2 | 10.0 | 0.0 |
| 30 | 2 | 0.2 | 10.0 | 0.0 |
| 40 | 2 | 0.2 | 10.0 | 0.0 |
| 50 | 2 | 0.3 | 9.9 | 0.0 |
| 60 | 2 | 0.3 | 9.9 | 0.0 |
| 70 | 2 | 0.4 | 9.8 | 0.0 |
| 80 | 2 | 0.4 | 9.8 | 0.0 |
| 90 | 2 | 0.5 | 9.7 | 0.0 |
| 1,200 | 2 | 2.6 | 7.6 | 0.0 |

Table 4.1: Pipette 1 results

Pipette 2, EO\# = 7.8

| Time <br> $[\mathrm{min}]$ | \# Phases | Vol Upper <br> $[\mathrm{ml}]$ | Vol Emulsion <br> $[\mathrm{ml}]$ | Vol Lower <br> $[\mathrm{ml}]$ |
| :--- | :--- | :--- | :--- | :--- |
| 0 | 1 | 0.0 | 10.3 | 0.0 |
| 10 | 2 | 0.0 | 8.0 | 2.4 |
| 20 | 2 | 0.0 | 6.6 | 3.7 |
| 30 | 2 | 0.0 | 5.7 | 4.6 |
| 40 | 2 | 0.0 | 5.3 | 5.0 |
| 50 | 2 | 0.0 | 5.1 | 5.2 |
| 60 | 2 | 0.0 | 5.0 | 5.3 |
| 70 | 2 | 0.0 | 4.9 | 5.4 |
| 80 | 2 | 0.0 | 4.8 | 5.5 |
| 90 | 2 | 0.0 | 4.7 | 5.6 |
| 1,200 | 2 | 0.0 | 3.7 | 6.6 |

Table 4.2: Pipette 2 results

Pipette 3, EO\# = 9.3

| Time <br> $[\mathrm{min}]$ | \# Phases | Vol Upper <br> $[\mathrm{ml}]$ | Vol Emulsion <br> $[\mathrm{ml}]$ | Vol Lower <br> $[\mathrm{ml}]$ |
| :--- | :--- | :--- | :--- | :--- |
| 0 | 1 | 0.0 | 10.3 | 0.0 |
| 10 | 2 | 0.0 | 7.2 | 3.1 |
| 20 | 2 | 0.0 | 5.7 | 4.6 |
| 30 | 2 | 0.0 | 5.4 | 4.9 |
| 40 | 2 | 0.0 | 5.2 | 5.1 |
| 50 | 2 | 0.0 | 5.1 | 5.2 |
| 60 | 2 | 0.0 | 5.0 | 5.3 |
| 70 | 2 | 0.0 | 4.9 | 5.4 |
| 80 | 2 | 0.0 | 4.9 | 5.5 |
| 90 | 2 | 0.0 | 4.9 | 5.5 |
| 1,200 | 2 | 0.0 | 4.2 | 6.1 |

Table 4.3: Pipette 3 results

Pipette 4, EO\# = 15.0

| Time <br> $[\mathrm{min}]$ | \# Phases | Vol Upper <br> $[\mathrm{ml}]$ | Vol Emulsion <br> $[\mathrm{ml}]$ | Vol Lower <br> $[\mathrm{ml}]$ |
| :--- | :--- | :--- | :--- | :--- |
| 0 | 1 | 0.0 | 9.9 | 0.0 |
| 10 | 2 | 0.0 | 4.6 | 5.3 |
| 20 | 2 | 0.0 | 4.1 | 5.8 |
| 30 | 2 | 0.0 | 4.0 | 5.9 |
| 40 | 2 | 0.0 | 3.9 | 6.0 |
| 50 | 2 | 0.0 | 3.9 | 6.0 |
| 60 | 2 | 0.0 | 3.8 | 6.1 |
| 70 | 2 | 0.0 | 3.8 | 6.1 |
| 80 | 2 | 0.0 | 3.8 | 6.2 |
| 90 | 2 | 0.0 | 3.7 | 6.2 |
| 1,200 | 3 | 0.0 | 3.6 | 6.3 |

Table 4.4: Pipette 4 results

### 4.5 Surface/ Interfacial Tension and Contact Angle

There is no branch of engineering to which capillary forces are as important as petroleum engineering. Capillary pressure is a basic reservoir characterization tool. It determines the equilibrium distribution of phases in a reservoir and is by far the major factor in determining the magnitude of residual phase saturations. In this experiment, students have to determine the interfacial tension between different fluids by using both ring method and spinning drop method. The lab also ask students to measure the contact angle between solid glass, liquid water and air.

### 4.5.1 Reduction

Wilhelmy plate tensiometer is not available in the laboratory. Thus, Wilhelmy Plate Method is no longer required in this lab. The contents has been removed to avoid confusion.

### 4.5.2 Modification

The equation to calculate interfacial tension in the Spinning drop method is incorrect. The conversion factor has been corrected based on derivation from the original equation.

$$
\begin{equation*}
\sigma=\frac{\Delta \rho \omega^{2} r^{3}}{4} \tag{4.5.1}
\end{equation*}
$$

Where
$\omega=$ angular speed $[1 / \mathrm{s}]$
$\mathrm{r}=$ radius [ cm ]
$\rho=$ density $[\mathrm{g} / \mathrm{cm} 3]$
$\sigma=$ IFT [dynes/cm]

In the lab, we measure:
$\mathrm{T}=$ Temperature $\left({ }^{\circ} \mathrm{C}\right.$, for density calculation)
$d$ = diameter of drop [mm]
$\mathrm{P}=$ period (millisecond per revolution) [ $\mathrm{s} / 1000]$

The Equation (4.5.1) can be simplified to:

$$
\begin{equation*}
\sigma_{L V}=1.2337 \times 10^{6} \frac{\Delta \rho d^{3}}{P^{2}} \tag{4.5.2}
\end{equation*}
$$

where
$d$ = diameter of drop [mm]
$\mathrm{P}=$ period (millisecond per revolution) [ $\mathrm{s} / 1000]$
$\rho=\operatorname{density}[\mathrm{g} / \mathrm{cm} 3]$

### 4.6 Compatibility of Oilfield Brines

Water flooding is an extremely common way to produce additional oil from a reservoir. One of the problems associated with water flooding is that the water being injected can damage the formation. In this experiment, the students are required to identify the scale by using solubility product, measured the minimum amount of inhibitor to prevent the scale formation, and explore the trade-off between plugging and scale treatment by using experiment data and economic calculation.

### 4.6.1 Modification

The lab materials of water flooding and scale treatment is an important topic in the Petroleum Engineering. However, most of the sophomores are not familiar with the concept of solubility product in chemistry. The original results section demanded the students to identify and calculate the scale using this unfamiliar chemistry concept. The modified results section guides the students to go through the identification and calculation process step by step. The modified discussion section helps the students focus on the engineering significance of the water flooding and scale treating.

Results:

1. Use the tabulated free energies to identify the scale resulting from the mixing in step one. Possible candidates are barium chloride BaCl 2 , barium sulfate BaSO4, sodium chloride NaCl , and disodium sulfate Na 2 SO 4 .
2. Use the tabulated free energies to estimate the concentrations and the amount of solid formed from the mixing in step one. Compare the results of your calculation to the amount measured in step 2 .
3. Using the estimated concentrations of the solid-saturated solutions, calculate how much of each solution can be mixed with the other to just initiate precipitation. Compare your results with those of steps 3 and 4 .

### 4.6.2 Addition

Along with the results section modification, a step-by-step supporting document is provided to the students to go through the chemistry calculation.

## Scale Identification and Calculation

a. Calculate the solubility product for each reaction

For product solubility constant

$$
\begin{gathered}
\mathrm{AaBb}(\mathrm{~s}) \leftrightarrow \mathrm{aA}^{\mathrm{b}+}+\mathrm{bB}^{\mathrm{a}-} \text { dissolution } \\
K_{s p}=\frac{\left\{A^{b+}\right\}^{a}\left\{B^{a-}\right\}^{b}}{\left\{A_{a} B_{b(s)}\right\}}
\end{gathered}
$$

$A_{a} B_{b(s)}$ goes to 1 due to activity of a solid
So the corrected reaction should be

$$
\begin{aligned}
& \mathrm{BaCl}_{2} \rightarrow B a^{2+}+2 \mathrm{Cl}^{-} \\
& K_{s p}=\exp \left(-\frac{\Delta G_{f-r x n}^{o}}{R T}\right) \\
& K_{s p}=\exp \left(-\frac{\left.\sum\left|v_{i}\right| \Delta G_{f-\text { product }}^{o}-\sum\left|v_{i}\right| \Delta G_{f-\text { reactant }}^{o}\right)}{R T}\right) \\
& K_{s p}=\exp \left(-\frac{1 * \Delta G_{f-B a^{2+}}^{o}+2 * \Delta G_{f-C l^{-}}^{o}-1 * \Delta G_{f-B a C l_{2}}^{o}}{R T}\right) \\
& K_{s p}=\exp \left(-\frac{-134000-2 * 31350+193800}{1.987 * 293}\right) \\
& =145.646
\end{aligned}
$$

Notation:
$\mathrm{Ksp}=$ solubility product constant
$\Delta G_{f-i}^{o}=$ standard gibbs free energy of formation of i (i can be reaction, products
etc.)
$\mathrm{vi}=$ Stoichiometric coefficient $(+$ for product, - for reactant $)$

For our sample reaction, the standard $\Delta \mathrm{G}$ is a negative number ( $-2900 \mathrm{cal} / \mathrm{mol}$ ), this is an indication of spontaneous reaction. Or you can consider it as BaCl 2 tend to stay in the way of separate ions rather than form a solid precipitate.
$\mathrm{K} s \mathrm{BaSO} 4=9.3 \mathrm{e}-10$
$\mathrm{K} s \mathrm{NaCl}=40.439$
Ksp Na2SO4 $=0.638$
b. Identify the scale that formed from Part A

$$
\begin{aligned}
& \mathrm{BaCl}_{2} \rightarrow \mathrm{Ba}^{2+}+2 \mathrm{Cl}^{-} \\
& \text {mole }\left[\mathrm{Ba}^{2+}\right]=0.01 \frac{\mathrm{~mole}}{l} * 50 \mathrm{ml} * \frac{1 l}{1000 \mathrm{ml}}=5 e-4 \text { mole } \\
& V_{\text {mixing }}=(50 \mathrm{ml}+50 \mathrm{ml}) * \frac{1 l}{1000 \mathrm{ml}}=0.1 \mathrm{l} \\
& C\left[\mathrm{Ba}^{2+}\right]=\frac{\operatorname{mole}\left[\mathrm{Ba}^{2+}\right]}{V_{\text {mixing }}}=5 e-3 \text { mole } / l \\
& \text { Similarily, } C\left[\mathrm{Cl}^{-}\right]=\frac{\text { mole }\left[\mathrm{Cl}^{-}\right]}{V_{\text {mixing }}}=0.01 \text { mole } / l \\
& K_{s p-a c t u a l}=C\left[\mathrm{Ba}^{2+}\right] C\left[\mathrm{Cl}^{-}\right]^{2}=5 e-7 \\
& K_{s p-a c t u a l}<K_{s p-B a C l_{2}}
\end{aligned}
$$

Thus, BaCl 2 will not be the scale.
The only scale formed is BaSO 4

$$
\begin{aligned}
& \operatorname{mole}\left[\mathrm{Ba}^{2+}\right]=0.01 \frac{\mathrm{~mole}}{l} * 50 \mathrm{ml} * \frac{1 l}{1000 \mathrm{ml}}=5 e-4 \mathrm{~mole} \\
& V_{\text {mixing }}=(50 \mathrm{ml}+50 \mathrm{ml}) * \frac{1 l}{1000 \mathrm{ml}}=0.1 \mathrm{l} \\
& C\left[\mathrm{Ba}^{2+}\right]=\frac{\text { mole }\left[\mathrm{Ba}^{2+}\right]}{V_{\text {mixing }}}=5 e-3 \mathrm{~mole} / l \\
& \text { Similarily, } C\left[\mathrm{SO}_{4}^{2-}\right]=\frac{\text { mole }\left[\mathrm{SO}_{4}^{2-}\right]}{V_{\text {mixing }}}=5 e-3 \text { mole } / l \\
& K_{s p-\text { actual }}=C\left[\mathrm{Ba}^{2+}\right] C\left[\mathrm{SO}_{4}^{2-}\right]=2.5 e-5 \\
& K_{s p-a c t u a l}>K_{s p-B a S O_{4}}
\end{aligned}
$$

c. Calculate the mass of the scale

$$
\begin{aligned}
& C_{\mathrm{BaSO}_{4}}=5 e-3 \frac{\mathrm{~mole}}{l} \\
& m_{\text {BaSO}_{4}}=C_{\mathrm{BaSO}_{4}} * M W_{\text {BaSO}_{4}} * V_{\text {mixing }} \\
& =5 e-3 \frac{\text { mole }}{l} * 233.3906 \frac{\mathrm{~g}}{\mathrm{~mole}} * 0.1 l \\
& =0.117 \mathrm{~g}
\end{aligned}
$$

## Appendix A: Mixing Properties Lab Manual

## Objectives

1. Give some idea about the behavior of binary mixtures
2. Clarify some esoteric (though important) things like partial molar quantities

## BACKGROUND

Because very few naturally occurring materials are pure, mixture properties play an everyday role in subsurface engineering. Hydrocarbons in particular are mixtures of many components, as are formation brines. One of the most relevant applications of mixture properties is the design and optimization of separation processes and equipment.

This discussion uses the background in Smith, van Ness, and Abbott (SvNA, 2001), Sec. 11.3 and Sec. 11.9 and largely reproduced below. When dealing with liquid solutions, it is often convenient to deal with properties that measure deviations from ideal solution behavior. This is the notion of an "excess property" defined by
$M^{E}=M-M^{\text {ideal }}$
where $\mathrm{M}_{\mathrm{E}}$ is the excess property of the solution
$M$ is the actual value of the property of the solution
$\mathrm{M}^{\text {ideal }}$ is the value of the property of the solution if the solution were ideal
SvNA discuss the application of this equation to all thermodynamic properties; we will deal only with volume here.

The molar volume of an ideal solution is simply the mole-fraction-weighted sum of the molar volumes of the solution components:

$$
V^{\text {ideal }}=\sum_{i} x_{i} V_{i}
$$

where $\mathrm{V}_{\mathrm{i}}$ is the molar volume of the pure component i
$\mathrm{x}_{\mathrm{i}}$ is the mole fraction of component i in the mixture (the composition)

The excess volume of a mixture is therefore given by
$V^{E}=V-\sum_{i} x_{i} V_{i}$
where $V^{\mathrm{E}}$ is the "excess volume" of the mixture
V is the molar volume of the mixture
The actual molar volume V is what one measures in the lab. The molar volume of a mixture is related to the partial molar volumes of the components of the mixture by the following equation:
$V=\sum_{i} x_{i} \bar{V}_{i}$
Where is the partial molar volume of component $i$ in the mixture.
For a binary mixture, like the ones in this lab, we have:
$V=x_{1} \bar{V}_{1}+x_{2} \bar{V}_{2}$

## Apparatus and Materials

The apparatus used in this experiment is very basic: graduated cylinders, pipettes, thermometers, and scales.

We will use the following chemicals:

| Chemicals | Specific Gravity | Molecular Weight $(\mathrm{g} / \mathrm{mol})$ |
| :--- | :--- | :--- |
| Isopropyl alcohol (IPA) | 0.786 | 60.11 |
| Calcium chloride (CaCl2) | 2.15 | 110.99 |
| Distilled water | 1.00 | 18 |
| Hexane | 0.66 | 86.18 |

## Procedure

The measured volumes for the components of the mixture should be the volumes provided in the charts. If the volumes you have measured are not exactly the volumes in the charts, then you must record the experimental volumes (as stated below).

You should record the initial and final temperatures for each mixture. Assume room temperature for the initial temperature, and measure the final temperature using the provided thermometer.

Part A
Use the table provided below to obtain volumes of mixtures.
Mole $\% \mathrm{CaCl} 2 \quad$ Mass $\mathrm{CaCl} 2(\mathrm{~g}) \quad$ Vol. $\mathrm{H} 2 \mathrm{O}(\mathrm{ml})$
$0 \quad 0 \quad 8$
$\begin{array}{lll}2 & 1 & 7.9\end{array}$
$\begin{array}{lll}4 & 2 & 7.8\end{array}$
$6 \quad 3 \quad 7.6$

8
4
7.5

10
5
7.3

1. Use the provided scales to obtain the desired masses.
2. Place a plastic weighing dish on the scale.
3. Tare the reading to zero.
4. Measure the desired amount of CaCl 2 .
5. Record the measured amount.
6. Repeat for the remaining masses listed above.
7. Use the pipettes provided to measure the volumes.
8. Pour the measured water into a small beaker.
9. Once the water has been poured in the beaker, carefully pour the CaCl 2 into the water.
10. Allow the CaCl 2 to dissolve completely. (You may need to swirl the mixture.)
11. Once the CaCl 2 has dissolved, pour the mixture into a 10 ml graduated cylinder.
12. Record the final volume.

## Part B

Use the table provided below to obtain volumes of mixtures.

| Mole \% IPA | Vol. IPA (ml) | Vol. H20 (ml) |
| :--- | :--- | :--- |
| 0 | 0 | 10 |
| 20 | 10 | 9.4 |
| 40 | 10 | 3.5 |
| 60 | 10 | 1.6 |
| 80 | 10 | 0.6 |
| 100 | 10 | 0 |

1. Use the provided pipettes to measure the volumes.
2. To minimize error, pour the measured IPA directly into a 25 ml graduated cylinder.
3. Record the volume.
4. Repeat for the remaining volumes listed above.
5. Use the pipettes provided to measure the volumes.
6. Record the volume.
7. Repeat for the remaining volumes listed above.
8. Once the IPA has been poured in the graduated cylinder, carefully pour the water into the appropriate graduated cylinder.
9. Allow the components to mix.
10. Record the final volume.

## Part C

Use the table provided below to obtain volumes of mixtures.
Mole \% IPA Vol. IPA (ml) Vol. Hexane (ml)

| 0 | 0 | 10 |
| :--- | :--- | :--- |
| 20 | 1 | 6.8 |
| 40 | 2 | 5.1 |
| 60 | 6 | 6.7 |
| 80 | 8 | 3.4 |
| 100 | 10 | 0 |

1. Use the provided pipettes to measure the volumes.
2. In order to minimize error, pour the measured IPA directly into a 25 ml graduated cylinder.
3. Record the volume.
4. Repeat for the remaining volumes listed above.
5. Use the pipettes provided to measure the volumes.
6. Record the volume.
7. Repeat for the remaining volumes listed above.
8. Once the IPA has been poured in the graduated cylinder, carefully pour the hexane into the appropriate graduated cylinder.
9. Allow the components to mix.
10. Record the final volume.

## Results

Make sure you label all data tables and graphs clearly. Don't forget units!!
Since the required volumes were already given, show calculations of how those values were found. Specifically, find the volumes of water for Part A and B, and find the volume of hexane for Part C. You need not show calculations for $0 \%$ and $100 \%$, pick one of the percentages for each mixture. Use the information provided in the "Materials" section of the lab, the given mole fractions, and masses/volumes of the given component to help you.

Construct a table with the following data included:
a. Specified mixture (i.e. IPA-Hexane)
b. Mole fraction (i.e. XIPA)
c. Ideal total volume (i.e. 10 ml )
d. Experimental total volume (i.e. 10.5 ml )

For each of the three mixtures, construct plots of the following:
a. Ideal molar volume vs. mole fraction of substance added
b. Actual molar volume vs. mole fraction of substance added
c. Excess molar volume vs. mole fraction of substance added
d. Partial molar volume vs. mole fraction of substance added

The ideal, actual, and excess molar volume plots should be on the same graph for each mixture. For part 3a, b, and c, this means that you will have a total of one graphs with three plots included.

The partial molar volume graphs should be for each mixture. You will have two plots for each graph (i.e. for the IPA-Hexane mixture, you will have both the IPA and Hexane partial molar volumes plotted vs. the mole fraction of IPA). There will be a total of three graphs for part 3d. Hint: To plot the partial molar volumes, you will need to find the slope of the ideal molar volume-use trend lines to approximate the equation.)

## DISCUSSION

1. Identify which of the fluid pairs are the closest to ideal mixtures. Explain why you chose that pair using the plots made above as reference.
2. Estimate the partial molar volumes of each component at infinite dilution.
3. Based on what you know about the chemicals and their underlying chemistry, discuss why the deviations from ideal behavior are as you have observed. That is, explain why a particular component should have a volume different than its pure state in each mixture. Be sure to describe the behaviors for each of the three mixtures. (Hint: don't forget to use the temperatures.)

## Appendix B: Thermochemistry: Measuring Heat of Reaction

## ObJectives

1. Become familiar with a simple method for measuring heat of chemical reaction
2. To measure the heat evolved in aqueous reaction
3. Determine enthalpy changes $(\Delta \mathrm{Hrxn})$ for a series of chemical reactions
4. Apply mass and energy balances

## Background

In this experiment, we investigate the energy changes in the form of heat that accompany chemical reactions; this area of physical chemistry is known as thermochemistry. The basic approach is to place prescribed volumes or masses of two different components (pure phases) into an insulated container, which is then closed, and the two components mixed.

The system is where primary changes like reactions or phase changes occur; the surroundings include everything outside the system. In this experiment the system is the reactants and products of the various reactions, i.e. the contents of the container. The surroundings consist of the reaction container (called a calorimeter), the room, the building about the room, and anything other than the reactants and products. What do you anticipate will be a convenient control volume for analyzing this experiment?

If a reaction produces energy in the form of heat, the reaction is exothermic. If the reaction container is not well insulated, then in general the energy released by the reaction flows from the system into the surroundings. Thus is negative, according to the usual convention. Reactions that absorb heat are endothermic. If the reaction container is not well insulated, then heat will flow into the system from the surroundings, and will be positive.

We will use cumulative (or batch) mass and energy balances here. The reaction container is closed after the reactants are placed within it. Thus, the cumulative balance for total moles n within the system (control volume is the reaction container) reduces to:

$$
\begin{equation*}
0=\left.n\right|_{t_{2}}-\left.n\right|_{t_{1}} \tag{1}
\end{equation*}
$$

Where t 1 is the time before the two components are added to the container, and t 2 is the time at which the experiment is halted (typically, when the temperature becomes constant). The energy balance reduces to

$$
\begin{equation*}
\left.(n H)\right|_{t_{2}}-\left.(n H)\right|_{t_{1}}=Q \tag{2}
\end{equation*}
$$

Where we have neglected all forms of energy except internal and enthalpy. The term H represents the molar enthalpy of the mixture. The term Q represents the cumulative heat transferred to or from the system between time t 1 and t 2 ; note the absence of the "dot" since we are working with a cumulative balance. The work term is absent since there are no moving parts.

Notation:
$\mathrm{ab}: \mathrm{a}$ * b
$a(b)$ : $a$ is a function of $b$
$\mathrm{a} \mid \mathrm{b}$ : a at condition b
For a binary mixture obtained by mixing n 1 moles of pure component 1 at initial temperature Tini with n 2 moles of pure component 2 at Tini, these two temperatures are not necessarily the same, the initial enthalpy of the system is
$\left.(n H)\right|_{t_{1}}=n_{1} H_{1}\left(T_{i n i}\right)+n_{2} H_{2}\left(T_{i n i}\right)$
And the final enthalpy is
$\left.(n H)\right|_{t_{2}}=\left(n_{1}+n_{2}\right) H\left(T_{\text {fin }}\right)$
The energy balance Eq. (2) can then be written

$$
\begin{equation*}
H\left(T_{f i n}\right)-x_{1} H_{1}\left(T_{i n i}\right)-x_{2} H_{2}\left(T_{i n i}\right)=\frac{Q}{n} \tag{3}
\end{equation*}
$$

Where. The left side of Eq. (3) appears to be the definition of the enthalpy of mixing:

$$
\Delta H_{m i x i n g} \equiv H^{E}=H-\left(x_{1} H_{1}+x_{2} H_{2}\right)
$$

But it is not, because in general the final temperature of the contents of the container T 2 will be different than the initial temperature. The enthalpy of mixing (also known as the excess enthalpy) is defined for a constant temperature and pressure, thus in the definition equation you don't see enthalpy as a function of temperature. To obtain the correct form of enthalpy of mixing, we add and subtract the enthalpies of the components at temperature T2 (i.e. at time t2) to the left side of (3):

$$
H\left(T_{f i n}\right)-x_{1} H_{1}\left(T_{i n i}\right)-x_{2} H_{2}\left(T_{i n i}\right)+\left[x_{1} H_{1}\left(T_{f i n}\right)-x_{1} H_{1}\left(T_{f i n}\right)\right]+\left[x_{2} H_{2}\left(T_{f i n}\right)-x_{2} H_{2}\left(T_{f i n}\right)\right]=\frac{Q}{n}
$$

Notice the equation does not change, the purpose is to match the definition. After gathering the enthalpies at time t 2 on the left side, we obtain

$$
H\left(T_{f i n}\right)-x_{1} H_{1}\left(T_{f i n}\right)-x_{2} H_{2}\left(T_{f i n}\right)=\frac{Q}{n}+x_{1} H_{1}\left(T_{i n i}\right)-x_{1} H_{1}\left(T_{f i n}\right)+x_{2} H_{2}\left(T_{i n i}\right)-x_{2} H_{2}\left(T_{f i n}\right)
$$

And finally

$$
\begin{equation*}
\Delta H_{\text {mixing }}=\frac{Q}{n}+x_{1}\left(H_{1}\left(T_{i n i}\right)-H_{1}\left(T_{\text {fin }}\right)\right)+x_{2}\left(H_{2}\left(T_{\text {ini }}\right)-H_{2}\left(T_{\text {fin }}\right)\right) \tag{4}
\end{equation*}
$$

In the ideal case of a perfectly insulated container, the cumulative heat transfer Q is zero. For real containers, even well insulated ones, Q is nonzero, because the temperature of the container itself changes from initial Tini to final Tfin.

## Analysis

Calorimeter constant

For the case of part A of Procedure, water is the only component in the system, and Eq. (3) becomes

$$
\begin{equation*}
\left(n_{1}+n_{2}\right) H\left(T_{\text {mix }}\right)-n_{1} H_{1}\left(T_{\text {cold }}\right)-n_{2} H_{1}\left(T_{\text {hot }}\right)=Q \tag{5}
\end{equation*}
$$

Where Q is the heat transferred to raise the calorimeter itself to T 2 . Since there is no phase change, each of the enthalpies can be replaced by a term involving a heat capacity such as

$$
\begin{equation*}
H=C_{p}\left(T-T_{r e f}\right) \tag{6}
\end{equation*}
$$

Where Tref is an arbitrary reference temperature. Also, the increase in temperature of the calorimeter itself corresponds to an increase in its enthalpy given by

$$
\begin{equation*}
Q=-\Delta H_{c a l}=-m_{c a l} C_{v, \text { cal }}\left(T_{m i x}-T_{c o l d}\right) \tag{7}
\end{equation*}
$$

The mass of the calorimeter cup and its heat capacity do not change for any of the experiments, and so we lump them together as the "calorimeter constant":

$$
A_{c a l} \equiv m_{c a l} C_{v, c a l}
$$

Putting (6) and (7) into (5) yields an expression with which we can calibrate the calorimeter constant

$$
\begin{equation*}
A_{\text {cal }}=\frac{\left(n_{1}+n_{2}\right) T_{m i x}-n_{1} T_{\text {cold }}-n_{2} T_{\text {hot }}}{T_{\text {cold }}-T_{m i x}} C_{p} \tag{8}
\end{equation*}
$$

Estimate the calorimeter constant from the data of part A of Procedure. Take Cp, the specific heat of water to be $1 \mathrm{Btu} / \mathrm{lb} /{ }^{\circ} \mathrm{F}=1 \mathrm{cal} / \mathrm{g} /{ }^{\circ} \mathrm{C}$. The units on Acal should be cal $/{ }^{\circ} \mathrm{C}$.

Heats of mixing and heats of reaction.
No phase changes occur in these experiments, and it is reasonable to take the heat capacity of each solution (or component) as a constant over the range of temperatures involved. Thus, we can substitute equations such as (6) into (4) to evaluate the enthalpy changes on the right side of the balance, e.g.

$$
\begin{equation*}
\Delta H_{\text {mixing }} n=Q+n_{1} C_{p, 1}\left(T_{i n i}-T_{f i n}\right)+n_{2} C_{p, 2}\left(T_{i n i}-T_{f i n}\right) \tag{9}
\end{equation*}
$$

The heat of mixing due to nonideality of the solution is often small and thus difficult to measure. On the other hand, the heat of reaction is often large and thus more convenient to measure. The cumulative energy balance Eq. (4) is written in essentially the same way whether the process causing the temperature change is a chemical reaction or nonideal partial molar enthalpies. That is, only the initial and final temperatures are needed to account for the changes in energy. Thus, the calorimeter can measure the heat of reaction if we simply interpret $\Delta$ Hmixing as $\Delta \mathrm{Hrxn}$. Heats of reaction are normally reported per mole of reactants.

Hint $1: \mathrm{n}$ is not necessarily in the unit of mol. n is the amount of substance. It can be in mole or mass or volume, depends on the equation.

Hint 2: Even in the same equation, n can be in different units. In Eq. (9), n1 and n2 have the same unit, however n at the left side has a different unit.

## Procedure

## Part A: Calorimeter Constant

1. Measure 100 ml of distilled water into a beaker. This will be n 2 in your calculations.
2. Place the beaker onto a hot plate and heat it to a temperature of $60-70$ degrees Celsius. (Try to aim for the same value when repeating trials.)
3. Meanwhile, measure another 100 ml of distilled water. This will be n 1 in your calculations.
4. Pour the water into the calorimeter.
5. Allow the water in the calorimeter to sit for at least 30 seconds.
6. Record the temperature of the water in the calorimeter. This will be Tcold in your calculations. We assume the liquid and container have the same temperature after 30s.
7. Once the hot water has reached an adequate temperature, remove the beaker from the hot plate and stir to ensure a uniform temperature.
8. Record the maximum temperature of the hot water. This will be Thot in your calculations.
9. Quickly pour the hot water into the calorimeter (that is mix with the cold water) and replace the lid; swirl briefly.
10. Watch the temperature until it does not change and record the final temperature. Be sure you do not take this reading too soon; wait at least 30 seconds. This will be Tmix in your calculations. Again, we assume the system (liquid + container) reached equilibrium.
11. Repeat the above steps for four additional trials. Between trials, rinse the calorimeter with cold water to bring the temperature back to room temperature.
12. After five trials, you must calculate your calorimeter constants. **For your unit to be cal $/{ }^{\circ} \mathrm{C}$, check the unit of n 1 and n 2 . (Hint: Take into account density of water.) Part B: Heats of reactions

The following reactions involve acids and bases. Be sure to use proper lab attire including gloves and goggles. Be sure to dispose of the chemicals in the proper waste bottles.

$$
\mathrm{HCl}+\mathrm{NH} 4 \mathrm{OH} \rightarrow \mathrm{Cl}-+\mathrm{NH} 4++\mathrm{H} 2 \mathrm{O}
$$

1. Measure 50 ml of 1 M NH 4 OH . (Density $=0.9 \mathrm{~g} / \mathrm{ml}$ )
2. Pour it into the calorimeter and replace the lid (with thermometer).
3. Measure 50 ml of 1 M HCl . $($ Density $=1.19 \mathrm{~g} / \mathrm{ml})$
4. Take and record the temperature of HCl with a second thermometer.
5. Take and record the temperature of NH 4 OH with the thermometer in the calorimeter.
6. Quickly and carefully pour the HCl into the calorimeter, closing the lid with the thermometer originally positioned.
7. Swirl the calorimeter for $5-10$ seconds.
8. Wait for the temperature to stabilize.
9. Estimate the time it takes for the temperature to stabilize.
10. Record the maximum temperature.
$\mathrm{HCl}+\mathrm{NaC} 2 \mathrm{H} 3 \mathrm{O} 2 \rightarrow \mathrm{H}++\mathrm{Cl}-+\mathrm{Na}++\mathrm{C} 2 \mathrm{H} 3 \mathrm{O} 2-$
11. Make sure the calorimeter is rinsed and dried.
12. Measure 50 ml of 1 M NaC 2 H 3 O 2 .
13. Pour the NaC 2 H 3 O 2 into the calorimeter and replace the lid.
14. Measure 50 ml of 1 M HCl .
15. Take and record the temperature of HCl with a second thermometer.
16. Take and record the temperature of NaC 2 H 3 O 2 with the thermometer in the calorimeter.
17. Quickly and carefully pour the HCl into the calorimeter, closing the lid with the thermometer originally positioned.
18. Swirl the calorimeter for 10 seconds.
19. Wait for the temperature to stabilize.
20. Estimate the time it takes for the temperature to stabilize.
21. Record the maximum temperature.

H 2 O (distilled) $+\mathrm{CaCl} 2 \rightarrow \mathrm{Ca} 2++2 \mathrm{Cl}-+\mathrm{H} 2 \mathrm{O}$

1. Make sure the calorimeter is rinsed and dried.
2. Measure 5 g of CaCl 2 .
3. Pour the CaCl 2 into the calorimeter and replace the lid.
4. Measure 50 ml of DI H 2 O .
5. Take and record the temperature of H 2 O with a second thermometer.
6. Take and record the temperature of CaCl 2 with the thermometer in the calorimeter.
7. Quickly and carefully pour the H 2 O into the calorimeter, closing the lid with the thermometer originally positioned.
8. Swirl the calorimeter for 10 seconds.
9. Wait for the temperature to stabilize.
10. Estimate the time it takes for the temperature to stabilize.
11. Record the maximum temperature.

H 2 O (distilled) $+\mathrm{NH} 4 \mathrm{NO} 3 \rightarrow \mathrm{NH} 4++\mathrm{NO} 3-+\mathrm{H} 2 \mathrm{O}$

1. Make sure the calorimeter is rinsed and dried.
2. Measure 10 g of NH 4 NO 3 .
3. Pour the NH 4 NO 3 into the calorimeter and replace the lid.
4. Measure 50 ml of DI H 2 O .
5. Take and record the temperature of H 2 O with a second thermometer.
6. Take and record the temperature of NH4NO3 with the thermometer in the calorimeter.
7. Quickly and carefully pour the H 2 O into the calorimeter, closing the lid with the thermometer originally positioned.
8. Swirl the calorimeter for 10 seconds.
9. Wait for the temperature to stabilize.
10. Estimate the time it takes for the temperature to stabilize.
11. Record the minimum temperature.

## Results

Make a table that includes the following information for Part A:

1. Trial number
2. Cold water volume (ml)
3. Hot water volume (ml)
4. Mixed volume (ml)
5. Temperature of cold water $\left({ }^{\circ} \mathrm{C}\right)$
6. Temperature of hot water $\left({ }^{\circ} \mathrm{C}\right)$
7. Final temperature $\left({ }^{\circ} \mathrm{C}\right)$

Indicate which trials were used to find the calorimeter constant. Report the calorimeter constant and include sample calculations used to find those values.

Make a table that includes the following information for Part B:

1. Reaction
2. Acid volume (ml)
3. Base volume $/$ mass $(\mathrm{ml} / \mathrm{g})$
4. Temperature of acid $\left({ }^{\circ} \mathrm{C}\right)$
5. Temperature of base $\left({ }^{\circ} \mathrm{C}\right)$
6. Final temperature $\left({ }^{\circ} \mathrm{C}\right)$

Make a table that includes the following information for Part B:

1. Reaction
2. Heat of reaction (cal/mol reactant)
3. Estimated stabilize time
4. Final temperature $\left({ }^{\circ} \mathrm{C}\right)$

You may assume that the specific heat capacities are constant (i.e. $\mathrm{Cp}, 1=\mathrm{Cp}, 2=1$ $\mathrm{cal} /{ }^{\circ} \mathrm{C}$ ). Make sure your units are consistent. (Hint: you must use molecular weights.)

## DISCUSSION

While deriving Equation (9), it was assumed that internal energies and enthalpies were the same. Show that this is a valid assumption by comparing the PV term to the heats of reactions. You may assume $\mathrm{P}=1 \mathrm{~atm}$. Remember the general equation is as follows:
$\mathrm{H}-\mathrm{U}=\mathrm{PV}$. Assume the total volume of mixture does not change after reaction. Show calculation for the first reaction: $\mathrm{HCl}+\mathrm{NH} 4 \mathrm{OH}$.

The following table contains the standard heats of formations:

| Substance | $\Delta H f(\mathrm{cal} / \mathrm{mol})$ |
| :--- | :--- |
| $\mathrm{NH} 4 \mathrm{OH}(\mathrm{s})$ | -86770.33493 |
| $\mathrm{OH}-(\mathrm{aq})$ | -55047.84689 |
| $\mathrm{NH} 4+(\mathrm{aq})$ | -31698.56459 |
| $\mathrm{NO} 3-(\mathrm{aq})$ | -49425.83732 |
| $\mathrm{NH} 4 \mathrm{NO} 3(\mathrm{~s})$ | -87464.11483 |
| HCl | -22057.41627 |
| H 2 O (liquid) | -68312.61950 |
| $\mathrm{H}+$ | 0 |
| $\mathrm{Cl}-$ | -39976.07656 |


| NaC 2 H 3 O 2 | -173803.8278 |
| :--- | :--- |
| $\mathrm{Na}+$ | -57535.88571 |
| $\mathrm{C} 2 \mathrm{H} 3 \mathrm{O} 2-$ | -116339.7129 |
| CaCl 2 | -190406.6986 |
| $\mathrm{Ca} 2+$ | -130000 |

Calculate the heats of reactions from the heats of formations. Compare your experimental values with these calculated values. Show calculation for the first reaction: $\mathrm{HCl}+\mathrm{NH} 4 \mathrm{OH}$. If your experimental values differ from the calculated values in \#2, explain possible reasons for the variations.

## Appendix C: Ternary Phase Behavior

## ObJectives

1. Observe the immiscibility of liquid phases and its dependence on composition
2. Learn the definitions of miscible, immiscible and semi-miscible fluids
3. Gain practice in constructing ternary diagrams
4. See an application of the phase rule
5. Understand the difference between overall and phase compositions
6. Learn about developed miscibility

## BACKGROUND

Liquid-liquid phase behavior is important for many subsurface applications: emulsion breaking, enhanced oil recovery, and contaminant removal. Many of these processes can be understood in terms of three-component phase behavior. Such ternary phase behavior is the subject of this experiment.

In this experiment we will construct the saturation line or binodal curve in the isopropyl alcohol/brine/hexane system and then attempt to put tie lines into the interior of the two-phase region. We can also illustrate the development of miscibility in a condensing gas drive displacement.

One of the simplest (and most important) results of thermodynamics is the Gibbs phase rule
$\mathrm{NF}=\mathrm{NC}-\mathrm{NP}$
For fixed temperature and pressure and no reactions occurring. NF $(\geq 0)$ is the number of "degrees of freedom" needed to specify the equilibrium state of a system consisting of NP phases and NC components. "Specify" means determine the number, identity and composition of the phases that will form. A ternary system $(\mathrm{NC}=3)$, therefore,
can have no more than NP $=3$ phases because such a system has zero degrees of freedom $(\mathrm{NF}=0)$. A ternary system that forms $\mathrm{NP}=2$ phases has one degree of freedom. To fix this degree of freedom we must determine the concentration of one component; once this is done, we have completely specified the equilibrium state of the system. In other words, we can calculate the amount of each phase and the concentration within them.

The overall or total volumetric concentration of a component $i$ in a ternary system that forms two phases $(\mathrm{NP}=2)$ is given by

$$
\begin{equation*}
\mathrm{Ci}=\mathrm{Ci} 1 \mathrm{~S} 1+\mathrm{Ci} 2 \mathrm{~S} 2 \tag{1}
\end{equation*}
$$

Where Sj represents the volume fraction (saturation) of the phase j , and the Cij are the phase concentrations. (The word composition refers collectively to all the concentrations in a system.) For a ternary (three component) system i will range from 1 to 3. For this three-component experiment there will be three total concentrations, $\mathrm{C} 1, \mathrm{C} 2$, C 3 , and similarly up to six values for the phase concentrations Cij.

The first part of the experiment deals with fluids that are saturated or just about to form a second phase. For example, if phase 2 is just about to form (phase 1 is saturated) we will have $\mathrm{S} 1=1$ and $\mathrm{S} 2=0$ so that $\mathrm{Ci}=\mathrm{Ci}$. For phase 1 about to form (phase 2 saturated) we will have $\mathrm{S} 2=1$ and $\mathrm{S} 1=0$ so that $\mathrm{Ci}=\mathrm{Ci} 2$. The compositions where saturation occurs define a binodal curve, which is what part A is intended to measure. Part B puts a few tie lines within the two-phase region.

## Apparatus and Materials

The chemicals you are to use in this experiment are $2 \mathrm{wt} . \% \mathrm{CaCl} 2$ brine (tinted with red food coloring to facilitate identification of phases) $(\mathrm{i}=1)$, hexane $(\mathrm{i}=2)$, and IPA $(\mathrm{i}=3)$. Use pipettes and beakers are provided. All measurements are to be based on visual observations of the onset of two-phase behavior at room temperature and pressure (part A)
or on a density-concentration calibration curve (part B). All the concentrations in this experiment are in volume fraction or percent.

## Procedure

Part A: Measuring the binodal curve
**Brine is colored with red dye to see the two phases clearly.
Using the provided test tubes, make IPA/hexane solutions with the following volumes:

IPA (ml) Hexane (ml)
$9 \quad 1$
$5 \quad 1$
$4 \quad 1$
$1 \quad 1$
$1 \quad 4$
15
$1 \quad 9$
Using a burette, titrate slowly and carefully with CaCl 2 brine ( $2 \mathrm{wt} . \%$ ). Record the initial and final volumes of brine used. The appearance of two phases will occur when a light phase separates from the colored phase. The organic phase is saturated at this point. For the last four titrations, very little brine is required, so titrate carefully!

Empty the solutions into the proper waste bottles and clean the test tubes and burette.

Make IPA/brine solutions with the following volumes:
IPA (ml) Brine (ml)

9
1

| 5 | 1 |
| :--- | :--- |
| 4 | 1 |
| 1 | 1 |
| 1 | 4 |
| 1 | 5 |
| 1 | 9 |

Using a burette, titrate slowly and carefully with hexane. Record the initial and final volumes of hexane used. Note: The volume of hexane added will also be very small, so titrate slowly!

## Part B: Measuring tie lines

Make three 2-phase solutions of CaCl 2 brine, IPA, and hexane using the following volumes:

| Solution | Brine vol. (ml) | IPA vol. (ml) | Hexane vol. (ml) |
| :--- | :--- | :--- | :--- |
| 1 | 50 | 100 | 100 |
| 2 | 130 | 65 | 65 |
| 3 | 200 | 25 | 25 |

Mix the solution with a magnetic stirrer.
Pour the mixed solution into a funnel and wait for the two phases to separate.
Empty the lower phase into a beaker and measure (and record) the volume.
We will measure the composition of the lower phase in the following two ways:
Density method and Refractive index-concentration calibration curve

Density—for each solution of Part B

Weigh and record the mass of a dry 10 ml graduated cylinder. Keep the graduated cylinder on the balance.

Pour 10 ml of the lower phase into the graduated cylinder.
Record the total mass (solution + cylinder).
Discard the 10 ml into the waste bottle.
Dry the graduated cylinder as best as you can.
Repeat \#1-6 for two more trials.
Below is Table 2-114 (that lists IPA \%, temperatures, and densities), which enables you to estimate the IPA concentration.



Figure C.1: Density Table

Refractive index—for each solution of Part B
Using the provided syringe, place 3 drops onto the measuring prism.

Close the prism cover and position the illuminating arm so the upper prism is fully illuminated.

Turn the dispersion wheel (silver wheel below the eyepiece) so that the crosshair adjustment access hole is positioned at six o'clock.

Rotate the adjustment control counterclockwise to move the shadow line to the bottom of the view.

Rotate the eyepiece to focus the crosshair.
Move the shadow line to the middle of the crosshair.
Rotate the dispersion correction wheel to eliminate any red or green around the shadow line.

Press the READ button and record the refractive index.
Press the TEMP button and record the temperature.
Clean the measuring prism with distilled water and Chemwipes. Make sure you clean the prism thoroughly!

Repeat \#1-10 for two more trials.
**The refractive index-IPA concentration calibrated curve is shown below. Use this to estimate IPA concentration.

calibration curve for refractive index of IPA/water mixtures for use in Lab 3.
Figure C.2: Refractive Index of IPA curve

## Results

## Part A

For each of the titrations, make a table of the volume fractions ( $\mathrm{C} 1, \mathrm{C} 2$, and C 3 ) of the three components at which two phases appear. This table should include the following:

1. IPA volume (ml)
2. Hexane volume (ml)
3. Brine volume (ml)
4. Total volume (ml)
5. $\quad \mathrm{C} 1$ (volume fraction)
6. C 2 (volume fraction)
7. C3 (volume fraction)

Construct a binodal curve on a ternary diagram. On the ternary diagram, put pure IPA (C3) at the top apex of the diagram, hexane (C2) at the lower right, and brine (C1) at
the lower left. Software such as Triplot greatly helps automate ternary diagram creation; check out http://mypage.iu.edu/~tthomps/programs/html/tnttriplot.htm

In your own words, define miscibility. Then, make a table that describes the miscibility of the IPA/Hexane, IPA/Brine, and Hexane/Brine. Use your ternary diagram to guide you. Include the following information:

1. Mixture name
2. Miscibility of each (miscible or immiscible)

Part B
The notation we use here is that Cij is the volume fraction (or percent) of component $i$ in phase $j$. We will let $\mathrm{j}=1$ be the heavy or aqueous phase and $\mathrm{j}=2$ be the light or oil rich phase. $(\mathrm{S} 1=$ lower phase and $\mathrm{S} 2=$ upper phase.)

Using the density formula, find the densities for each trial of each solution. Use the density table to find the IPA \%. Assume 20 deg. C. Find an average of the best three. Show sample calculations. Report values in a table with the following included:

1. Solution
2. Trial
3. Initial mass (g)
4. Final mass (g)
5. Total mass (g)
6. Volume (ml)
7. Density (g/ml)
8. IPA \% from chart
9. Average

Using the refractive index curve, find the IPA volume fractions for each trial of the solutions. Find an average of the values. Report your values in a table with the following included:

1. Solution
2. Trial
3. Refractive Index
4. IPA vol. fraction
5. Average

Make a table reporting the IPA amounts for each of the methods. Include the following information:

1. Solution \#
2. Using density method
3. Using refractive index curve

Using the refractive index values, make a table of the volume fractions for each of the three samples. This should include the following:

1. C 1 (brine)
2. C 2 (hexane)
3. C 3 (IPA)
4. S1 (lower phase)
5. S2 (upper phase)
6. C11 (brine in lower phase)
7. C 21 (hexane in lower phase)
8. C31 (IPA in lower phase)
9. C 12 (brine in upper phase)
10. C22 (hexane in upper phase)
11. C32 (IPA in upper phase)

Use the measured volumes from Part B to find S1 and S2. You can assume ideal mixing.

## DISCUSSION

For each of the following pairs, state and explain which pair is more miscible:

1. IPA and water versus tertiary butyl alcohol $(\mathrm{C} 4 \mathrm{H} 9 \mathrm{OH})$ and brine
2. IPA and hexane versus tertiary butyl alcohol $(\mathrm{C} 4 \mathrm{H} 9 \mathrm{OH})$ and hexane
3. Methane and crude oil versus nitrogen and crude oil

Justify your answers using molecular weight, polarity, etc. It may help to look at the structure of the molecules.

Suppose you have an "oil" reservoir that contains equal amounts (by volume) of hexane and brine and that you could, in some fashion, mix this with a solvent that is itself a binary mixture. Consider the following solvents:

1. pure IPA
2. $1 / 1$ mixtures of IPA and brine
3. $1 / 1$ mixture of IPA and hexane

How much of each solvent must be added to the reservoir to attain miscibility?

## Appendix D: Treating Emulsion

## ObJectives

The behavior of emulsions is ultimately dictated by the thermodynamics of interfaces and immiscible fluids. Thus, this experiment will:

1. Illustrate surfactant properties
2. Reinforce ternary phase behavior properties
3. Introduce emulsions and their properties
4. Illustrate the methods used to break emulsions

## Background

Mayonnaise is perhaps the most familiar example of an emulsion. In many surface facilities the co-production of oil and water yields emulsions. Breaking these emulsions so the oil can be sold, and the water disposed can be a severe problem, and several technologies have been developed to treat this problem. Emulsions have also been employed as a clever means of transporting heavy (high viscosity) crude oil. One very large oil company field tested the idea of injecting emulsions for enhanced recovery of viscous crudes. This experiment is intended to introduce you to this interesting and useful topic.

Produced emulsions form a major nuisance in production operations. An emulsion is a dispersed mixture of one phase in another that together appear as a single phase. Produced emulsions can result in

Loss of oil suspended in an aqueous phase. Oil suspended in this fashion can be difficult to inject in waterflood operations.

Contamination of the oil product because of suspended water. Most hydrocarbon processors can tolerate no more than around $2 \%$ water suspended in the oil.

Difficulties in handling because produced emulsions can be highly viscous.

Surfactants can also cause a suspension of solid material that is equally detrimental to subsequent operations.

Not all crudes form emulsions; a naturally occurring surfactant must be present. By the same token, surfactants can be used to break--that is to revert or return the oil and water to their unsuspended forms--with other surfactants.

## Apparatus and Materials

Hexane, $2 \% \mathrm{CaCl} 2$ brine, and various surfactants will be used. The surfactants may be oil soluble or water soluble, depending on the hydrophilic/hydrophobic properties. The added surfactant is simulating a natural surfactant. The surfactants will be ethoxylated nonylphenol with ethylene oxide (EO \#) numbers ranging from 5.0 to 15.0 Surfactants with low EO \#s are dominated by its hydrophilic properties (dissolves in water or brine), whereas surfactants with high EO \#s are dominated by its hydrophobic properties.

## Procedure

1. The hexane phase will look very clear and appear as the upper phase.
2. The emulsion phase will look milky, cloudy and appear as the middle phase.
3. The brine phase will look clear and appear as the lower phase.
4. The brine is a $2 \%$ solution of CaCl 2 and de-ionized water.
5. Label all your pipettes appropriately.

## Part A: Pasteur Capillary Pipette Calibration

For each pipette you use:

1. Fill a $10-\mathrm{ml}$ graduated cylinder with DI water.
2. Put the rubber pipette bulb on the pipette while squeezing the bulb so that it is deflated.
3. Keep the bulb compressed until you submerge the tip of it in the graduated cylinder.
4. Slowly release the bulb until you have extracted 0.5 ml of water.
5. Keeping the bulb compressed, have a partner mark the water level on the pipette.
6. Now the pipette is calibrated to 0.5 ml and can only be used for one surfactant.
7. Make three more calibrated pipettes with the same method

Part B: No surfactant

1. Add 10 ml of hexane into the small cylindrical bottle (with cap on it).
2. Add 10 ml of brine.
3. Replace the cap and shake for 20 seconds.
4. Record any observations (i.e. phases, miscibility, etc)
5. Now add a pinch of sand to the mixture.
6. Shake the bottle again.
7. Record any observations.

Part C: Unknown surfactants
For each surfactant:

1. Obtain four flame sealed pipettes.
2. Label each accordingly as unknowns $1,2,3$, and 4.
3. Begin with a clean cylindrical bottle (with cap on it).
4. Add 10 ml of hexane.
5. Obtain the unknown surfactant from the TA using the calibrated pipette.
6. Using rubber pipettes marked in Part A, add 0.5 ml of surfactant to the hexane.
7. Cork the volumetric flask and shake the solution thoroughly. **It is very important that all the surfactant is dissolved into the hexane. Do not continue the procedure until the surfactant is completely dissolved.
8. Add 20 ml of brine to the solution.
9. Cork the solution to prevent evaporation.
10. Shake the mixture for one minute. ${ }^{* *}$ It is very important that the solution is thoroughly mixed.
11. Quickly, using a pipette, withdraw 10 ml and add that to a flame-sealed pipette. ${ }^{* *}$ When withdrawing solution, completely immerse the pipette until the tip touches the bottom of the flask.
12. Cork the pipette to prevent evaporation.
13. Observe and record the initial composition of the mixture. Specifically, record the number of phases, volume changes, and time.
14. Repeat readings every 10 minutes (or after volume changes are observed) until the end of lab.

## Results

For each unknown pipette, create a table and include the following information:

1. Time (min)
2. Number of phases
3. Volume of upper phase (ml)
4. Volume of emulsion phase (ml)
5. Volume of lower phase (ml)

For each unknown pipette, plot the volumes of each phase versus the time.

## DISCUSSION

Describe what you observed in Part B. What did the addition of sand do to the miscibility of the liquids? From your observations, what problems may petroleum engineers need to account for downhole? Provide examples.

For the first unknown:

1. How many phases occurred?
2. What were the phases? (i.e. brine, emulsion, hexane)
3. About how long did it take for the phases to separate?
4. Predict the EO \# for this surfactant. Justify your answer.

For the second unknown:

1. How many phases occurred?
2. What were the phases? (i.e. brine, emulsion, hexane)
3. About how long did it take for the phases to separate?
4. Predict the EO \# for this surfactant. Justify your answer.

For the third unknown:

1. How many phases occurred?
2. What were the phases? (i.e. brine, emulsion, hexane)
3. About how long did it take for the phases to separate?
4. Predict the EO \# for this surfactant. Justify your answer.

If the oil/water mixture is produced at a rate of 1000 bpd , how large must the volume of the separator tank be if the mean residence time in the tank should be 10 times the time for the emulsion to break. You should answer this question for each of the unknown samples. The mean residence time is given by

$$
\mathrm{t}_{\text {residence }}=\frac{\mathrm{V}}{\mathrm{q}}
$$

If the intent is to minimize the volume of facilities-as might be the case on an offshore platform-which of the three treatment options works best? Show your work.

## Appendix E: Surface/ Interfacial Tension and Contact Angle

## ObJectives

1. Gain practice in measuring surface tension
2. Understand the nature and magnitude of surface forces
3. See what typical values of surface tension are
4. Understand what factors affect contact (and thereby the wettability of a medium)
5. Gain practice in experimental techniques used to measure contact angle
6. Understand the nature of contact angle hysteresis

## Background for Surface/ Interfacial Tension

There is no branch of engineering to which capillary forces are as important as petroleum engineering. Capillary pressure is a basic reservoir characterization tool. It determines the equilibrium distribution of phases in a reservoir and is by far the major factor in determining the magnitude of residual phase saturations. Capillary pressure determines when a shale or a fault acts as a seal to trap migrating hydrocarbons and thus create a reservoir. Capillary pressure also determines the amount of water a sand or soil may retain. Fundamentally, capillary pressure is a manifestation of thermodynamics, as this experiment will show.

The interface separating two phases is in tension. This tension causes small blobs of liquid immersed in another fluid to be spherical in the absence of external forces. The tension also causes the difference in pressure (capillary pressure) between coexisting water and oil phases within porous media. The purpose of this experiment is to measure the surface or interfacial tension using two different techniques-the ring method (a du Nouy tensiometer), and the spinning drop-and to compare the results obtained using the two approaches. The principles of these methods are covered in Adamson and Gast.

## Ring Method

The du Nouy tensiometer measures the force needed to withdraw a platinumiridium ring from the surface of a liquid. As the ring is slowly withdrawn from the liquid, the liquid sticks to the surface of the ring as shown in Fig. 1. As the ring is further raised, the liquid film becomes unstable and ruptures. The shape of the liquid film at the point of rupture is depicted in Fig. 1. Measuring the downward force at the point of rupture gives the surface tension.


Figure E.1: Condition of drop at breaking point.

## Spinning Drop Method

This method was developed at The University of Texas. It is probably the most common interfacial tension measurement in use today because it can measure very low interfacial tensions. It is a little more involved than the other methods, however.

The method consists of inserting a bubble or drop of gas into a tube that is spun at a very high rate. The spinning causes the drop to elongate and from the diameter ( d in cm ) of the now almost cylindrical drop, the rate of spin ( P in milliseconds per revolution) and the density difference ( $\Delta \rho$ in $\mathrm{g} / \mathrm{cm} 3$ ) the interfacial tension follows from

$$
\begin{equation*}
\sigma_{L V}=1.2337 \times 10^{6} \frac{\Delta \rho d^{3}}{P^{2}} \tag{1}
\end{equation*}
$$

The constant in this equation is to account for optical effects of the tube and the liquid filling the tube.

## Background for Contact Angle

Figures. 2 and 3 show a liquid drop resting on a solid surface. At the edges of the drop, three phases are in contact: solid S , liquid L and vapor V . A condition for static equilibrium is

$$
\begin{equation*}
\sigma_{\mathrm{SV}}=\sigma_{\mathrm{SL}}+\sigma_{\mathrm{VL}} \operatorname{Cos} \theta \tag{2}
\end{equation*}
$$

Where $\sigma \mathrm{SV}, \sigma$ SL and $\sigma \mathrm{VL}$ denote the respective interfacial tensions (free energies per unit area) of the solid-vapor, the solid-liquid, and the liquid-vapor interfaces.


Figure E.2: Contact angle between a solid, a vapor and a liquid

The contact angle $\theta$, shown in Fig. 3, is a thermodynamic property since it depends on the free energies per unit of area from Eq. 1. Thus, if one coats the solid surface with a
material which tends to decrease the difference ( $\sigma \mathrm{SV}-\sigma \mathrm{SL}$ ), then $\theta$ increases and the "wettability" of the solid surface to that material is said to decrease. The contact angle is, therefore, a measure of the tendency of the liquid to spread. If the vapor is replaced by oil and if the drop is water, then $\theta$ measured on a mineral surface represents the wettability of that surface. $\theta$ is related to the capillary pressure and subsequently the relative permeabilities that would be expected within the reservoir.

One reason that the contact angle provides only an indication rather than a direct measure of the relative permeabilities and capillary pressures in permeable media is that the contact angle exhibits a strong hysteresis. If we add more liquid to a drop resting on a solid surface, then the drop size increases and the liquid tends to spread over the solid surface. The contact angle measured at the contact line, after allowing the drop to come to equilibrium, for this case is called an advancing contact angle $\theta$ a.


Figure E.3: Expanded view of three-phase contact zone.

If, on the other hand, liquid is removed from the drop, the three-phase contact line contracts or recedes. Now, the contact angle measured is the receding contact angle $\theta$ r. In general, $\theta \mathrm{r}<\theta \mathrm{a}$. The difference between these two contact angles is attributed to heterogeneities in the solid surface, adsorption and the formation of liquid films. The
heterogeneities can arise either because of surface roughness or because of variations in the chemical composition of the surface. Both types of heterogeneities will be present in abundance in soils, aquifers, and oil reservoirs.

## Apparatus and Materials for Surface Tension

The apparatuses you will be using are described above. The liquid-vapor system to be studied in this lab is very simple: air, DI water, isopropyl alcohol (IPA) and $2 \% \mathrm{CaCl} 2$ brine.

## Apparatus and Materials for Contact Angle

The experimental apparatus is an NRL-Contact Angle Goniometer, which consists of an optical bench on which is mounted a variable intensity light source, a sample holder, and a telescope that produces an image of the drop. The telescope has a protractor, calibrated in one-degree increments, and independently rotating cross hairs within the lens, which are divided into divisions of 0.02 mm so that the dimensions of the drop can be determined. The position of the sample holder can be adjusted.

Also attached to the optical bench above the sample holder is a micro-syringe to be used to continuously add or withdraw fluid from the drop to form advancing or receding contact angles.

This array of equipment will be mounted on the optical bench before you come to the laboratory. Do not attempt to use the equipment without first consulting the TA.

## Procedure

Part A: Surface Tension
a. Spinning Drop Method

Note: Because the process of filling the tube with liquid and an air bubble is timeconsuming and tedious, the machine will already be running. And the only surface tension will be measured is between air and DI water.

1. Record the speed and temperature.
2. Look into the eyepiece and find the bubble.
3. To measure the height of the bubble:
4. Move the $==$ lines so that they line up with the upper edge of the bubble.
5. Take the reading.
6. Move the $==$ lines so that they line up with the lower edge of the bubble.
7. Take the reading.
8. To take the reading:
9. Use the set of numbers on the left dial first (these should range from 0-35).
10. Whichever number that the tic mark intercepts is the value you use.
11. The decimal point value that you will use is the second dial.
12. Find the tic mark that intercepts a value ( $0-10$ ) and that becomes your decimal value.
13. If the tic mark falls between two numbers on either dial, use the value that precedes it.
14. Subtracting the two will give you the height (units: micrometers).

## b. Ring Method

Given:
Solution Surface Tension Range (dynes/cm) Weight Range (dynes/cm)
Brine 59.0-61.0 0.177-0.183

IPA 23.5-24.5 0.080-0.090

Solution Density
Air $\quad 1.222 \mathrm{~kg} / \mathrm{m} 3$
Water $\quad 1 \mathrm{~g} / \mathrm{cm} 3$
Brine $\quad 2.15 \mathrm{~g} / \mathrm{cm} 3$
IPA $\quad 0.7855 \mathrm{~g} / \mathrm{cm} 3$
Solution $1 \quad 1.023 \mathrm{~g} / \mathrm{cm} 3$
Solution $2 \quad 1.011 \mathrm{~g} / \mathrm{cm} 3$
Solution $3 \quad 0.999 \mathrm{~g} / \mathrm{cm} 3$
Solution $4 \quad 0.987 \mathrm{~g} / \mathrm{cm} 3$
Solution $5 \quad 0.976 \mathrm{~g} / \mathrm{cm} 3$
Units: 1 dyne $/ \mathrm{cm}=0.001 \mathrm{~N} / \mathrm{m}$
Note: The du Nouy tensiometer must be calibrated. Ask the TA for assistance.

For all five solutions, repeat the following steps for three trials each:

1. Pour 20 ml of solution into the clear evaporating dish.
2. Place the dish on the sample table.
3. Raise the table until the ring is totally immersed in the solution, but do not allow the ring to touch the bottom of the dish. ${ }^{* *}$ The ring is very delicate and expensive, so be very gentle when handling it.
4. Make sure the ring is parallel to the solution surface.
5. The scale should read zero and the needle should be flush with the mirror line.
6. Slowly lower the table until the ring is just below the solution surface. (The needle should still be flush with the mirror line.)
7. Begin to slowly lower the table and raise the ring in such a way that the needle remains flush with the mirror line.
8. Keep one hand under the sample table and the other on the scale dial.
9. Focus on the mirror line, not the scale values.
10. If the needle falls below the mirror line, you have lowered the table too much.
11. If the needle rises above the mirror line, you have raised the ring too much.
12. Do not raise/lower the needle too quickly or your readings will be inaccurate.
13. Continue rotating both dials until the ring breaks the solution surface.
14. Record the reading at the breaking point. See the TA if you have questions.
15. Find the zero on the inner dial. This will be your reference point.
16. Wherever the zero has stopped, read the outer number (i.e. 30-80).
17. If the zero mark has stopped in between two numbers, use the closest number that it has passed. For example, if it has stopped between 34 and 35 , use 34 as your number.
18. Using the inner dial now, begin from the zero reference point.
19. Find the point where one of the division marks lines up with an outer mark.
20. Your number will range only from 1-10. (This is the decimal part of your value.)
21. Your final reading will consist of a whole number and one decimal place (i.e. 34.5) in dynes/cm.
22. Pour the solution back into its relevant flask.
23. Repeat \#1-10 for the remaining solutions. **Note: Use the solutions in increasing order so that you only need to clean the ring and dish at the end of all your trials.
24. To clean the ring, use a DI water bottle and dish.
25. Carefully spray the water around the ring and use the dish to catch the excess.
26. Be very careful with the ring-it is fragile and expensive.
27. Clean the evaporating dish with DI water and dry with Chemwipes.

Contact Angle: DI water and air

1. Begin with the smooth glass slide. Make sure it is clean.
2. Place the slide on the sample holder.
3. Slide the eyepiece back and forth to focus the edge of the slide.
4. Make sure the horizontal baseline (reference line) is even with the bottom edge of the slide. Notice that the drop is seen upside-down.
5. Using the suspended micro-syringe, let 3-4 drops of DI water fall until they form one large drop.
6. Allow it to come to its equilibrium shape.
7. Slide the eyepiece to now focus the drop.
8. Measure the left contact angle of the drop using the 'measuring' cross-line and the cross-travel dial.
9. Line the edge of the drop with the vertical 'measuring' cross-line.
10. Rotate the 'measuring' cross-line so that it is approximately tangent to the base of the drop.
11. Slowly move the 'measuring' cross-line and the cross-travel dial until the 'measuring' cross-line is exactly tangent to the base of the drop.
12. Record the contact angle.
13. Move the measuring line back to its vertical position.
14. Align the edge of the bubble with it using the cross-travel dial.
15. Record the reading in mm .
16. Note that one revolution of the dial represents 1 mm , so keep track of the revolutions.
17. Now move the drop so it lines up with the right side.
18. Take the second reading of the diameter.
19. Find the right contact angle as explained above.
20. Record that angle.
21. Ideally, your values for the left and right contact angles should be the same.
22. Now we want to measure the height of the drop.
23. Move the drop to the center of the cross-lines.
24. Take the bottom height reading using the vertical fine adjustment knob.
25. Note that the increments represent 0.02 mm .
26. Move the drop up so the highest point is flush with the horizontal cross-line.
27. Take that height reading.
28. Move the slide back to its original height.
29. Withdraw about half of the drop with the micro-syringe.
30. Repeat the above procedures for measuring the left and right contact angles, diameter, and height.
31. These measurements are for the receding contact angles.
32. Add 1 or 2 drops to the original drop.
33. Repeat the above procedures for measuring the left and right contact angles, diameter, and height.

## Results

Part A
Prepare a table for the Spinning Drop Method with the following included:

1. Temperature (deg. C)
2. Spinning velocity ( $\mathrm{ms} / \mathrm{rev}$ )
3. Reading 1 ( $\mu \mathrm{m}$ )
4. Reading $2(\mu \mathrm{~m})$
5. Height $(\mu \mathrm{m})$
6. Surface tension (dynes/cm)

Prepare a table for whichever remaining method you chose and include the following:

1. Method used
2. Solution \#
3. Trial \#
4. Surface tension (dynes/cm)
5. Average surface tension for each solution (dynes/cm)

Part B
Prepare a table for the contact angles with the following included:

1. Trial (i.e. Equilibrium, Receding, Advancing)
2. $\theta 1$
3. $\theta \mathrm{r}$
4. Diameter (mm)
5. Height (mm)

## DISCUSSION

Answer the following question that pertains to the method:
Spinning Drop Method: $\sigma=\frac{\Delta \rho \omega^{2} r^{3}}{4}$
$\omega=$ angular speed $[1 / \mathrm{s}]$
$\mathrm{r}=$ radius $[\mathrm{cm}$ ]
$\rho=$ density $[\mathrm{g} / \mathrm{cm} 3]$
$\sigma=$ IFT $[$ dynes $/ \mathrm{cm}$ ]

Derive Eq. 1 from this original form.
Ring Method: Discuss the possible errors involved in performing this method.

From the results you have obtained in Part A, you should notice a trend. Describe what that trend is. Using past experiments, given densities and prior knowledge of brine and IPA, make an educated guess as to what the solutions are. Justify all answers.

If the drops are spherical, the contact angle may be estimated from
$\theta=\sin ^{-1}\left\{\frac{2 h R}{R^{2}+h^{2}}\right\}$
See Fig.2. This equation provides a means to determine contact angle entirely from length measurements R and h . Using your measurements of R and h , find the theoretical values of $\theta$.

In a table, compare the measured contact angles with those predicted by Eq. 3.
In general, would you say that the drops in your experiment are spherical? Why?

## Appendix F: Compatibility of Oilfield Brines

## Objectives

1. Demonstrate the formation of solids caused by the mixing of waters
2. Illustrate the accuracy of the estimations of the onset of solid formation
3. Demonstrate the effectiveness of scale inhibition treatments.
4. Explore the trade-off between plugging and scale treatment

## Background

Waterflooding is an extremely common way to produce additional oil from a reservoir. One of the problems associated with waterflooding is that the water being injected can damage (that is, cause a loss of injection rate) the formation. There are many causes of damage, but one of these is the formation of inorganic precipitates caused by mixing incompatible waters. Incompatible waters are those that form a solid upon mixing. These solids can cause plugging of the formation, as well as fouling of injection lines, and surface equipment. Solids that form in this fashion are sometimes called scale.

The background for this experiment is the chemical reaction equilibria. From the theory of reaction equilibrium, we know that the solubility product of a mineral determines the concentrations of cations and anions at which scale will start to form. One way to suppress scale formation is to use a small amount of a chemical called an inhibitor. Inhibitors bind with metal cations in an aqueous solution (usually with several metal cations) thereby removing them from being able to participate in the precipitation reaction. The cation-inhibitor complex remains in solution and does not interfere with water injection. The inhibitor we are to use is ethlylenediaminetatracetic acid or simply EDTA.

## Apparatus and Materials

Use glassware as provided by the TA. The experiment is designed to test the compatibility of a synthetic "formation" brine with a potential "injection" brine.

| Solution | Molar Weight $(\mathrm{g} / \mathrm{mol})$ | Molarity, (mol/L) |
| :--- | :--- | :--- |
| Na2SO4 injection brine | 142.04 | 0.01 |
| BaCl2 formation brine | 244.28 | 0.01 |
| EDTA inhibitor | 372.24 | 0.1 |

## Procedure

Part A: Weigh the scale

1. Obtain samples of 50 ml formation brine and 50 ml injection brine. Mix these samples and observe and record changes in physical properties.
2. Weigh a clean, dry filter. Use a filtration funnel to separate out the solid from the initial solution. Keep filtering the water until it returns to its initial clarity. Dry the filtration paper in the oven. Obtain the weight of this sample when it is dry.

Part B: Inhibit the scale formation

1. Beginning with 50 ml of seawater, add just enough of the produced water to attain the onset of precipitation. Record the amount of produced water added at this point.
2. Beginning with 50 ml of produced water, add just enough of the seawater to attain the onset of precipitation. Record the amount of seawater added at this point.
3. Repeat step 1 , and add 1 ml of the previously prepared solution of EDTA. Let this sit and observe changes in physical properties for at least 10 min . Keep adding EDTA in 1 ml increments until the solution is clarified.

## Results:

1. Use the tabulated free energies to identify the scale resulting from the mixing in step one. Possible candidates are barium chloride BaCl , barium sulfate BaSO 4 , sodium chloride NaCl , and disodium sulfate Na 2 SO 4 .
2. Use the tabulated free energies to estimate the concentrations and the amount of solid formed from the mixing in step one. Compare the results of your calculation to the amount measured in step 2.
3. Using the estimated concentrations of the solid-saturated solutions, calculate how much of each solution can be mixed with the other to just initiate precipitation. Compare your results with those of steps 3 and 4.

## DISCUSSION:

Why was it necessary to add NH 4 OH to the solution?

Consider the reaction that formed the solid. Which of the ions making up this solid are in excess in the mixture you made in lab?

What are the possible sources of error that could account for discrepancies between the results of the calculations (in the Results section) and the results of the laboratory mixings (in the Procedure section)?

You are about to conduct a waterflood using a 50-50 (by volume) mixture of the injection water and formation water. The waterflood recovers 1 barrel of oil for every 2 barrels of water injected and the well you are injecting into should take 5,000 barrels of water per day. You have two operational alternatives to remedy the scaling problem:
a. You can inject the waters even though you know they form precipitates. In this case the well will gradually plug up. The injection rate will fall linearly with time for about one year to 100 barrels at which time you will must treat the well to restore the injection rate to its original value. Treating the well costs $\$ 300,000$.
b. You can add just enough EDTA (determined by your experiment) to prevent scaling. The EDTA costs $\$ 2$ per pound.

Which of the two options yields the largest net profit over the space of a year?

## References

1. UCSD. (n.d.). Lab 7 - Determination of the Molar Mass of an Unknown Solid by Freezing Point Depression. Reading. Retrieved December 6, 2017, from http://www.webassign.net/labsgraceperiod/ucscgencheml1/lab 7/manual.html
2. Stanford. (n.d.). Freezing Point Depression. Reading. Retrieved December 6, 2017, from http://labsci.stanford.edu/images/Freezing-Point-Depression-SA.pdf
3. Klent, J. (n.d.). Freezing Point Depression. Reading. Retrieved December 6, 2017, from http://www2.ohlone.edu/people/jklent/labs/101a labs/frptdepression.pdf
4. Gorin, G. (1994). "Mole and chemical amount: A discussion of the fundamental measurements of chemistry". J. Chem. Educ. 71 (2): 114. Bibcode:1994JChEd..71..114G
5. Barnes, H.A.; Hutton, J.F.; Walters, K. (1989). An introduction to rheology (5. impr. ed.). Amsterdam: Elsevier. p. 12. ISBN 0-444-87140-3.
6. Lake, L. (2007). Lab Manual for PGE 421 Physical and Chemical Behavior of Fluids II. The University of Texas at Austin.
