CERTIFICATION OF APPROVAL

Thermal Stability and Heat Capacity Characterization of 1,6-Bis(Trioctylphosphonium-1-yl)Decane Chloride

By

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CERTIFICATION OF ORIGINALITY

This is to certify that I am responsible for the work submitted in this project, that the original work is my own except as specified in the references and acknowledgments, and that the original work contained herein have not been undertaken or done by unspecified sources or persons.

FARAHIYAH BINTI JASMI

ABSTRACT

Manmade carbon dioxide, (CO_2) emission to the atmosphere is expected to increase in the next 100 years and this will seriously have a huge impact on the environment in the future. Fossil fuel is one of the most important sources of energy in the world today. This includes petroleum, coal and natural gas. In the oil and gas industry, natural gas exists in two forms, which are sweet gas (lowly contaminated) and sour gas (highly contaminated), usually by CO_2 and H_2S. To make use of this sour gas which is available in abundance, separation processes are required to first purify them. Currently used absorbents for CO_2 absorption such as amines have been found to be effective in the removal of CO_2; however they have notable flaws i.e high energy requirement for reactivation, corrosion due to formation of acid, and amine degradation and loss. On the other hand, ionic liquid, (IL) is another potential absorbent for separation of CO_2 from natural gas stream and flue gas stream. ILs are in liquid state under atmospheric conditions at room temperature with specific properties that make them extremely effective as CO_2 absorbents. The unique properties of IL can possibly counter the flaws of amine absorption for this purpose. Dicationic ionic liquid (DCIL) is a newer type of ionic liquid which possess higher thermal stabilities and non-volatility. This new IL is needed to be characterized in term of heat capacity and thermal stability since the data is not much publicly reported for researchers to consult. Characterization on these thermophysical properties will be done on dicationic phosphonium-based symmetrical ionic liquid that is **1,6-bis(trioctylphosphonium-1-yl)decane chloride** through lab experiments by using equipment such as **Bomb Calorimeter and Fourier Transform Infrared (FTIR) Spectroscopy.** Additional experiment is done to evaluate performance of CO_2 solubility in the DCIL sample at room temperature and ambient pressure using CO_2 absorption system.

ACKNOWLEDGMENT

Completing this project was a tremendous fun, researching it even more so. I am exceedingly grateful to Allah who gives me never ending strength and courage whenever the hurdles came around.

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CHAPTER 1: INTRODUCTION

1.0 Project Background

Room temperature ionic liquid (RTIL) posseses many desirable properties as absorbent in CO_2 removal from natural gas and flue gas streams. RTIL exhibits high affinity towards CO_2, thermal stability in which it can be a liquid over a range of 350°C and negligible vapor pressure. Due to immeasurably low vapor pressure of RTIL, it is referred to as 'environmentally benign' [1]. RTIL also has minimal potential of explosion because it has little or no flammability [2]. By providing nonvolatility at high temperatures as well as nonflammability, ILs are suitable alternatives to the commonly used organic solvents. Other advantages of RTIL are no corrosion problems and high regeneration efficiency [3]. In addition, RTILs have thermophysical properties that may be suitable for heat transfer and absorption. Two of thermal properties important for heat transfer applications (i.e. heat exchanger) and separation applications (i.e. absorber) are thermal stability and heat capacity. It is a strong need to find liquids usable as heat transfer fluids from normal ambient temperature to very high temperatures. However these days, various studies have proven that dicationic ionic liquid (DCIL) is much better than monocationic ionic liquid (MCIL) [4]. It appears to be more stable and nonvolatile at temperature range higher than 240°C due to its higher thermal stability as compared to MCIL, up to 400 °C [5]. This is because producing bulkier cation and dicationic salts rather than monocationic salts greatly improves the thermal stability of IL. The bulky cation is big in size and hence molar volume will be increased. Compared with imidazolium-based ionic liquids (ILs), phosphonium-based ILs have been proven to be more stable in thermodynamics and less expensive to manufacture [4]. In this work, a kind of phosphonium-based DCIL, **1,6-bis(trioctylphosphonium-1-yl)decane chloride** is studied under several characterization tests in order to determine its thermal stability and heat capacity.

1.1 Problem Statement

The main advantage of DCILs is that they have a higher thermal stability compared to traditional MCILs, up to 400°C. In the literature, most work has focused on MCILs based on different anions but less attention has been paid to DCILs with respect to heat transfer applications and powerful organic solvents. However, recent work with DCILs has focused on the characterization and application of certain kinds of DCILs, and provided a large amount of useful data as well as regulations. Today, the IL research continues to be dominated by imidazolium salts. Although phosphonium-based RTIL was recently reported to be chemically stable and remain inert, studies of phosphonium systems, however, are much rare. It is believed that these ILs would potentially provide the needed chemical stability as useful media for organic synthesis and relevant applications. Hence, this prompts for further investigation on phosphonium-based ILs. Several ILs, especially those based on imidazolium ions have been known to be chemically reactive. In addition, quaternary phosphonium salts were known to be more stable to high temperatures for longer periods of time than those nitrogen-based cations [4]. Since phosphonium-based DCIL is still new, number of values and materials reported regarding its thermopysical properties are limited and less. The values of the specific properties important for heat transfer and separation applications are difficult to find. In fact, there is no such specific listing for the properties and comprehensive database publicly available for researchers to consult [6]. Hence, it is decided to characterize the phosphonium-based DCIL in question, **1,6-bis(trioctylphosphonium-1-yl)decane chloride** in term of thermophysical properties (i.e. heat capacity and thermal stability), via experimental research. It is hoped that the data obtained will support the research and development of phosphonium based DCILs. Since this type of IL is a potential absorbent for removal of CO_2 from natural gas and flue gas streams, an additional experiment is done to determine the performance of CO_2 solubility in DCIL sample at 25°C and 1 atm.

1.2 Objectives of Project

- To characterize dicationic ionic liquid in term of:
    - Thermal stability
    - Heat capacity

- To carry out performance test on CO_2 solubility in dicationic ionic liquid at room temperature and ambient pressure

These characterizations are to be determined through laboratory experiments and research.

CHAPTER 2: LITERATURE REVIEW

2.1 Ionic Liquid

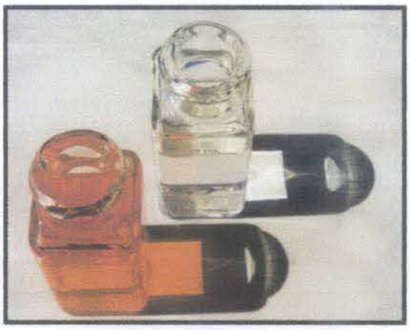


Figure 1: Ionic Liquid

Ionic liquids are typically organic salts that, in their pure state, are liquid under atmospheric conditions at room temperature. They have unusual properties that suggest they could be extremely effective as carbon dioxide absorbents, possibly replacing current amine-based technology to capture carbon dioxide from power plants stacks. Unlike amines, which are corrosive and costly to operate and organic salts are typically benign. [7]

A molten salt is generally referred to a high melting, highly viscous and corrosive medium. But ionic liquids as shown in Figure 1 are liquids at low temperatures and have relatively low viscosity. Among the various known ILs, those on imidazolium, quaternary ammonium or phosphohium salts are most commonly used because of their particular set of properties. ILs exhibit high ionic mobility, negiligible vapor pressure and high thermal stabilities. [2]

A diverse range of organic, inorganic and organometallic compounds are soluble in ILs. The solubility of gases such as oxygen, benzene, nitrus oxide, ethylene, ethane, carbon dioxide and ethane is also good. Ionic liquids tend to have a good thermal stability and can be a liquid over a range of 300°C. This wide liquid range is a distinct advantage over traditional solvent systems that have a much narrower liquid range, for example water that has a liquid range of 100°C and toluene of 206°C. [7]

2.2 *Dicationic Ionic Liquid (DCIL)*

Dicationic ionic liquid (DCIL) is the newer type of ionic liquid and based on various researches it has been proved that DCIL exhibits desirable properties as compared with monocationic ionic liquid (MCIL). The structure of DCIL is more stable due to the bulky size of the cation on the IL [5]. For example, in Figure 2, imidazolium based dicationic ionic liquid is stronger than its MCIL due to having two imizadolium rings and hence there is an increment in size. This shows that size plays the important role to stabilize the IL.

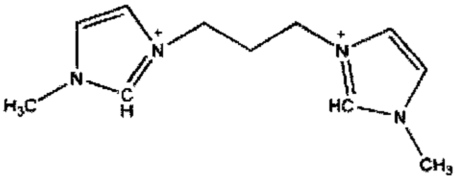


Figure 2: Imidazolium Based Dicationic Ionic Liquid

Due to this feature also, the thermal stability of DCIL is higher than MCIL. Thermal stability is important when it involves reaction or process that operates at high range of temperature without being decomposed. The volatility of DCIL is almost none. However as the size of DCIL gets bigger and more stable, the solubility of CO_2 in DCIL will be less. This is because as the molar attraction constant and Henry's constant increase, the solubility of CO_2 in IL will also increase. [8]

2.3 *Imidazolium versus Phosphonium Based DCIL*

Benefits of phosphonium based DCIL:

Figure 3: Phosphonium Ion

This type of ionic liquid has enhanced chemical stability under varied conditions, more thermally stable than ammonium and imidazolium-based ionic liquid [1]. It also has tunable cation can be modified to alter physical properties such as miscibility and freezing point. The dicationic phosphonium ILs are more thermally stable than dicationic imidazolium IL. With these results, researchers may choose to use the more robust phosphonium IL columns instead of nitrogen-based ILs when high temperatures are needed [4].

Drawbacks of imidazolium based DCIL:

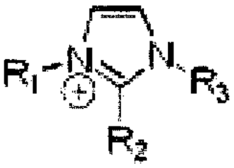


Figure 4: Imidazolium Ion

Imidazolium is slightly less thermally stable. The imidazolium cation contains proton which are not entirely inert. They are somewhat acidic which can result in carbene formation. Phosphonium salts have no such acidic proton.

Based on these reasons, it is decided to characterize phosphonium based symmetrical DCIL rather than imidazolium based DCIL. In this case, 1,6-bis(trioctylphosphonium-1-yl)decane chloride is investigated through experimental research.

2.4 Absorption Theory

Absorption is a separation process where two contacting phases are a gas and a liquid. The process involves molecular and turbulent diffusion or mass transfer of a solute in the gas phase into a stagnant absorbent in liquid. The reverse of absorption is called desorption, and the same theories and basic principles hold.

2.5 Amine Solutions

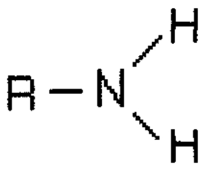


Figure 5: Amine structure

Amines are basic organic compounds and functional groups that contain a basic nitrogen atom with a lone pair. They are derivatives of ammonia in which one or more hydrogens are replaced by a substituent such as an alkyl or aryl groups and still retain its class as an amine [7]. Figure 5 shows the amine structure as described earlier.

Table 1: Types of Amines [7]

Amines	Description	Example
Primary amines	One alkyl or aryl group on the nitrogen	MEA, butylamine
Secondary amines	Two groups on the nitrogen	DEA
Tertiary amines	Three groups on the nitrogen	MDEA, dimethylcyclopentylamine
Quaternary ammonium salts	Four groups on the nitrogen	Tetramethylammonium hydroxide

The nitrogen atom features a lone electron pair that can bind H^+ to form an ammonium ion R_3NH^+. Alkyl group raises the energy of the lone pair of electrons, thus elevating the basicity while aryl groups diminish it. Thus the basicity of an amine may be expected to increase with the number of alkyl groups on the amine. [7]

The amine solutions are primarily used in industries for natural gas purification. Aqueous monoethanolamine (MEA), diglycolamine (DGA), diethanolamine (DEA), diisopropanolamine (DIPA) and methyldiethanolamine (MDEA) are widely used industrially for removing carbon dioxide (CO_2) and hydrogen sulfide (H_2S) from natural gas streams and refinery process streams. They may also be used to remove CO_2 from combustion gases or flue gases. For example, MEA in such solutions that acts as a weak base will neutralize weak acidic compounds such as H_2S and CO_2 that are dissolved in the solution to turn the molecules into an ionic form, making them polar and considerably more soluble in a cold solution. Thus, this keeps such acidic gases dissolved in this gas-scrubbing solution. MEA will re-release H_2S or CO_2 when the scrubbing solution is heated. Same goes to alkanolamines. They are weak basic compounds that react with certain acid gases, forming weak chemical bonds. These bonds are easily broken upon mild heating or regeneration. The strength of the alkanolamine's bond and the corresponding heat needed to break it depends on the number of organic hydrocarbon groups attached to the nitrogen atom.

2.6 Process Chemistry

2.6.1. Absorption

The direct chemistry of CO_2 sequestration using absorbents is the carbamate-reaction, which results in the formation of carbamate. H_2S and CO_2 are 'acid gases' because they dissociate in water or aqueous solutions to form weak acids. Aqueous amines are bases. Thus for CO_2 removal, the basis of the chemistry is a combination of acid-base reaction and carbamate reaction for primary and secondary amines, while only acid-base reaction for tertiary amines. Removal of CO_2 using IL does not involve acid-base reaction due to the fact that there are no water molecules for CO_2 to dissociate into and behave like a weak acid. The acid-base reaction is kinetically slow because of the carbonic acid dissociation to the bicarbonate is relatively slow. This is different from the carbamate reaction where the rate of CO_2 absorption is very rapid. All these reactions are shown as below.

2.6.2. CO_2 Absorption via Acid-Base Reaction

$CO_2 + H_2O \rightleftharpoons H_2CO_3$

Using Amines:

$H_2CO_3 + [Amine] \rightleftharpoons HCO3^- + [Amine]^+$ [9]

2.6.3. CO_2 Absorption via Carbamate Reaction

Primary and Secondary Amines:

$CO_2 + 2[\text{Amine}] \rightleftharpoons [\text{Amine}]^+ + [\text{Amine}]\,CO_2^-$

Ionic Liquid:

$CO_2 + 2[\text{Anion}]^+ \rightleftharpoons [\,[\text{Amine}]^+ + [\text{Amine}]\,CO_2^-\,]^{++}$ [9]

2.7 Thermal Stability

Thermal stability is the stability of a molecule at high temperatures such that a molecule with more stability has more resistance to decomposition at high temperatures. Thermal decomposition is defined as a chemical reaction in which a chemical substance breaks up into at least two chemical substances when heated. The reaction is usually endothermic as heat is required to break chemical bonds in the compound undergoing decomposition. The decomposition temperature of a substance is the temperature at which the substance decomposes into smaller substances or into its constituent atoms.

Figure 6: FTIR (Fourier Transform Infrared) Spectroscopy

FTIR (Fourier Transform Infrared) Spectroscopy is an analysis technique that provides information about the chemical bonding or molecular structure of materials, whether organic or inorganic. The technique works on the fact that bonds and groups of bonds vibrate at characteristic frequencies. The bonds can stretch, contract and bend. A molecule that is exposed to infrared rays absorbs infrared energy at frequencies which are characteristic to that molecule. There is a correlation between the wavenumbers at which a molecule absorbs infrared radiation and its structure. This allows the structure of an unknown molecule to be determined from its infrared spectrum, and allows spectra of different samples to be compared to each other to see if they are the same. During FTIR analysis using FTIR spectrometer, a spot on the specimen is subjected to a modulated IR beam. The specimen's transmittance and reflectance of the infrared rays at different frequencies is translated into an IR absorption plot consisting of reverse peaks. [10]

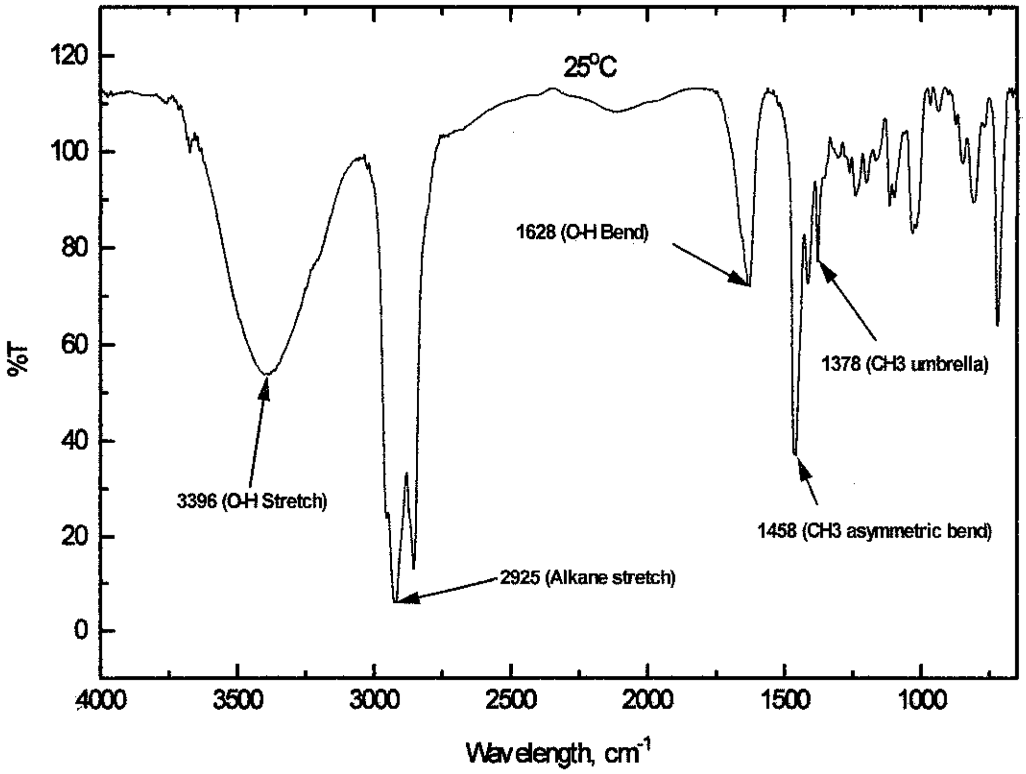


Figure 7: Example of Infrared Spectrum

A plot of measured infrared radiation intensity versus wavenumber is known as an infrared spectrum. Infrared spectra are conventionally plotted with high wavenumber on the left and low wavenumber on the right. This means that as a spectrum is read from left to right, one is reading from high energy to low energy.

2.8 Heat Capacity

Heat capacity, C is a measurable physical quantity that characterizes the amount of heat that is required to change a body's temperature by a given amount. When heat is removed from an object, the temperature of the object decreases [11]. The relationship between the heat (q) that is transferred and the change in temperature (ΔT) is

$$q = C\,\Delta T = C\,(T_f - T_i)$$

The proportionality constant in this equation is called the heat capacity (C). The heat capacity is the amount of heat required to raise the temperature of an object or substance one degree. The temperature change is the difference between the final temperature (T_f) and the initial temperature (T_i).

2.9 CO_2 Solubility in Phosphonium-based Ionic Liquids

Lee Ferguson and Paul Scovazzo in their study stated that gas solubility of the phosphonium-based ionic liquids is of the same magnitude as the gas solubility for the most familiar imidazolium-based ionic liquids. Henry's law constants in both the imidazolium- and phosphonium-based ionic liquids are similar for CO_2 solubility. In imidazolium-based RTILs, the solubility increases as the number of solute carbons increases and when the number of carbon double bonds increases for the hydrocarbon solutes with the same number of carbons. This trend is also observed in phosphonium-based RTILs. [12]

Henry's Law is one the gas laws, states that at a constant temperature, the amount of a given gas dissolved in a given type and volume of liquid is directly proportional to the partial pressure of that gas in equilibrium with that liquid. An equivalent way of stating the law is that the solubility of a gas in a liquid at a particular temperature is proportional to the pressure of that gas above the liquid. Henry's Law has been shown to apply for a wide range of dilute solutions, not merely those of gases. [13]

The Henry's law constants are different in values at different temperatures. It can be seen that the Henry's law constant of all the studied systems increases with increasing temperature, which indicates the solubility of CO_2 decreases with increasing temperature. [14]

CHAPTER 3: METHODOLOGY

3.1 Research Methodology

3.1.1 Experimental

All DCIL samples were prepared in glass vials and closed with screw caps fitted with silicone septum, to ensure a secure seal and preventing their contact with moisture in air. The samples were taken from the vials with a syringe and immediately placed into the apparatus for each experimental measurement to avoid the humid effect of atmosphere.

3.1.2 Hazards and Safety

Toxicology: It is harmful if swallowed, inhaled or absorbed through the skin. It may cause cancer or reproductive defects and also burns.

Personal protection: Safety glasses, gloves, good ventilation. It must be handled as a possible carcinogen.

3.1.3 Thermal Stability Measurement

Many of IL properties are very sensitive to impurities like halides or water. Halides, also free acids or amines can be responsible for a substantial corrosion behavior. Since chloride and water were analyzed in the ionic liquid sample, this will contribute to corrosion in TGA equipment. Hence, instead of using TGA to measure thermal stability of DCIL in question, it is decided to perform direct heating of the sample and analyze it based on resulted FTIR spectra. In addition, TGA equipment is not available and broke down and thus, made it unable for thermal stability determination. The step by step procedure of investigating the thermal stability of DCIL sample is as per below:

Figure 8: Thermal Stability Experiment Setup

Chemical:

1. Ionic liquid sample
2. Diethyl ether
3. Acetone

Apparatus and equipments:

1. Small glass container
2. Retort
3. Syringe
4. Hot plate
5. Thermometer
6. Polishing cloth
7. Perkin Elmer FTIR Spectroscopy

Procedure:

1. Ionic liquid sample is filled into a small glass container to one quarter full by using a syringe.
2. Experiment setup is arranged in the fume hood as shown in Figure 8.
3. The sample area is ensured clean, empty and dry (from cleaning with acetone).
4. FTIR Background spectrum is run.
5. Sample at room temperature is taken from the container and a small drop of the sample is placed on ZnSe plate. It is spread and layered to obtain a nice even film.
6. The plate is placed into the sample holder and a spectrum is run. FTIR spectrum of the sample under investigation is recorded in the wavenumber range 4000 – 650 cm^{-1} using Perkin Elmer system. The spectrum of each sample represents an average of 4 scans.
7. The ZnSe plate is thoroughly cleaned after the above procedure to prevent contamination of future samples. The window is wiped with a tissue, then is washed several times with diethyl ether (solvent that takes off the sample), then acetone.
8. Polishing cloth is used to polish the window surface. Gloves are worn to prevent fogging. Cleaned surface should be clear and free from scratches.
9. Sample is continued to heat up to next temperature, 40°C. When it reaches the desired temperature, the sample is immediately taken and layered on ZnSe plate to be tested using FTIR.
10. Steps 5 to 8 are repeated.
11. Experiment is repeated for temperatures (°C): 70, 90, 120, 150, 170, 190, 240, 270, 290, 320, 350, 370, 390, 410, 430, 450, 470, 490, and 510.
12. Along the experiment, any physical change on ionic liquid sample is observed. The effects of temperature on ionic liquid structure are studied using FTIR spectra.

Infrared Spectral Interpretation [10]:

1. Information about the sample is found out as much as possible beforehand (i.e. molecular structures).
2. The spectrum is quickly read from left to right noting the presence or absence of the intense group wavenumber and quickly deny or confirm the presence of a large number of important functional groups.
3. The intense bands are assigned first using the tables from other sources of information. The intense bands are intense for a reason; they are important and carry important information.
4. The functional groups that exist in the sample are written down. Then the pieces are put together to come up with proposed chemical structures for the molecules in the sample. This must follow the laws of chemistry when writing proposed structures.
5. Get help from the spectral atlases, library searching or interpretation software. The proper point in the interpretation process is to obtain outside help after thoroughly examining the spectrum.

3.1.4 Heat Capacity Measurement

Figure 9: Bomb Calorimeter

Procedure for liquid samples:

1. The ignition cup is weighed to +/- 0.1 mg with and without the liquid sample. Those masses are recorded and the net mass of the liquid sample is determined.
2. The cup and liquid sample is put in place between the electrodes.
3. The two ends of ignition wire are wrapped around the two electrodes, and the wire is looped into the liquid sample. Let the wire touches the liquid but not the edges of the ignition cup.
4. While keeping the wire connected to the electrodes and in contact with the sample, it is gently placed in the body of the bomb and the head is screwed into place.
5. The outlet valve on the bomb's top is closed but not over tightened. With the valves on the oxygen tank closed, the inlet tube from the tank is attached to the bomb.
6. Slowly 20 atm of oxygen is let into the bomb by opening the valve on the oxygen tank. Then the tank valve is closed.
7. The gas is bleeded out of the bomb by slowly opening the outlet valve on the bomb head until a hissing sound no longer be heard. This fill-and empty cycle is repeated two more times at least.

8. Slowly 25 atm of oxygen let into the bomb. This is the final fill. The gas must not be emptied from the bomb this time.
9. The bucket is placed into the insulating jacket and it is ensured to sit flat.
10. 2 L of water is measured with a volumetric flask and place it into holding bucket. The temperature of this water is ensured to be near the lower end of the temperature range visible on the thermometer that is inserted into the calorimeter.
11. The lead wires are attached to the bomb while holding the bomb above the water.
12. The bomb is lowered gently into the bucket and it is ensured to sit flat.
13. The lid is put into place and the lid is clamped down until snug.
14. The ignition button and the timer button are pushed at the same time.
15. Temperature readings are taken every one minute for about 10 minutes prior to the firing the charge.
16. When the run is complete, the stirring motor is turned off, lift and the cover is moved. The metal bucket is lift out of the calorimeter and the bomb is removed from the bucket. The bomb is carefully dried, and the gas outlet valve is gently opened to relieve the inside pressure. Once the pressure has decreased (no more hissing), the top of the bomb is removed.
17. The inside walls of the bomb is checked for beads of water or soot.

3.1.5 CO_2 Solubility Measurement

This research methodology is adapted based on the method presented by Suojiang Zhang *et al* [9]. for measuring CO_2 solubility in sulfonate ionic liquids at high pressure. The apparatus used for CO_2 solubility measurement consists of a stainless steel pressure cell, a CO_2 gas storage tank, a pressure gauge, a pressure transducer, a vacuum pump, a thermometer and a temperature-constant water bath; a schematic diagram of the experimental apparatus is shown in Figure 10. The system is designed so that CO_2 absorption measurements could be repeated several times with the same ionic liquid sample.

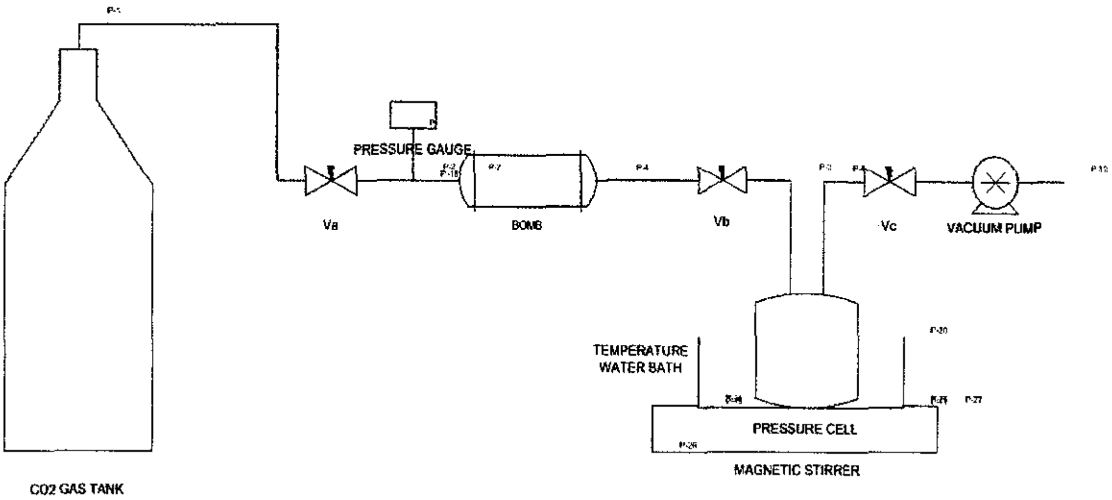


Figure 10: Schematic Diagram of the CO_2 Absorption System

Procedure:

1. An accurate amount (0.25-0.28mL) of DCIL is loaded in the pressure cell using micropipette and degassed in the temperature-constant water bath.
2. The system is evacuated using the vacuum pump by opening valve V_c until the pressure cell pressure reaches constant value (equilibrium condition).
3. Valve V_c is closed.
4. CO_2 gas is introduced into the system by opening the valve V_a. (The equilibrium condition is judged when there is no change in pressure or pressure change is negligible).
5. Valve V_b is opened so that DCIL sample could be in contact with CO_2 gas.
6. Valve V_c is kept closed throughout series of run.
7. Ambient pressure of 1 atm is measured before opening valve V_b and after equilibration with valve V_b is opened.
8. The system is let to run for 3 hours before the DCIL sample is taken for test using FTIR.
9. Temperature was measured by a thermometer with an accuracy of better than ±0.01 K and pressure by a pressure transducer with an accuracy of ±0.025 MPa.

Instead of using pressure drop to measure solubility of CO_2 in phosphonium-based DCIL in question, the FTIR will be utilized to see the interaction between DCIL and CO_2. Any change in the structure of examined DCIL sample is noted.

3.2 Tools and Equipment

Table 2: Tool and Equipment

Experiment/Test	Equipment/Apparatus
Thermal stability	1. Direct Heating Apparatus 2. Fourier-transform Infrared Spectroscopy (FTIR)
Heat Capacity	Bomb Calorimeter
CO_2 Solubility in DCIL	1. CO_2 Absorption System 2. Fourier-transform Infrared Spectroscopy (FTIR)

CHAPTER 4: RESULT AND DISCUSSION

4.1 Thermal Stability Measurement

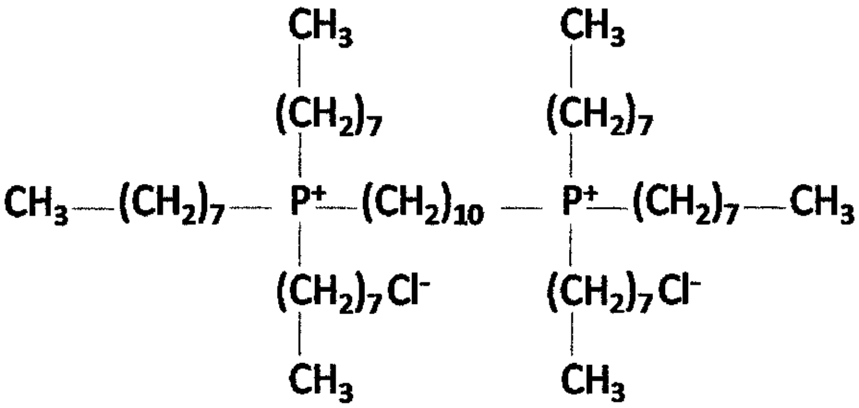


Figure 11: 1, 6-bis (trioctylphosphonium-1-yl) decane chloride structure

From the known molecular structure in Figure 11, it is confirmed that initially the molecular bondings exist in the ionic liquid are C-H bond (alkane), C-CL (Halogenated Organic Molecules) and C-P. However, chloride and water content were detected in the ionic liquid sample based on FTIR spectrum at room temperature in Figure 12. Ionic liquids are more difficult to purify than volatile organic solvents, and thus are often contaminated with one or more of the starting materials or water (generally absorbed from the atmosphere). Chloride and alkali metal ions have dramatic effects on transport properties.

The IR spectrum of DCIL at room temperature is shown in Figure 12 below. The absorption in the region around 3396 cm^{-1} in the IR spectra can be assigned to O-H stretch. The appearance of a peak around 721 cm^{-1} suggested that the DCIL have C-CL stretch for halogenated organic molecules. The other major peaks which can be clearly observed are around 2925 and 1458 cm^{-1} indicating the structure of alkane. At the wavelength of 1377 cm-1 and 1628 cm^{-1}, CH_3 umbrella bend and O-H bend can be assigned respectively.

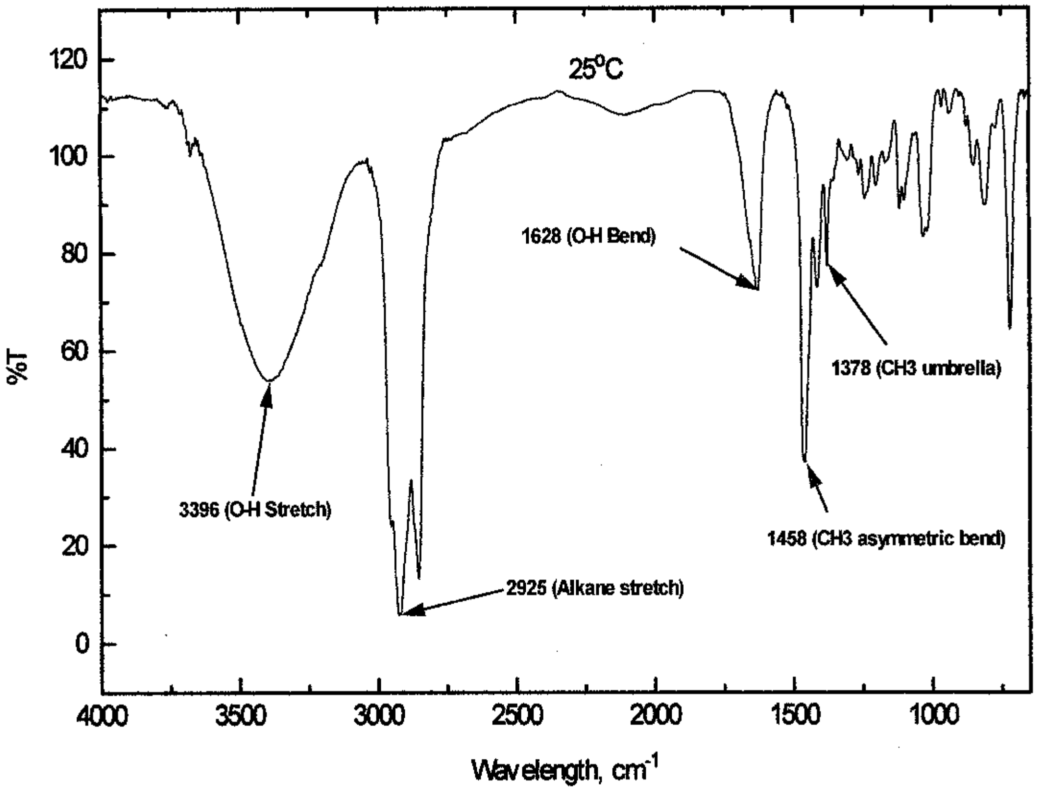


Figure 12: FTIR Spectra at Room Temperature

Following table contains the characteristic examples which are referred in order to become familiar with the intensity and shape absorptions bands for respective absorptions.

Table 3: Characteristic Infrared Absorption Frequencies [10]

Frequency Range (cm^{-1})	Compound Type
3500 - 3200	O-H Stretch
1630	O-H Bending
2960 - 2850	C-H Aliphatic Stretch
1375± 10	CH_3 Umbrella Bending Mode
1470 – 1350	C-H (Alkanes) Bending
800-600	C-CL Stretch for Halogenated Organic Molecules

Infrared spectra are recorded as a function of temperature from room temperature to 510°C. An analysis of the temperature-induced changes in the structures is performed based on changes in the ionic liquid bands.

At room temperature, it is observed that DCIL is clear and faintly yellow in colour. During the heating period from room temperature to 120°C, there is no colour change of the ionic liquid sample; it remains yellowish and honey-like in colour. The viscosity of the sample is very much the same as compared to its previous state at room temperature. No smoke or smell is detected in the fume hood during the heating process. At temperature of 120°C and above, the colour of the ionic liquid sample begins to change slowly to dark yellow and then brownish. The sample becomes more viscous. At 380°C onwards, smoke and petrol-like smell can be detected and it is blackish in colour. At 510°C, no more ionic liquid sample is left in the container since it changes into solid state and sticky.

Although the spectra (i.e. structures) after complete thermal decomposition are clearly different, the spectrum of DCIL after first stage of heating (at 40 °C) is the same as that at room temperature and clearly shown in Figure 13 below.

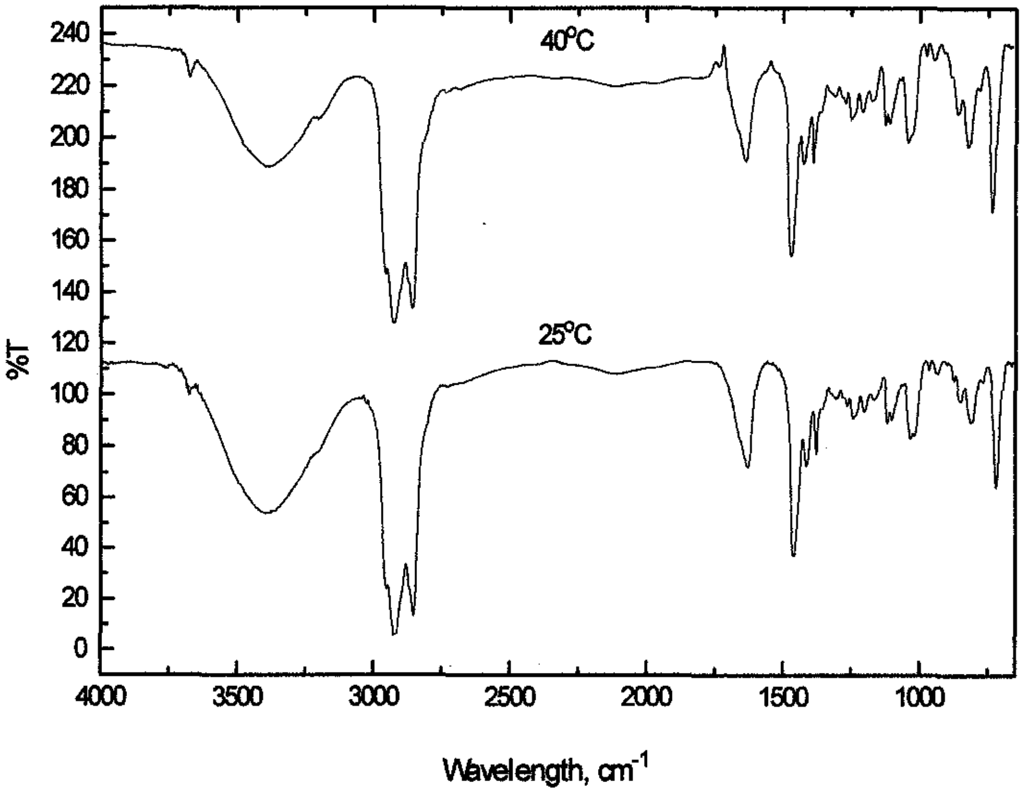


Figure 13: FTIR Spectra at 25 °C and 40 °C

The DCIL is proved to be stable when heated from room temperature up to some temperatures that can be considered as the temperature at which the decomposition of DCIL starts (i.e. at 490°C). A study of temperature effect on this DCIL revealed that it has a high thermal stability at temperature close to 490 °C corresponds to the start of the thermal decomposition as shown in Figure 14. Effect of temperature rise on other IR spectra of DCIL is shown in Appendix A.

However, the condition may not 100% represent at the particular temperature since the sampling time not on isothermal condition, that can give better representative profile at isothermal as well as reaching an equilibrium condition. This means that it should be reinvestigated in order to achieve good understanding on the DCIL tested.

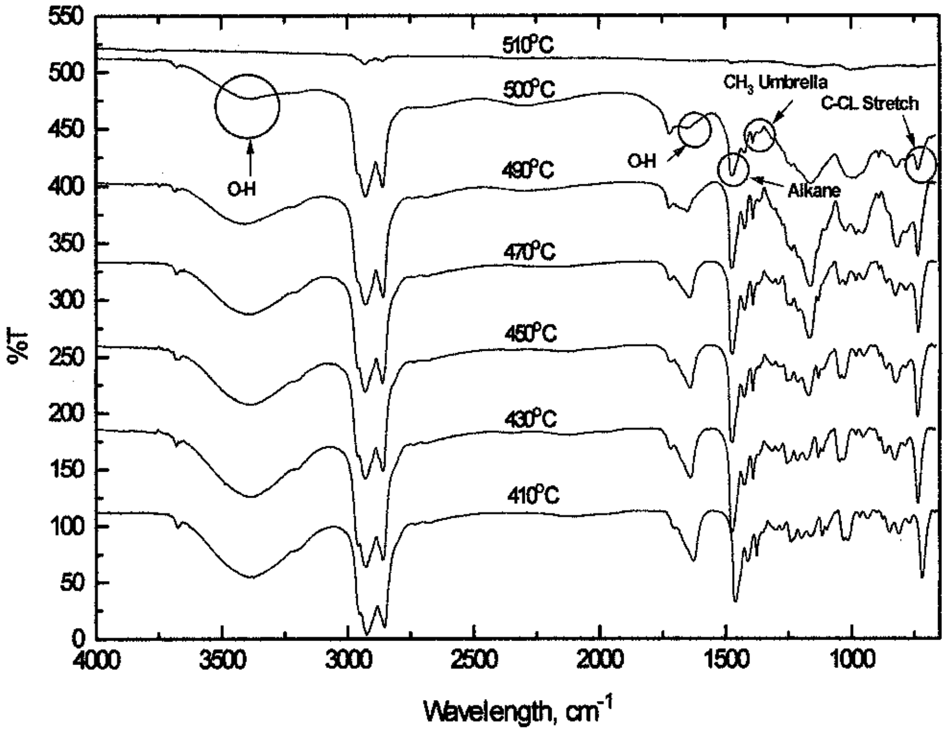


Figure 14: FTIR Spectra at Temperatures 410°C to 510°C

Bond energy is a measure of the strength of a chemical bond. The amount of energy required to break a bond is called bond dissociation energy or simply bond energy. The bond energy is essentially the average enthalpy change for a gas reaction to break all the similar bonds. The larger the bond energy is, the stronger the bond. Distances between centers of bonded atoms are called bond lengths, or bond distances. The smaller the distance between the participating atoms, the higher is the bond dissociation energy and bond energy; that is more energy is required to break the bond.

Table 4 below shows the values of bond energies and bond lengths for all the possible bonds exist in this DCIL structure. Relatively high bond strength is seen at room temperature.

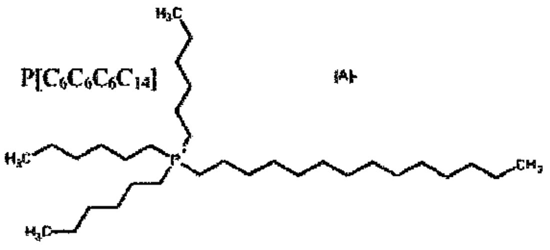
Table 4: Bond Energy and Bond Length [15]

Bond	Bond Energy, kcal/mol	Bond Length, pm
C-C	83 - 85	154
C-H	98	106 - 112
C-Cl	79	177
H_3C-H	105	-
O-H	110	92 - 98

At temperature 25 to 470°C, the bond strength leveled off and remained constant as the temperature is increased, as can be seen in Figure 14. At temperature in the range of 490°C, a reduction in the bond strength is seen for all of the bonds stated in Table 4 above as a consequence of heating. Experiments are stopped at around 510°C. At higher temperature (470 °C and above), the DCIL structure begins to decompose, no mechanical properties can be expected at these temperatures.

Referring to the visible changes in peak intensities of IR spectra in Figure 14, C-Cl stretch is the most sensitive to temperature rise and loses its bond strength rapidly as compared to other bonds. This is due to its low bond energy which is the least one, 79 kcal/mol. Loss of ~50% of C-H bend (alkane) bond strength is seen at temperature of 500°C since it has the second weakest bond energy; 98 kcal/mol. This is different from C-H aliphatic stretch that undergoes almost no change in its peak intensity under temperature rise. This is because methyl C-H bond is one of the strongest aliphatic C-H bonds with 105 kcal/mol of bond energy. Rapid reduction in bond strength is also seen for CH_3 bend in which most of the reduction is in the 500°C range. The reduction in bond strength of the O-H stretch and O-H bend occurred over a wider range, from low temperature and extended up to 500°C. An additional increase in the temperature produced a very moderate additional loss of bond strength. In conclusion, the effect of the elevated temperature is more critical for C-Cl stretch.

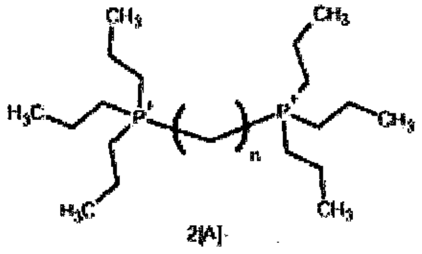
This thermal stability result is then compared with other types of phosphonium-based ILs from a reliable literature published in Springerlink [4]. One of the study focuses is to investigate thermal stability of both phosphonium-based MCIL and DCIL. Figure 15 and Figure 16 below show the structures for the ionic liquids studied in this analysis.



A1 = $[A]^- = [Cl]^-$ **A4** = $[A]^- = [NTf_2]^-$
A2 = $[A]^- = [BF_4]^-$ **A5** = $[A]^- = [NCNCN]^-$
A3 = $[A]^- = [TfO]^-$ **A6** = $[A]^- = [SAC]^-$

Figure 15: Phosphonium-based MCIL

$C_n(P[C_3C_3C_3])_2$



D1 = n = 10 ; $[A]^- = [NTf_2]^-$
D2 = n = 12 ; $[A]^- = [NTf_2]^-$

Figure 16: Phosphonium-based DCIL

Table 5 below shows the approximate thermal stabilities for both types of IL under study, which are phosphonium-based MCIL and DCIL.

Table 5: Thermal Stability for Phosphosnium-based MCIL and DCIL [4]

Ionic Liquid		**Approximate Thermal Stability, °C**
Monocations		
A1	$P[C_6C_6C_6C_{14}]$ Cl	335
A3	$P[C_6C_6C_6C_{14}]$ TfO	405
A4	$P[C_6C_6C_6C_{14}]$ NTf_2	380
Dications		
D1	$C_{10}(P[C_3C_3C_3])_2$ NTf_2	425
D2	$C_{12}(P[C_3C_3C_3])_2$ NTf_2	425
E1	$PEG_3(P[C_3C_3C_3])_2$ NTf	410

From the above table, dicationic phosphonium ILs show increased thermal stability possessing decomposition temperatures up to 425 °C and liquid ranges well over 400 °C. These RTILs have not been reported in the literature before and will prove to be very useful as high thermal stability solvents and stationary phases.

Figure 17 shows four representative thermal stability curves for a variety of phosphonium-based ILs. The first three curves represent the thermal stability of phosphonium MCILs, whereas the last curve represents a phosphonium DCIL. The lowest thermal stability is observed for the chloride IL **A1**. The most thermally stable phosphonium MCIL was **A3**, with an approximate decomposition temperature of 405 °C. The phosphonium DCILs show increased thermal stability possessing decomposition temperatures up to 425 °C and liquid ranges well over 400 °C. These RTILs have not been reported in the literature before and will prove to be very useful as high thermal stability solvents. The thermal stability and robustness of the phosphonium IL columns dominates nitrogen-based IL columns in every aspect. It is expected that the preceding will persuade and attract many researchers to phosphonium RTILs. [4]

However, if a comparison has to be made between D3 phosphonium-based DCIL and our DCIL under study, 1,6-bis(trioctylphosphonium-1-yl)decane chloride, it is clear that thermal stability of the latter one is much higher, up to 470°C. This indicates that it is approximately 45°C more thermally stable than D3. Hence, this type of phosphonium-based DCIL is very potential as high thermal stability solvents and stationary phases.

Thermal stability tests indicate a significant advantage for the phosphonium-based ILs. Phosphonium MCILs are approximately 200 °C more thermally stable than imidazolium MCILs. Newly synthesized phosphonium DCILs also offered increased thermal stability and resulted in RTILs with liquid ranges greater than 400 °C. The lowest thermal stability was observed for the chloride IL **A1**. The most thermally stable phosphonium MCIL was **A3**, with an approximate decomposition temperature of 405 °C. Comparing the phosphonium MCILs with nitrogen MCILs, it is clear that the phosphonium ILs are more thermally stable. In general, phosphonium MCILs can be about twice as stable as imidazolium MCILs. For example, the phosphonium Cl and NTf_2 ILs **A1** and **A4** were stable to 335 °C and 380 °C, respectively, whereas their imidazolium-based analogs BMIM Cl and BMIM NTf_2 are only stable to approximately 145 °C and 185 °C, respectively. Also, the phosphonium DCILs are more thermally stable than imidazolium DCIL. With these results in mind, it is easy to believe that researchers may choose to use the more robust phosphonium IL columns instead of nitrogen-based ILs when high temperatures are needed. [4]

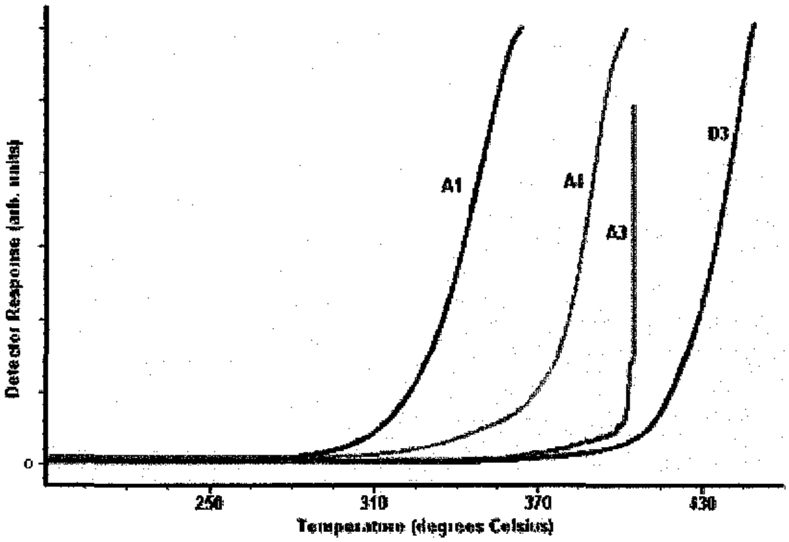


Figure 17: Thermal Stability of Examined IL [4]

4.2 Heat Capacity Measurement

The energy needed to increase the temperature of a kilogram of substance by 1K (the specific heat capacity) is a quantity considerable interest for many industrial applications. Bomb calorimeter has been used for many fluids in order to determine this heat capacity. In the adiabatic method, heat exchange between the calorimeter and its environment is eliminated as long as a temperature gradient does not exist. [15]

After a successful ignition, the temperature of the calorimeter rises quickly. After the several minutes, the rate of change of temperature becomes small. Temperature difference for the run is determined by plotting Temperature versus Time using the data in Table A.1 and Table A.2 in Appendix B. A linear least square fit over the regions of the pre- and post-ignition and extrapolate the result over the entire time period as shown in Figure 18. The distance ($T_2 - T_1$) is taken as temperature difference for the combustion reaction. [15]

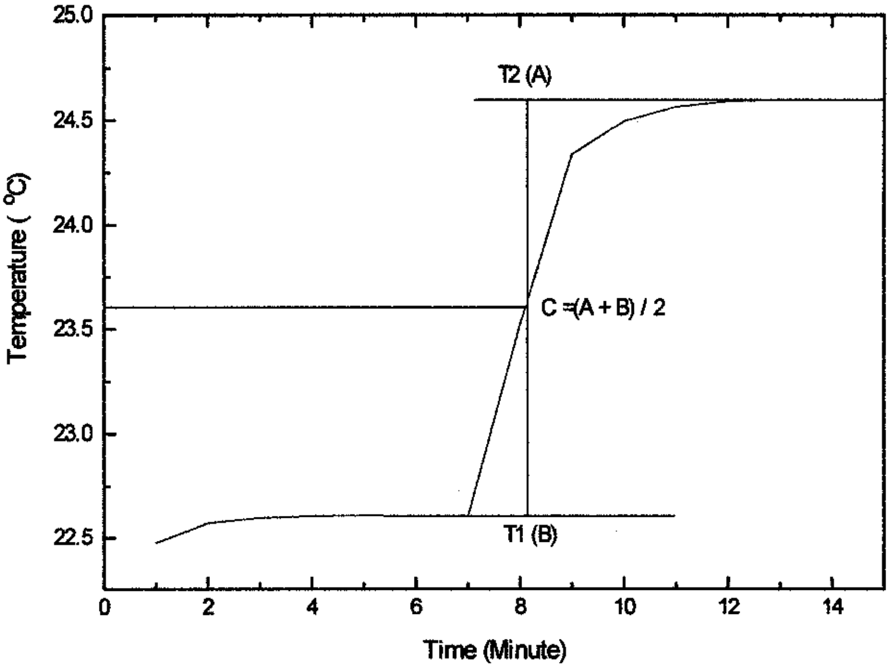


Figure 18: Temperature vs. Time Plot for Average Data

The equation that governs the energy calculation is:

$$E = -mc\Delta T$$

However, the question above is used in a slightly modified form in order to calculate the specific heat capacity:

$$Q = mC\Delta T + e$$

$$Q = \frac{(m_{H_2O}C_{H_2O} + m_{IL}Co)(T_2 - T_1) + e}{m_{IL}}$$

Where,

Q = Heat released by the bomb per mass, cal/g

m_{H_2O} = Mass of water = 2L = 2000g

C_{H_2O} = Specific heat capacity of water = 1 cal/g°C

m_{IL} = Mass of ionic liquid sample tested, g

C_o = Specific heat capacity of calorimeter (bomb and contents, can, immersed portion of thermometer etc.), cal/g°C

T_2 = Final temperature, °C

T_1 = Initial temperature, °C

e = Pre-determined ignition wire energy = 50 J = 11.95 cal

Referring to the heat capacity calculation in Appendix D, heat capacity of the DCIL tested using Bomb Calorimeter is 36.6506 kJ/g°C. Data for this calculation is taken as average of Trial 1 and Trial 2. Consider a standardization test in which 0.5742g of standard benzoic acid with heat of combustion of 26.434kJ/g produces a temperature rise of 1.27°C. The calculated heat capacity of bomb calorimeter is 20.92 kJ/g°C. Comparing this value to heat capacity of examined DCIL, the latter one can be said as small. Hence, it can be concluded that the DCIL can easily gain heat and easy to lost it.

4.3 CO_2 Solubility in Phosphonium-based DCIL Measurement

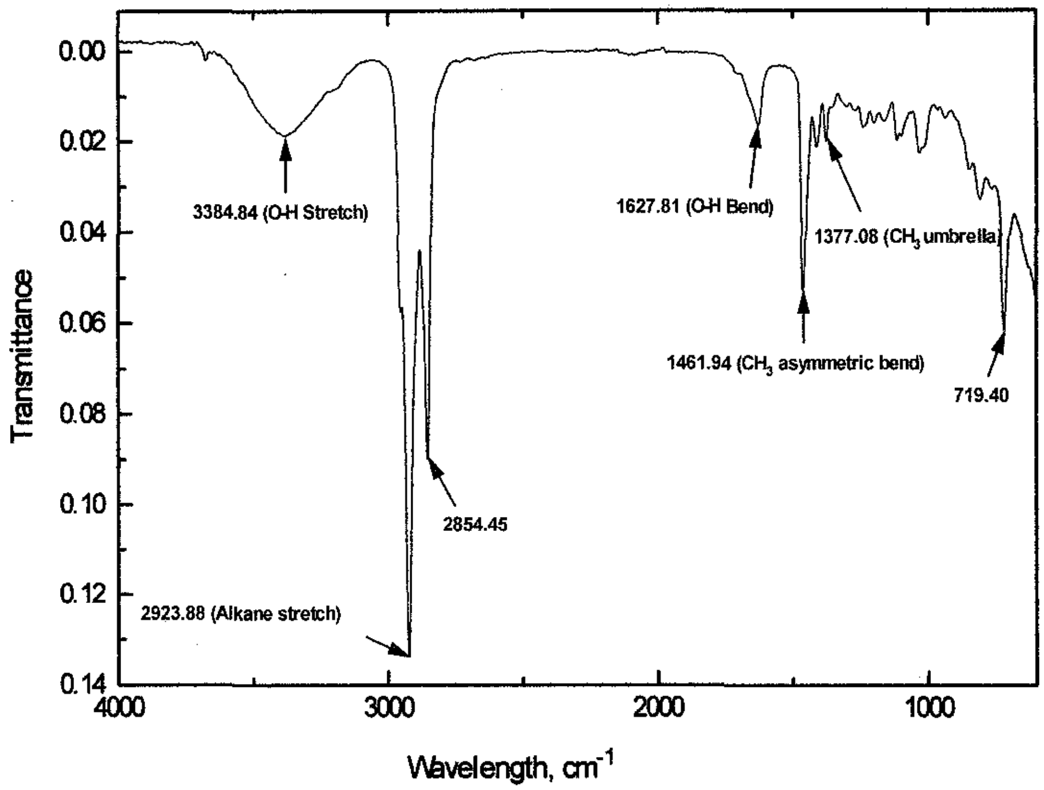


Figure 19: FTIR Spectrum after bubbled with CO_2 at RT and 1 atm

The experiment involves bubbling of CO_2 on the phosphonium-based DCIL in question at room temperature and ambient pressure using the pressure cell for three hours. Then, the FTIR spectrum of the sample is analyzed to see whether there is any chemical absorption of CO_2 by the DCIL sample.

Based on the FTIR test result in Figure 19, it shows the same trend for DCIL in contact with and without CO_2. There is no presence of C-O species in DCIL structure in the 2400-2000 cm^{-1} region. Thus, this can be concluded that no chemical absorption occurs between CO_2 and DCIL sample at room temperature and ambient pressure. CO_2 chemical absorption in DCIL sample might occur at higher pressure than 1 atm.

CHAPTER 5: CONCLUSION & RECCOMENDATION

From the two experiments done by using FTIR Spectroscopy and Bomb Calorimeter, both thermal stability and heat capacity of the tested 1,6-bis(trioctylphosphonium-1-yl)decane chloride had been revealed. Thermal stability of DCIL in question is high; up to 470°C, whereas its heat capacity is quite small with 36.6506 kJ/g°C. The determination and understanding of basic thermophysical properties of DCILs such as thermal stability (to set the feasible temperature operating range) is vital for the process design and development of contacting equipments. The thermal stability of the IL investigated here indicates that it is suited for use as heat transfer fluid as well as as solvent for separation purpose. In many ways it is superior to present commercial heat transfer fluids. Contamination of IL due to water and chloride might have minimal impact on the physical and thermal properties. It is abundantly clear that physical properties must be measured on pure samples, and that the samples be analyzed for the contaminants mentioned above. Otherwise, the values reported for physical properties will be suspected. In spite of the importance and utility of DCILs, accurate data for many of their fundamental physical, chemical and thermodynamic properties are either insufficient or even more absent for both theoretical research and industrial application. In the recent past, the investigation on the properties of DCILs has increased considerably. The establishment of the database will definitely promote the research and development of DCILs. However, due to large inconsistency for characterization data of DCILs in the published literature, there is and huge need of generating reliable and accurate data along with stability of the investigated DCILs samples.

REFERENCES

1. Bradaric C. J, Downard A., Kennedy C, Robertson A. J., Zhou Y, 2003, *Green Chem.* (5)143

2. Kenneth R. Seddon, Robin D. Rogers, 2002, *Ionic Liquids Industrial Applications to Green Chemistry,* Washington, American Chemical Society

3. Chinn Daniel, Boudreau Laura, Michael S, Vu De Q, 2006, "CO_2 Removal from Gas using Ionic Liquid Absorbents", *FreePatentOnline.com*

4. Daniel W. Armstrong, Zachary S. Breitbach, 2008, "Characterization of Phosphonium Ionic Liquids through a Linear Solvation Energy Relationship and Their Use as GLC Stationary Phases", *Analytical and Bioanalytical Chemistry* 390(6): 1605-1617

5. Aleksandar Matic, Anna Martinelli, Fausto Croce, Jagath Pitawala, Per Jacobsson, Victor Koch, 2009, "Thermal Properties and Ionic Conductivity of Imidazolium Bis(trifluoromethanesulfonyl)imide Dicationic Ionic Liquids", *J. Phys. Chem B* 113: 10607-10610

6. Ning Sun, Suojiang Zhang, Xiangping Zhang, Xingmei Lu, Xuezhong He, 2006, "Physical Properties of Ionic Liquids: Database and Evaluation", *J Phys. Chem. Ref. Data* 35(4)

7. Chinn Daniel, Boudreau Laura, Michael S, Vu De Q, 2006, "CO_2 Removal from Gas using Ionic Liquid Absorbents", *FreePatentOnline.com*

8. Abu Bakr, Postgraduate student of Universiti Teknologi PETRONAS, Perak. Personal Interview. Sep. 10. 2009

9. Irza Hairani, 2009, *Carbon Dioxide Removal Using Ionic Liquid,* Final Year Project Thesis, Universiti Teknologi PETRONAS, Malaysia

10. Brian Smith, 1999, *Infrared Spectral Interpretation: A Systematic Approach,* New York, CRC Press

11. <http://science.jrank.org/pages/3265/Heat-Capacity.html>

12. Lee Ferguson, Paul Scovazzo, 2007, "Solubility, Diffusivity, and Permeability of Gases in Phosphonium-Based Room Temperature Ionic Liquids: Data and Correlations", *Ind. Eng. Chem. Res.* 46 (4): 1369–1374

13. International Union of Pure and Applied Chemistry, 1993, *Quantities, Units and Symbols in Physical Chemistry,* (2):50, Oxford: Blackwell Science

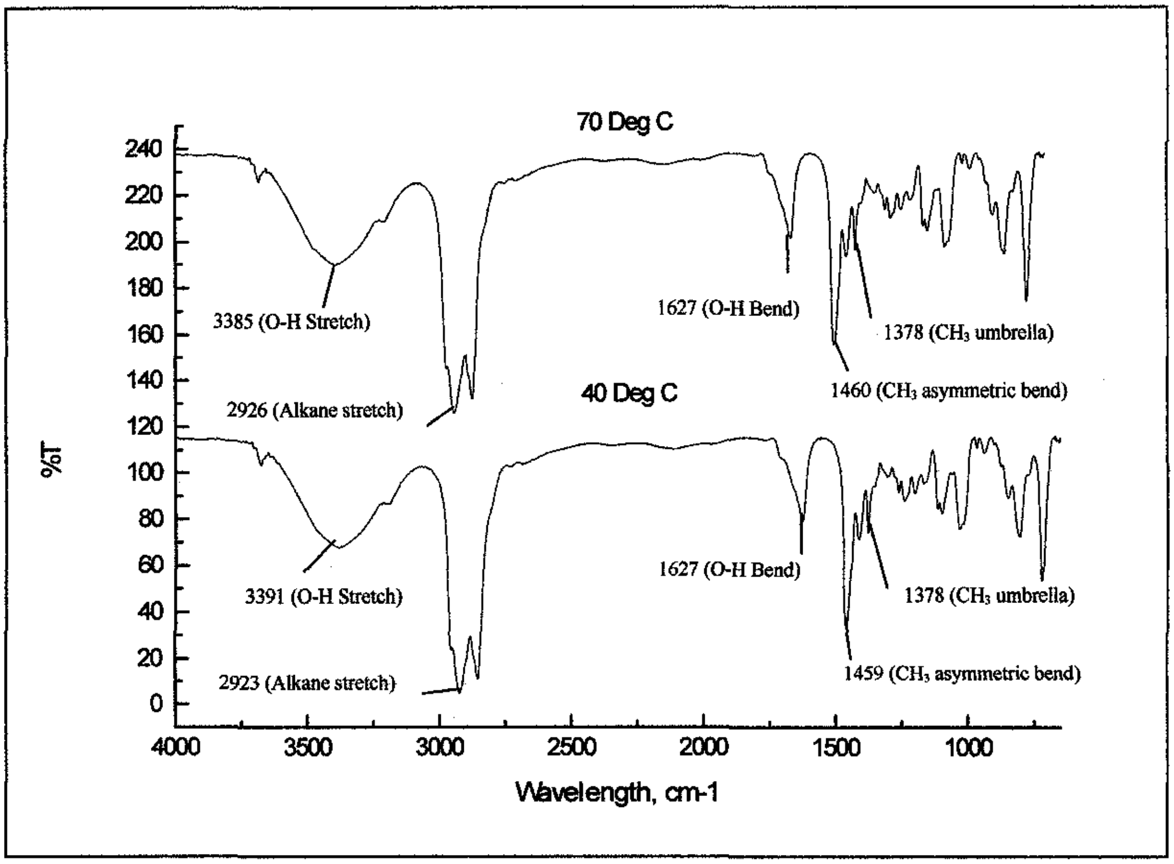
14. Jianmin Zhang, Rex X.-F. Ren, Suojiang Zhang, Xiangping Zhang, Yanqiang Zhang, Yuhuan Chen, 2005, "Solubility of CO_2 in Sulfonate Ionic Liquids at High Pressure", *J. Chem. Eng. Data* 50: 230-233

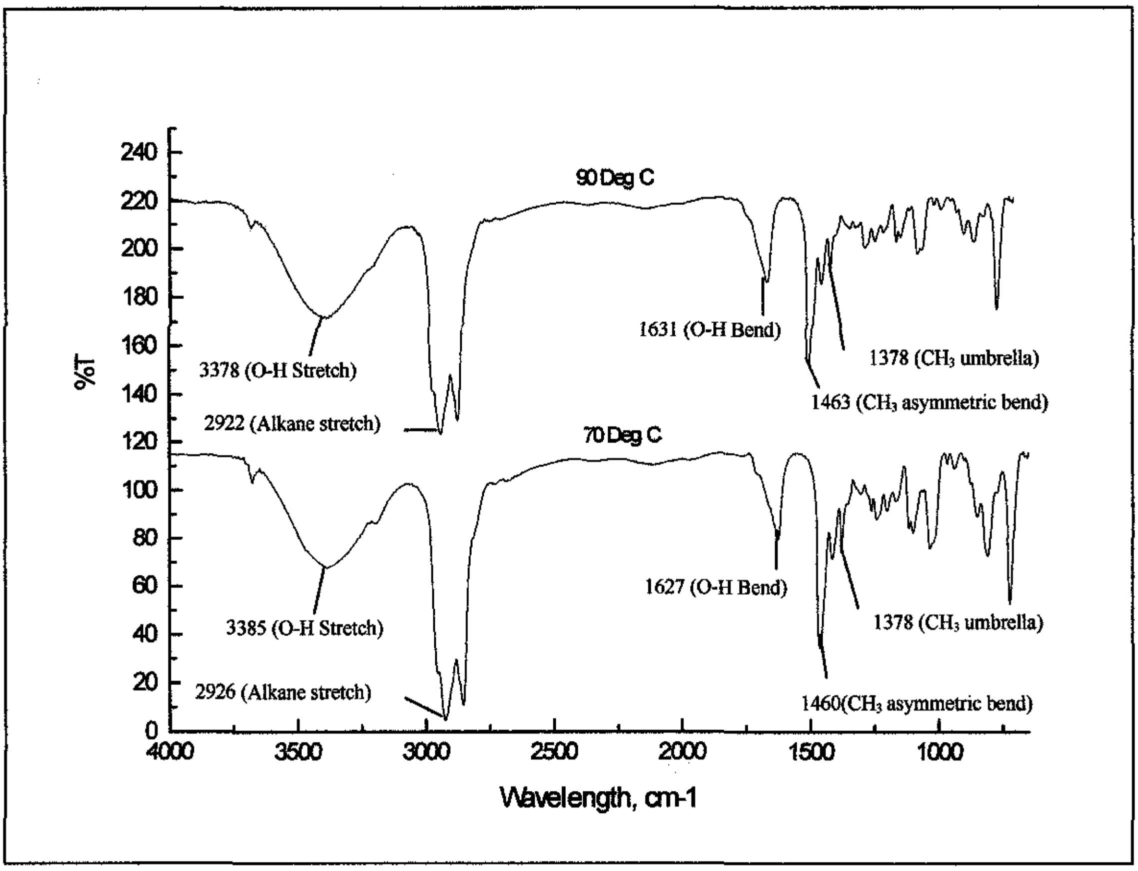
15. <http://www.chem.hope.edu/~polik/Chem345-2000/bombcalorimetry.htm>

16. Amir Shafeeq , Ayyaz Muhammad, C.D. Wilfred, M.I. Abdul Mutalib and T. Murugesan, 2008, "Thermophysical properties of 1-hexyl-3-methyl imidazolium based ionic liquids with tetrafluoroborate, hexafluorophosphate and bis(trifluoromethylsulfonyl)imide anions", *The Journal of Chemical Thermodynamics* 40(9): 1433-1438

APPENDICES

Appendix A: Interpreted FTIR Spectra

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%T
240
220
200
180
160
140
120
100
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60
40
20
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2922 (Alkane stretch)
1631 (O-H Bend)
1378 (CH_3 umbrella)
1463 (CH_3 asymmetric bend)
3385 (O-H Stretch)
2926 (Alkane stretch)
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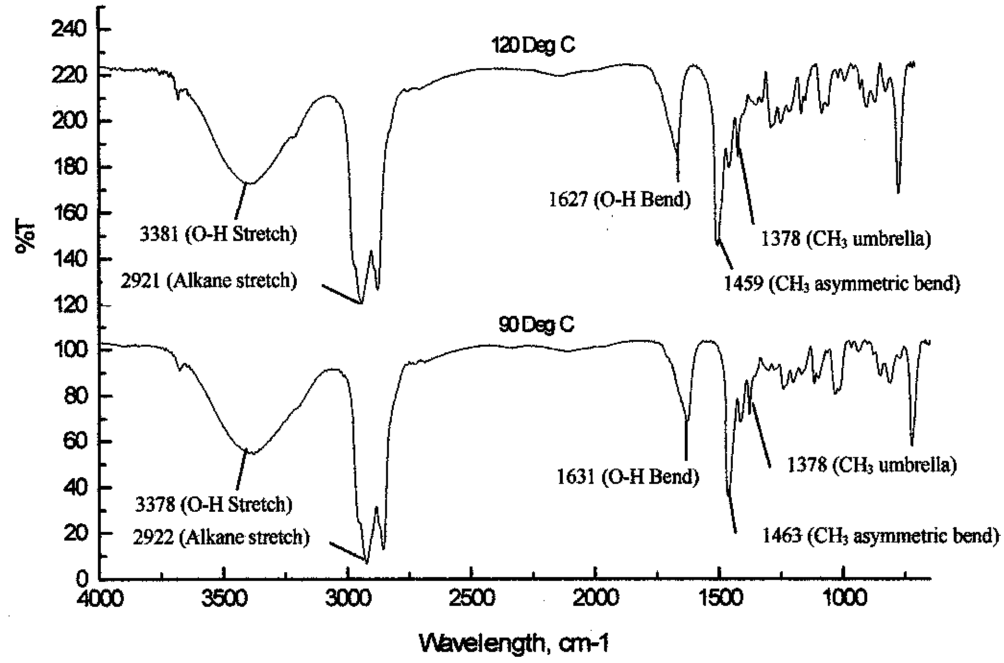
3000
2500
2000
1500
1000
Wavelength, cm-1



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160
140
120
100
80
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40
20
0
%T
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3381 (O-H Stretch)
2921 (Alkane stretch)
1627 (O-H Bend)
1378 (CH3 umbrella)
1459 (CH3 asymmetric bend)
90 Deg C
3378 (O-H Stretch)
2922 (Alkane stretch)
1631 (O-H Bend)
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3000
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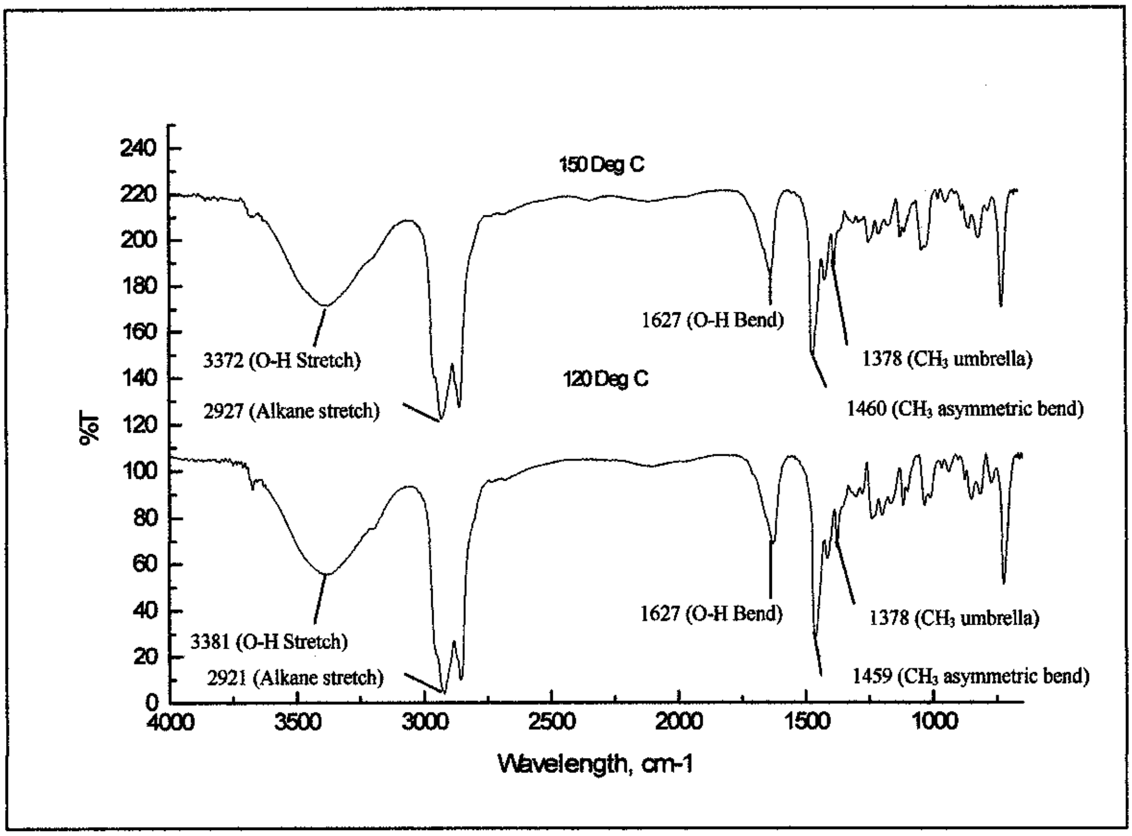
2000
1500
1000
Wavelength, cm-1



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1627 (O-H Bend)
1378 (CH$_3$ umbrella)
1459 (CH$_3$ asymmetric bend)
%T
0
20
40
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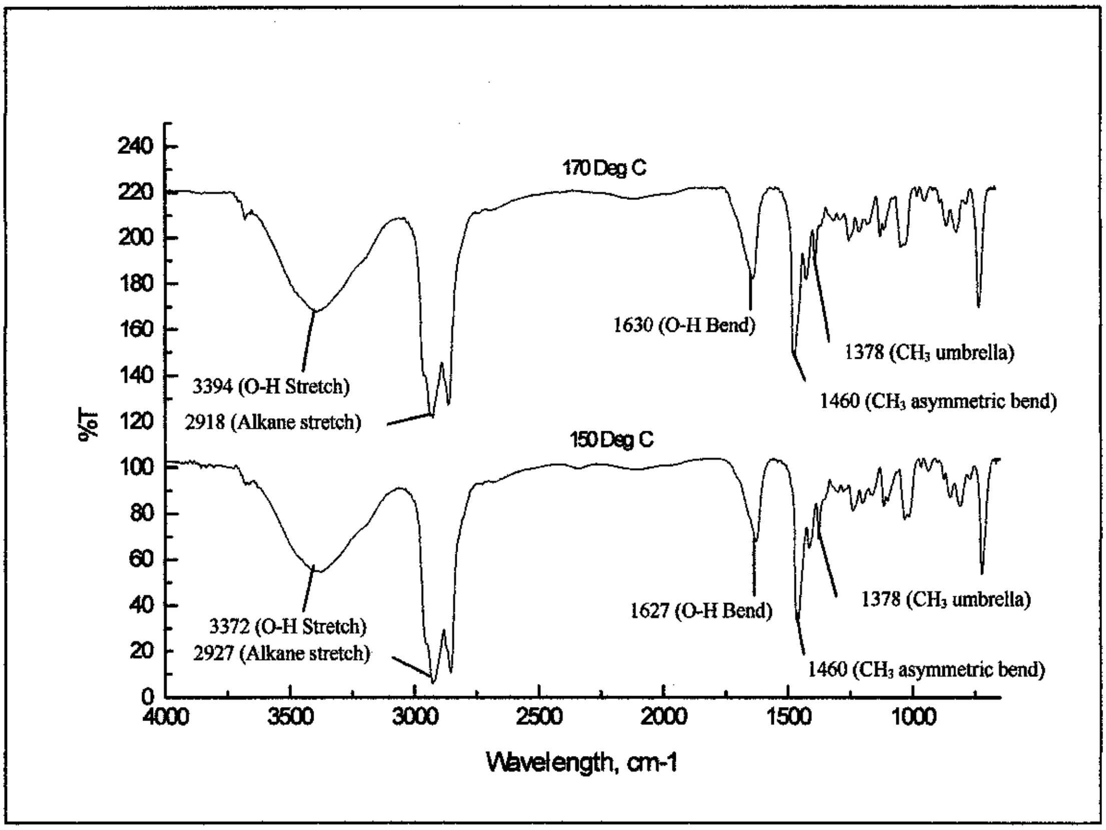
1000
Wavelength, cm-1



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160
140
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100
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60
40
20
0
%T
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1630 (O-H Bend)
1378 (CH₃ umbrella)
1460 (CH₃ asymmetric bend)
150 Deg C
3372 (O-H Stretch)
2927 (Alkane stretch)
1627 (O-H Bend)
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1460 (CH₃ asymmetric bend)
4000
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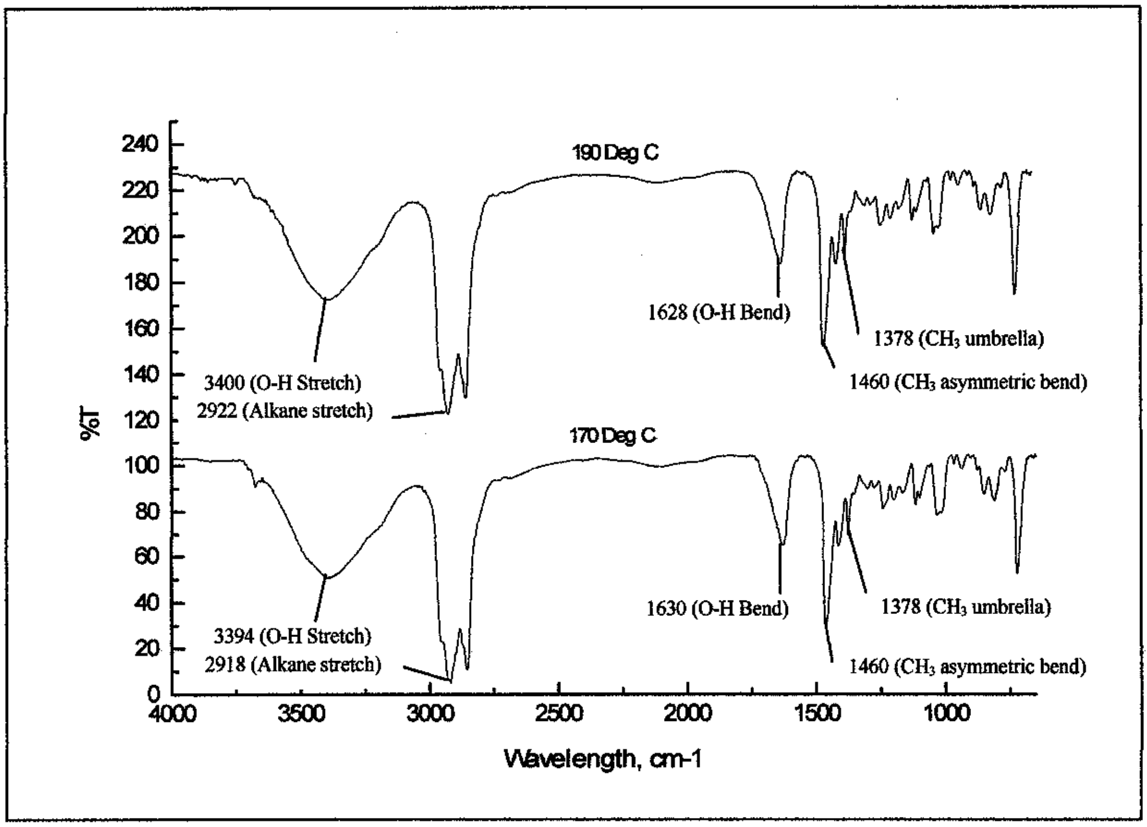
3000
2500
2000
1500
1000
Wavelength, cm-1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1378 (CH₃ umbrella)
1460 (CH₃ asymmetric bend)
%T
240
220
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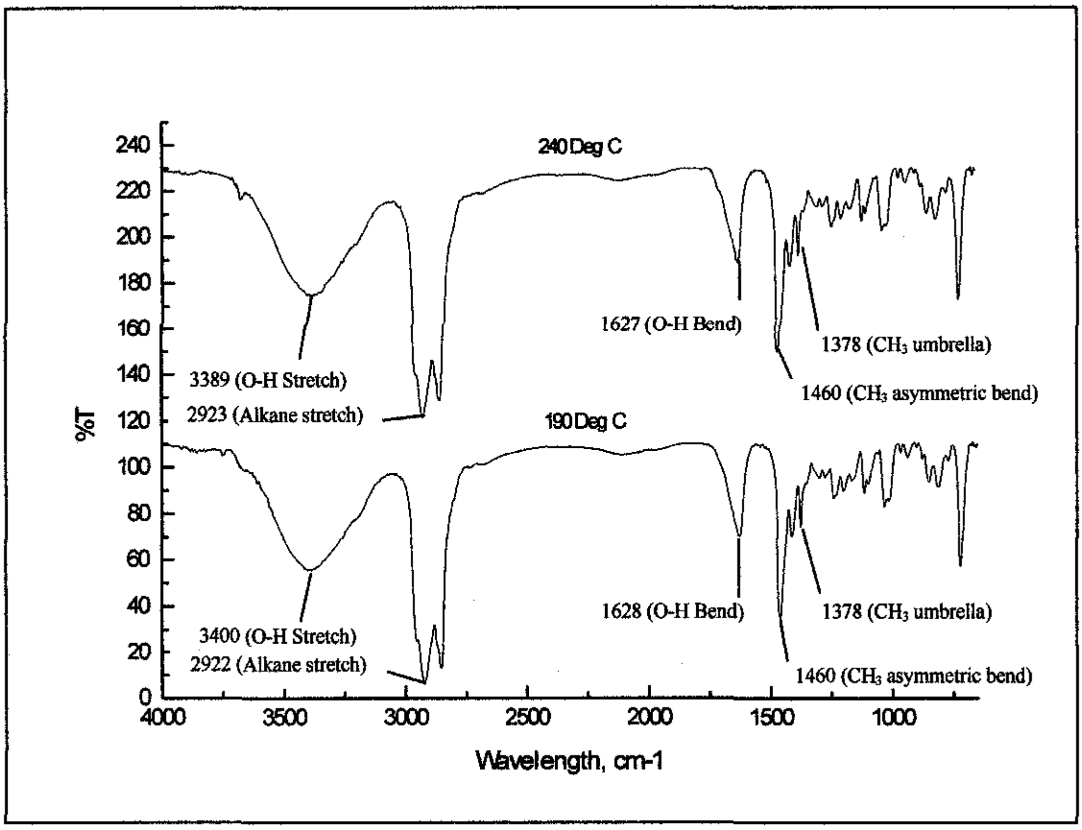
Wavelength, cm-1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1628 (O-H Bend)
1378 (CH_3 umbrella)
1460 (CH_3 asymmetric bend)
%T
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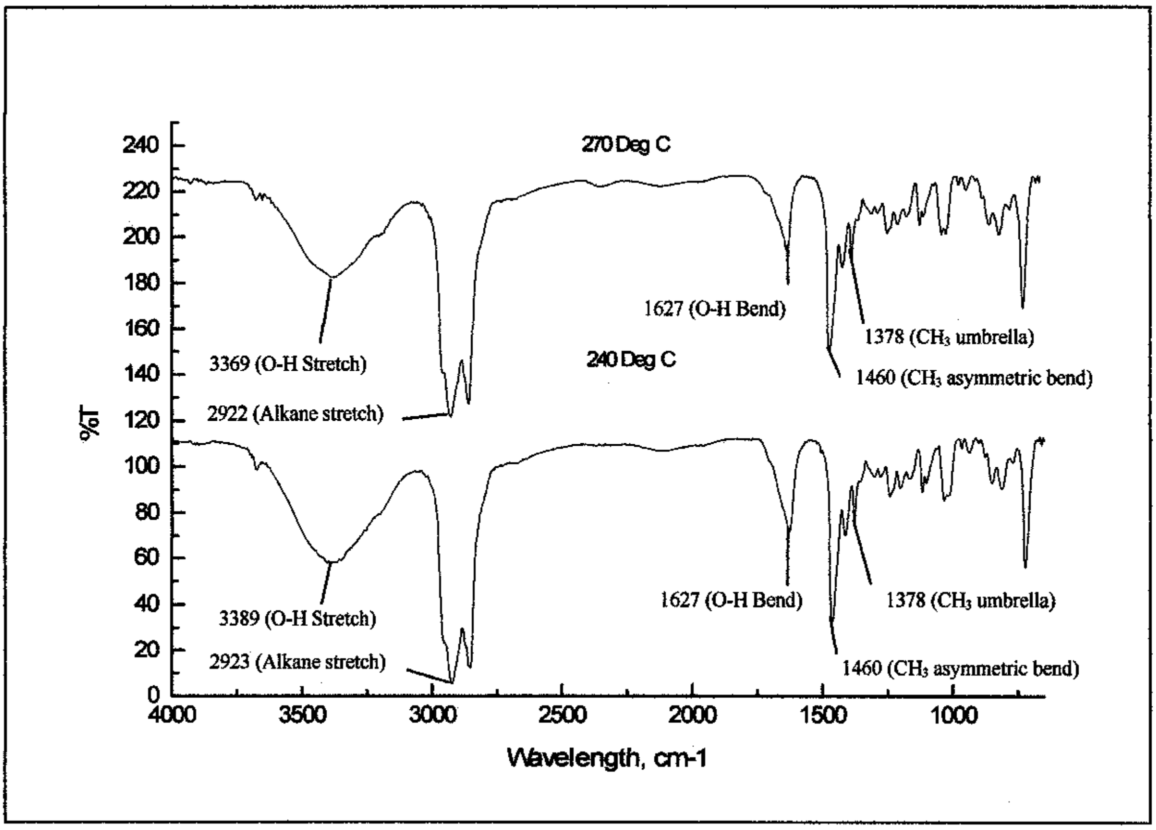
Wavelength, cm-1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1627 (O-H Bend)
1378 (CH₃ umbrella)
1460 (CH₃ asymmetric bend)
%T
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20
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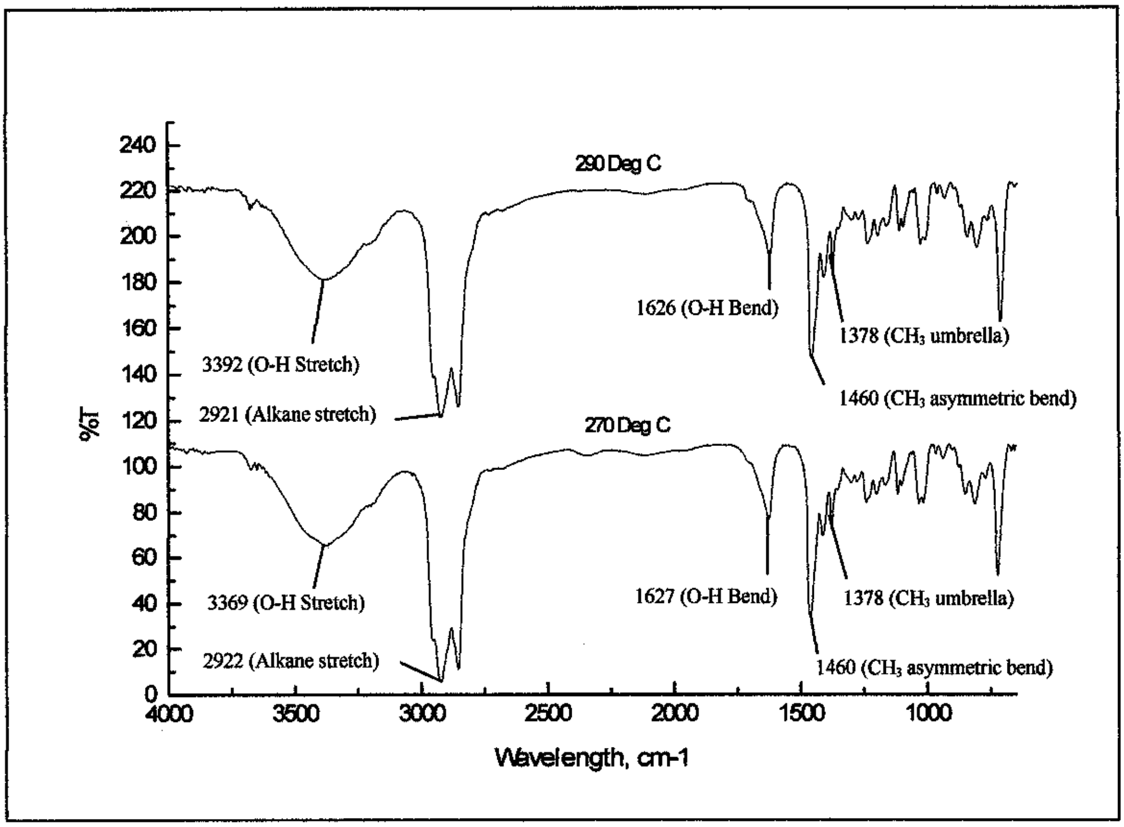
Wavelength, cm-1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20
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%T
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3000
2500
2000
1500
1000
Wavelength, cm-1
290 Deg C
3392 (O-H Stretch)
2921 (Alkane stretch)
1626 (O-H Bend)
1378 (CH3 umbrella)
1460 (CH3 asymmetric bend)
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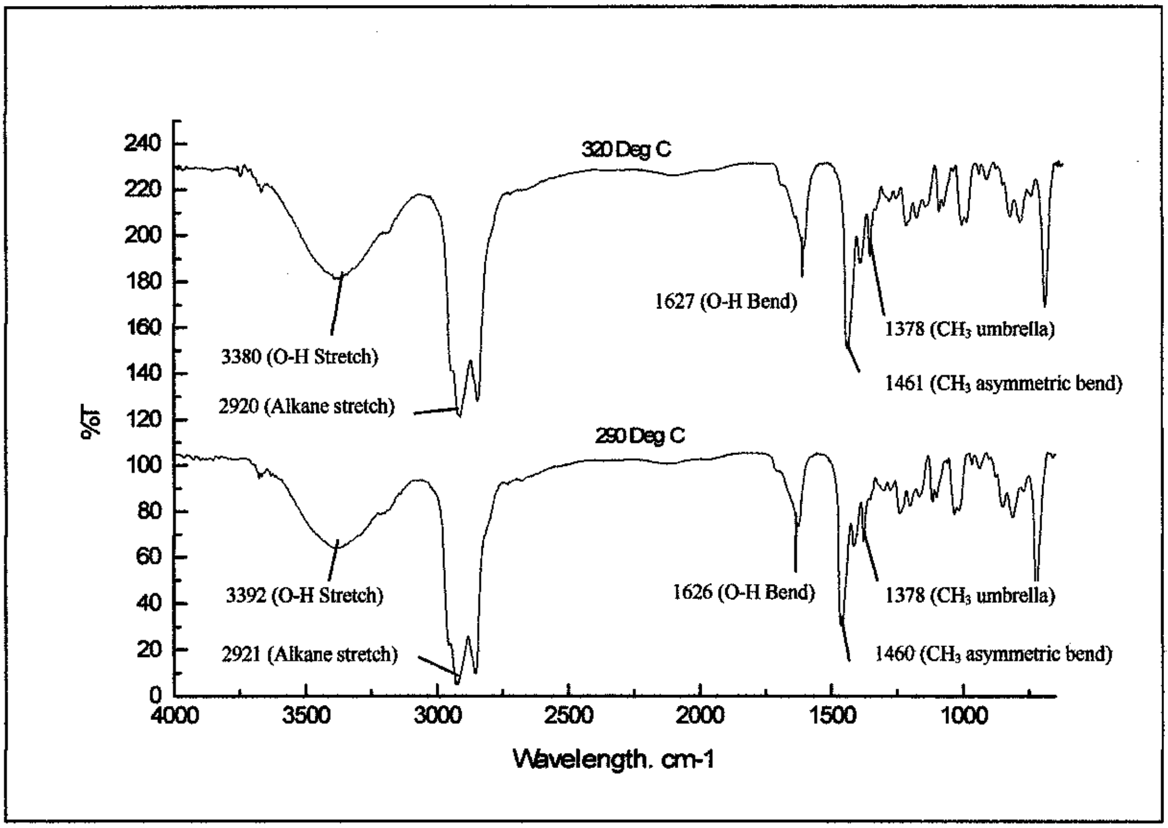
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1626 (O-H Bend)
1378 (CH3 umbrella)
1460 (CH3 asymmetric bend)
%T
240
220
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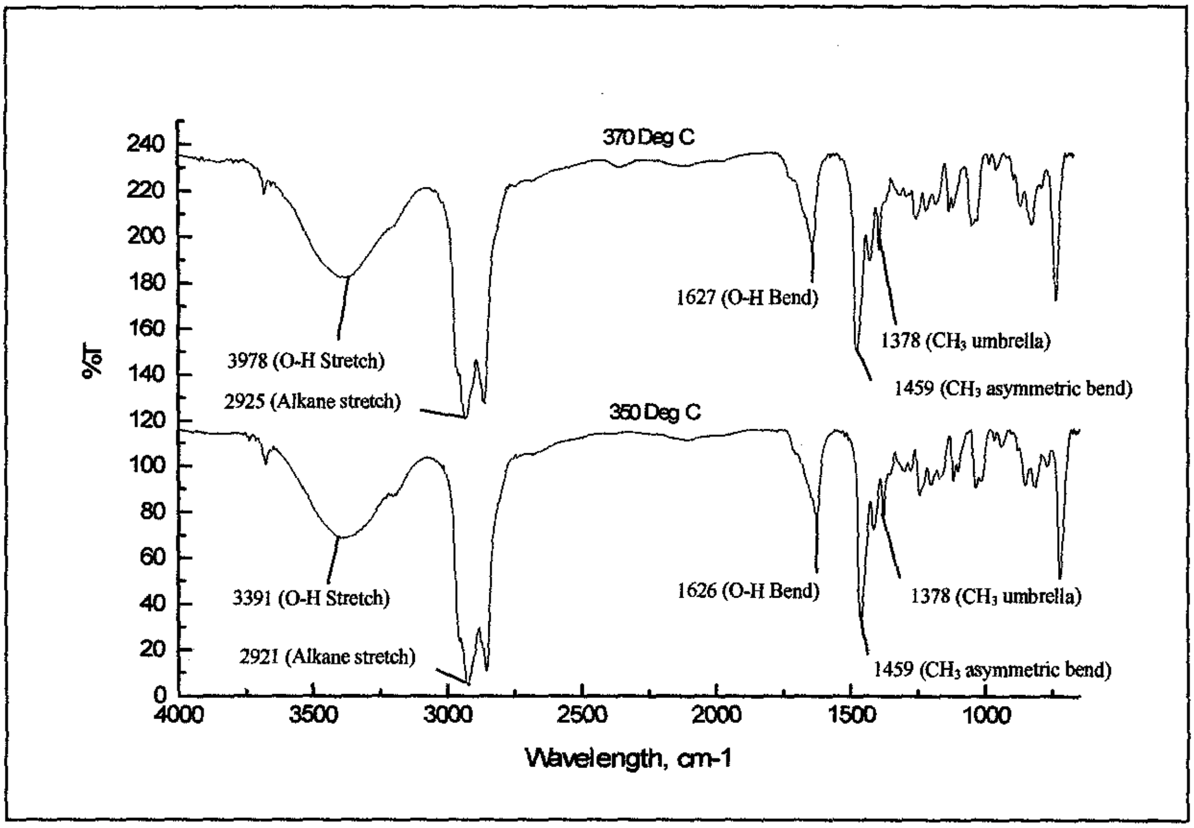
Wavelength. cm-1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1500
1000
Wavelength, cm-1
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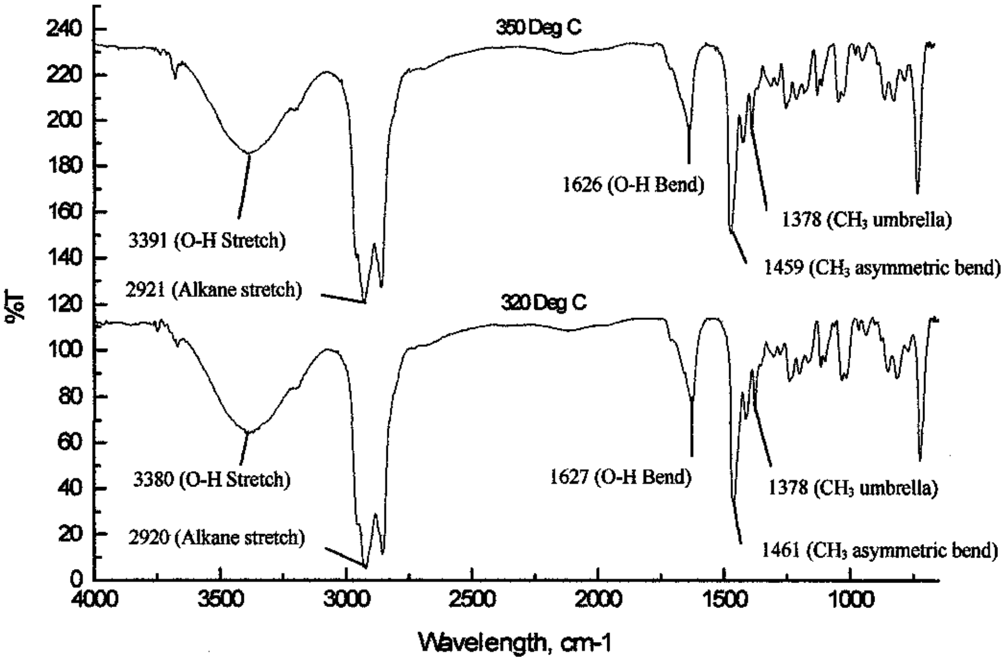
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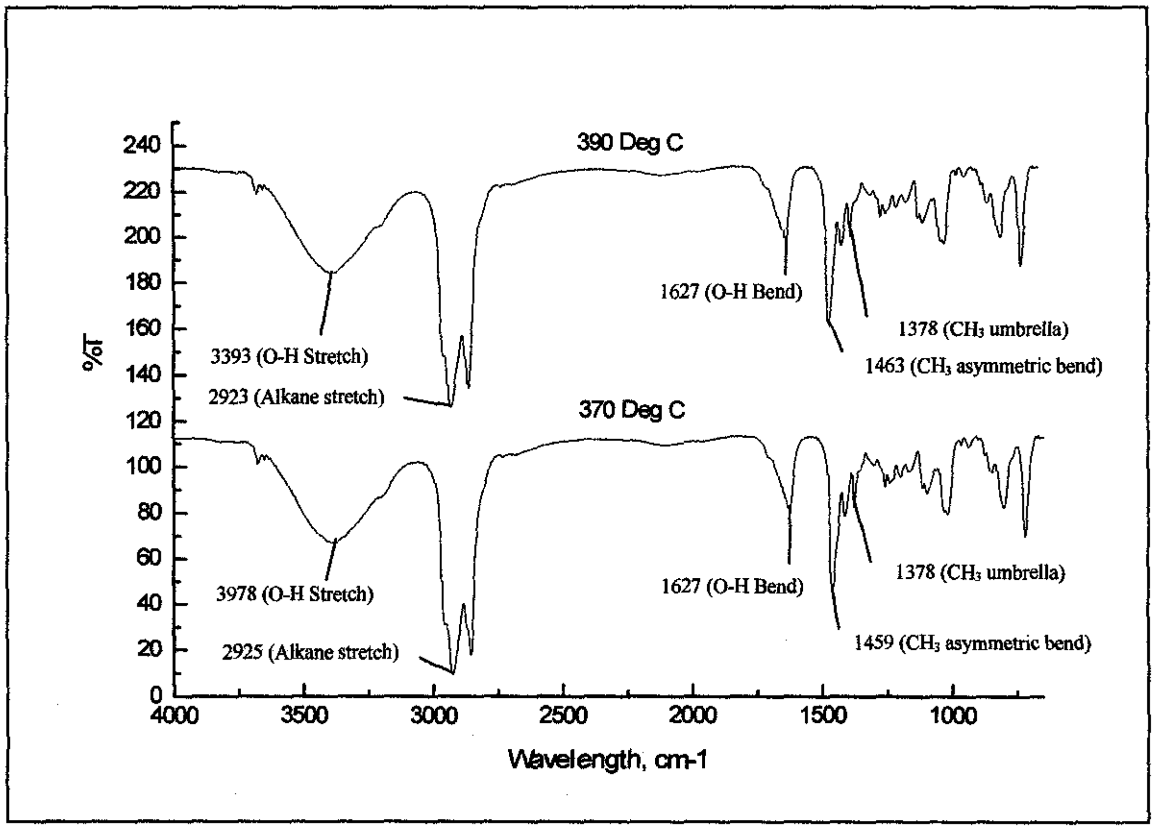
100
80
60
40
20
0
4000
3500
3000
2500
2000
1500
1000
Wavelength, cm-1
3391 (O-H Stretch)
2921 (Alkane stretch)
1626 (O-H Bend)
1378 (CH3 umbrella)
1459 (CH3 asymmetric bend)
3380 (O-H Stretch)
2920 (Alkane stretch)
1627 (O-H Bend)
1378 (CH3 umbrella)
1461 (CH3 asymmetric bend)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370 Deg C
%T
240
220
200
180
160
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120
100
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40
20
0
4000
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3000
2500
2000
1500
1000
Wavelength, cm-1
3393 (O-H Stretch)
2923 (Alkane stretch)
1627 (O-H Bend)
1378 (CH_3 umbrella)
1463 (CH_3 asymmetric bend)
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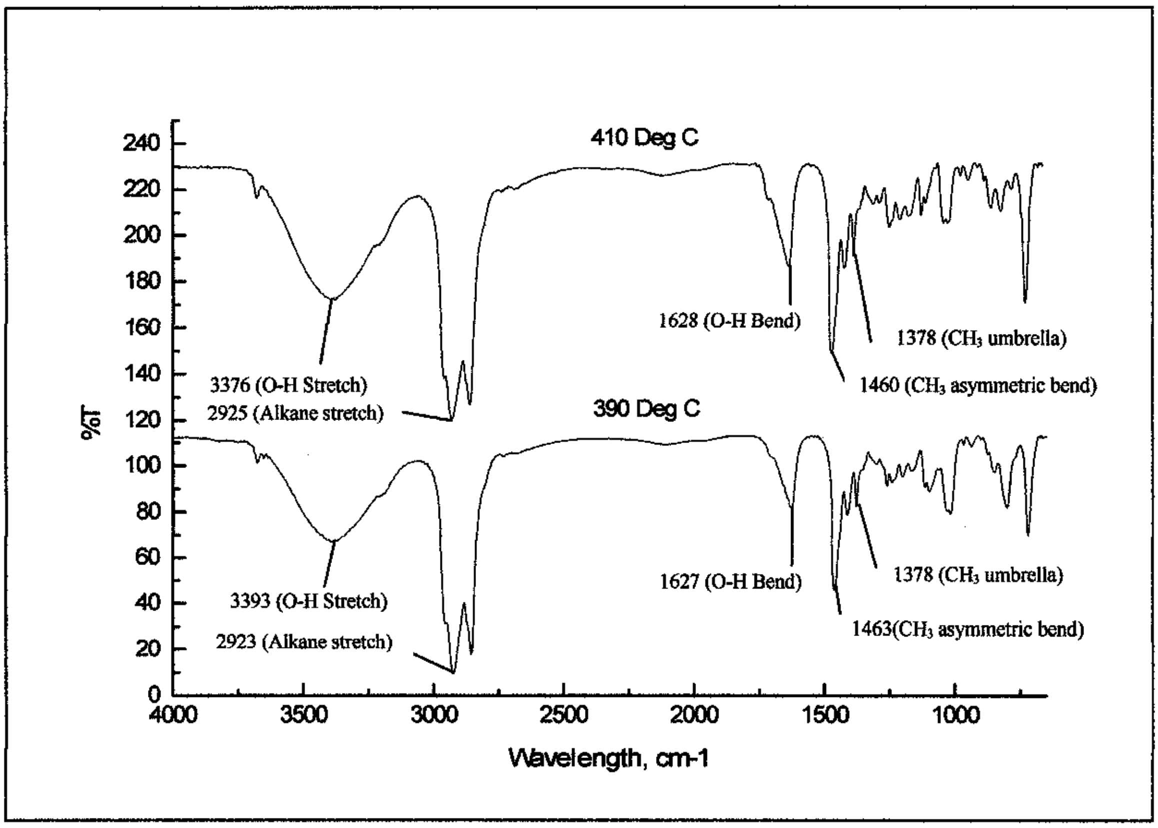
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390 Deg C
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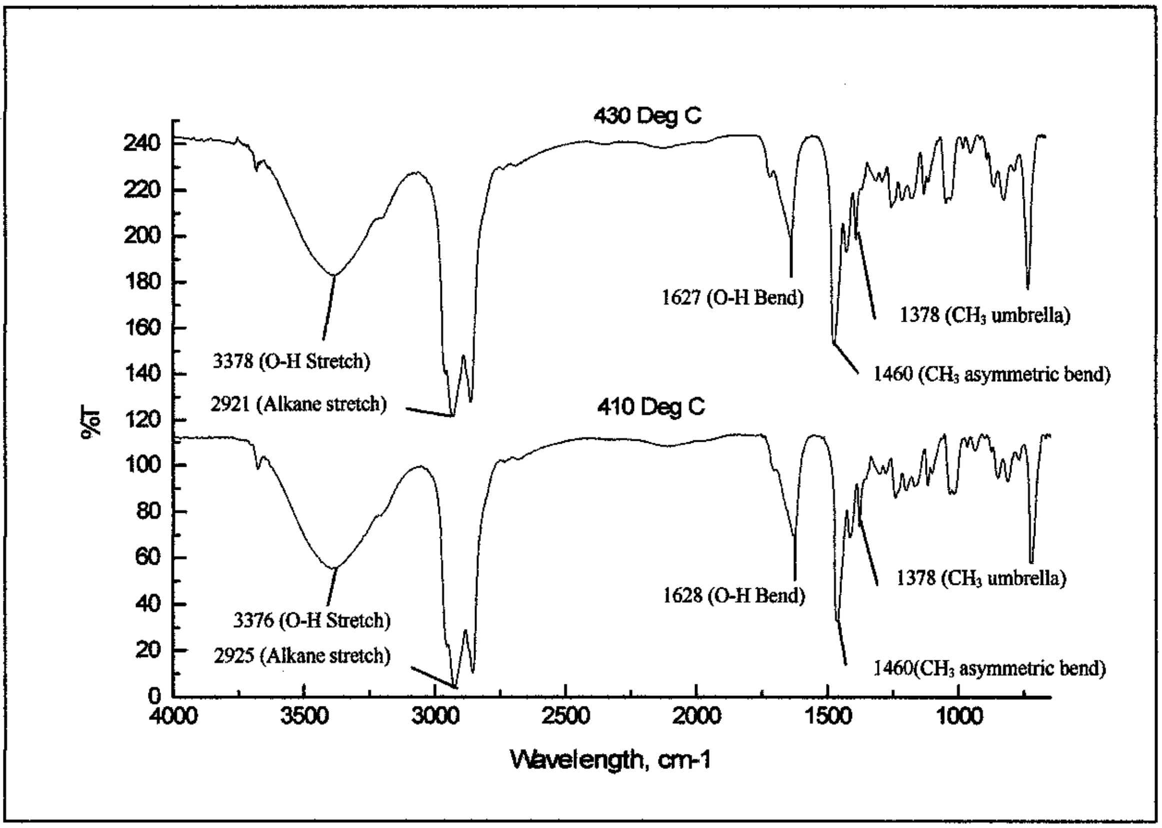
3393 (O-H Stretch)
2923 (Alkane stretch)
1627 (O-H Bend)
1378 (CH_3 umbrella)
1463(CH_3 asymmetric bend)
%T
240
220
200
180
160
140
120
100
80
60
40
20
0
4000
3500
3000
2500
2000
1500
1000
Wavelength, cm-1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410 Deg C
%T
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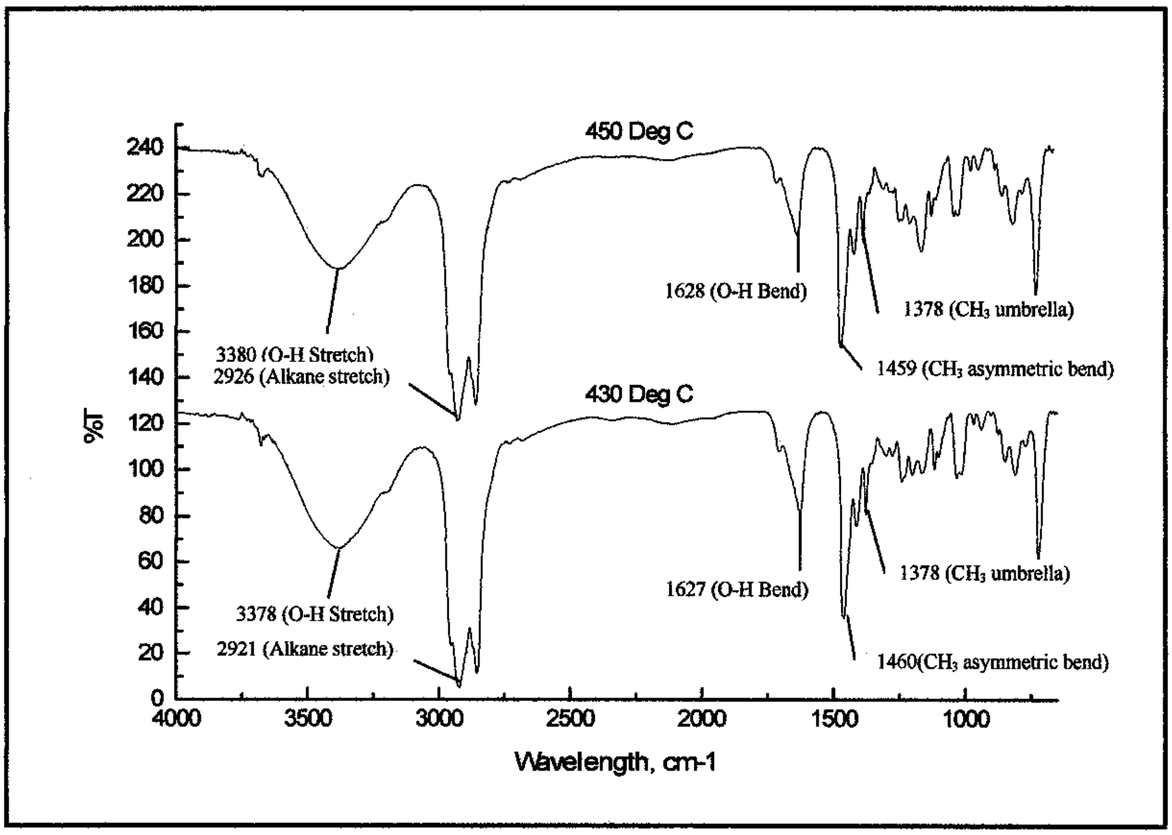
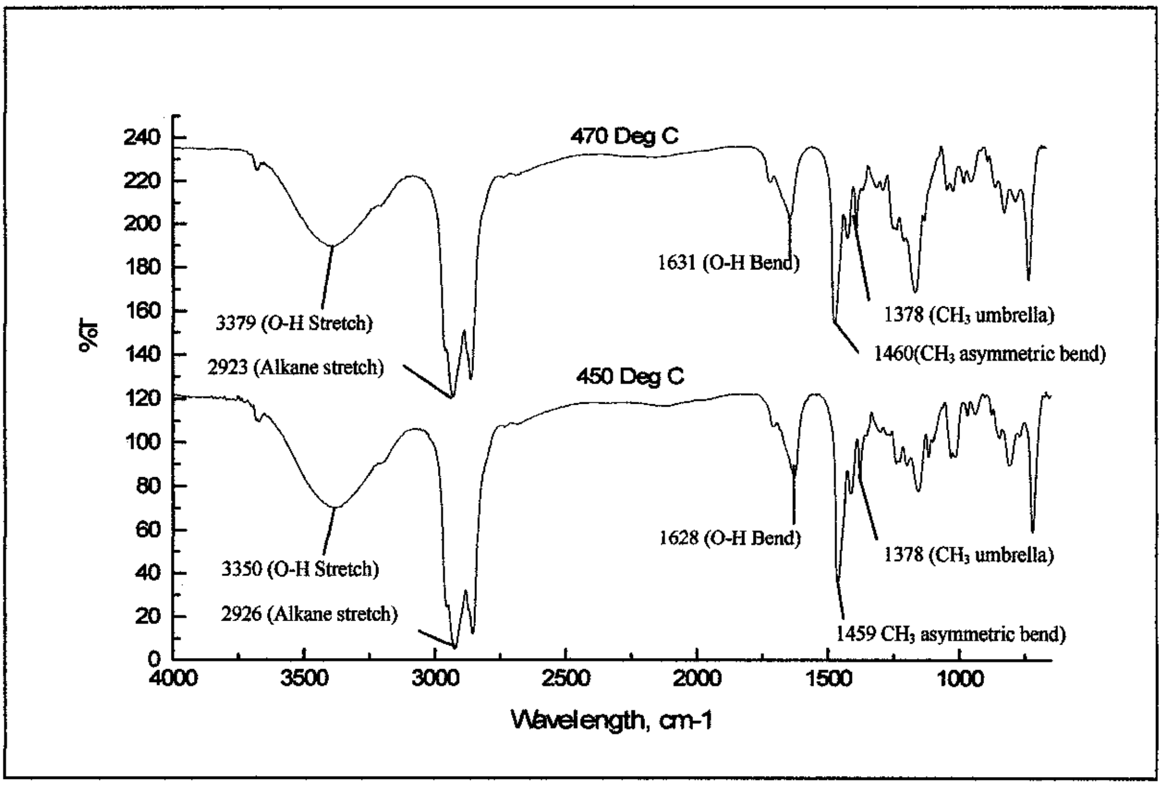
3000
2500
2000
1500
1000
Wavelength, cm-1
3378 (O-H Stretch)
2921 (Alkane stretch)
1627 (O-H Bend)
1378 (CH_3 umbrella)
1460 (CH_3 asymmetric bend)
3376 (O-H Stretch)
2925 (Alkane stretch)
1628 (O-H Bend)
1378 (CH_3 umbrella)
1460(CH_3 asymmetric bend)


450 Deg C
430 Deg C
%T
240
220
200
180
160
140
120
100
80
60
40
20
0
4000
3500
3000
2500
2000
1500
1000
Wavelength, cm-1
3380 (O-H Stretch)
2926 (Alkane stretch)
1628 (O-H Bend)
1378 (CH3 umbrella)
1459 (CH3 asymmetric bend)
3378 (O-H Stretch)
2921 (Alkane stretch)
1627 (O-H Bend)
1378 (CH3 umbrella)
1460(CH3 asymmetric bend)


470 Deg C
450 Deg C
3379 (O-H Stretch)
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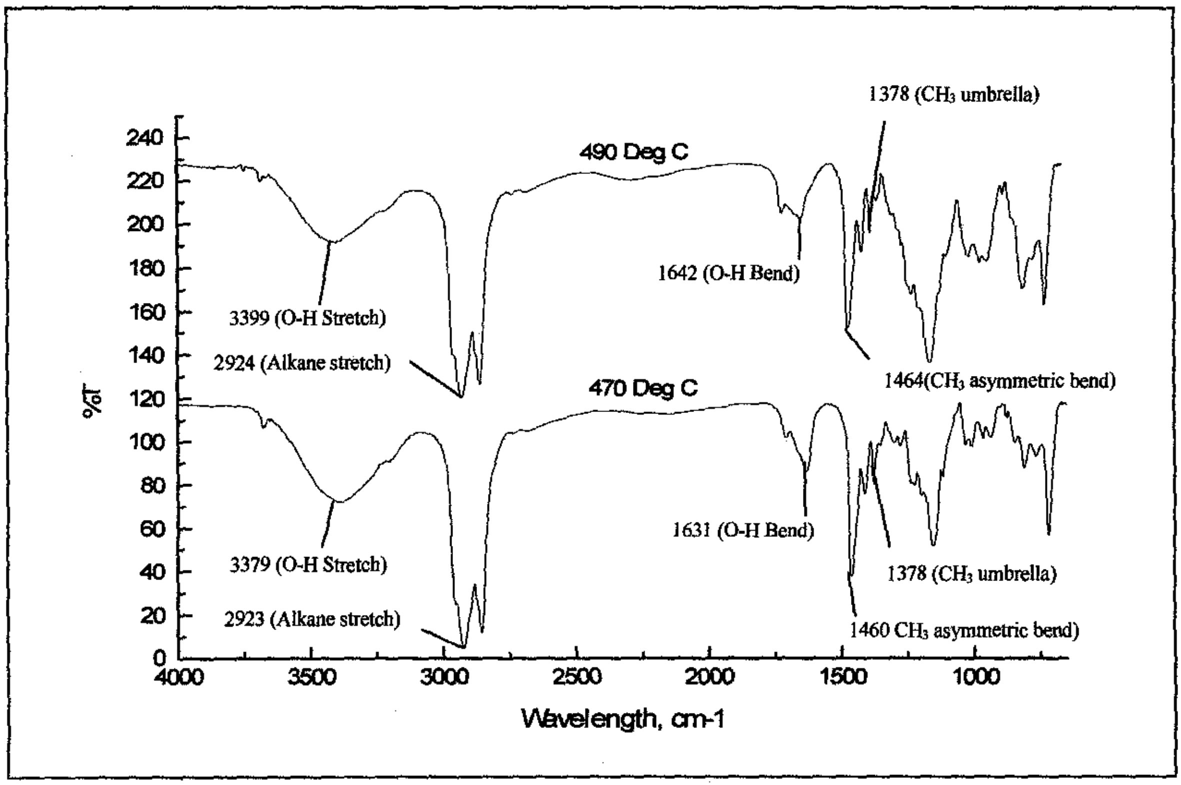
1631 (O-H Bend)
1378 (CH₃ umbrella)
1460(CH₃ asymmetric bend)
3350 (O-H Stretch)
2926 (Alkane stretch)
1628 (O-H Bend)
1378 (CH₃ umbrella)
1459 CH₃ asymmetric bend)
%T
0
20
40
60
80
100
120
140
160
180
200
220
240
4000
3500
3000
2500
2000
1500
1000
Wavelength, cm-1



490 Deg C
470 Deg C
1378 (CH_3 umbrella)
3399 (O-H Stretch)
2924 (Alkane stretch)
1642 (O-H Bend)
1464(CH_3 asymmetric bend)
3379 (O-H Stretch)
2923 (Alkane stretch)
1631 (O-H Bend)
1378 (CH_3 umbrella)
1460 CH_3 asymmetric bend)
%T
240
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Wavelength, cm-1

Appendix B: Data for Heat Capacity Calculation

Table A. 1: Temperature vs. Time Data

Time (Min)	Temperature, °C		
	Trial 1	Trial 2	Average
1	22.3928	22.5583	22.47555
2	22.4877	22.6532	22.57045
3	22.513	22.6785	22.59575
4	22.5214	22.6869	22.60415
5	22.5246	22.6901	22.60735
6	22.525	22.6905	22.60775
7	22.5235	22.689	22.60625
8	23.4377	23.6032	23.52045
9	24.3168	24.3572	24.337
10	24.44	24.5508	24.4954
11	24.507	24.6209	24.56395
12	24.5304	24.6513	24.59085
13	24.5388	24.6578	24.5983
14	24.5402	24.661	24.6006
15	24.5408	24.6624	24.6016

Table A. 2: Data Gained during Bomb Calorimeter Experiment

	Trial 1	Trial 2	Average
Sample, g	0.5282	0.5129	0.52055
H, J/g	- 41109	-41111	-41110
Thread energy, J	-50	-50	-50

Appendix C: Plot of Temperature versus Time

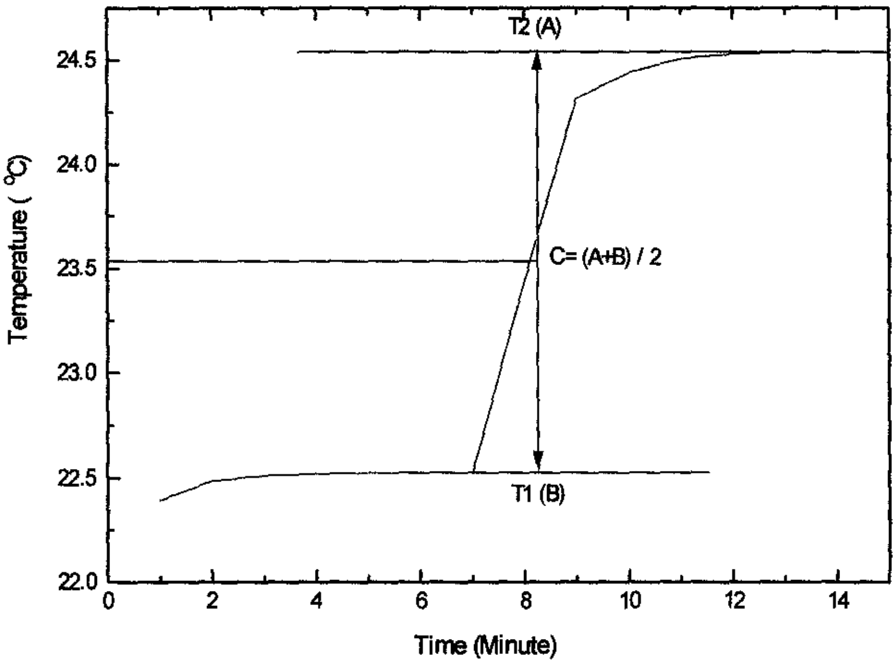

Figure A. 1: Temperature vs. Time Plot for Trial 1

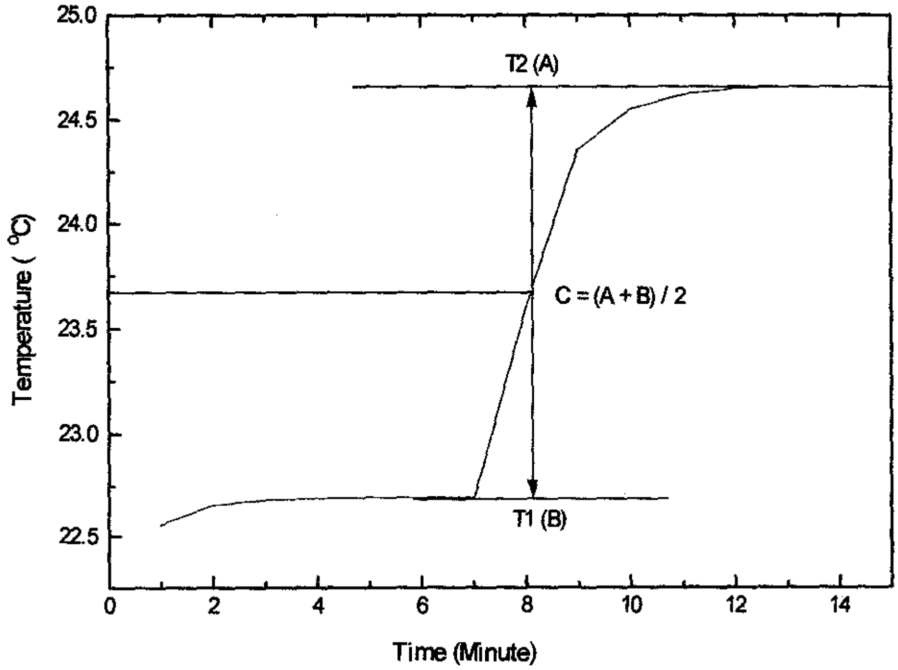

Figure A. 2: Temperature vs. Time Plot for Trial 2

Appendix E: Project Activities and Gantt Chart

Project Activities:

- Executing experimental research through experiments
- Undertake independent study on interpretation of experiment results
- Understanding the concept of chemistry

Key Milestone:

- Lab experiment on thermal stability measurement and result interpretation
- Lab experiment on heat capacity measurement and result interpretation
- Lab experiment on CO_2 solubility in dicationic ionic liquid at room temperature and ambient pressure and result interpretation

Gantt Chart for Final Year Project II:

No.	Progress According to Milestone/ Week	1	2	3	4	5	6	7		8	9	10	11	12	13	14
1	Lab experiment on thermal stability measurement and result interpretation	🟥	🟥	🟥	🟥	🟥			MID SEMESTER BREAK							
2	Submission of Progress Report I					⬛										
3	Lab experiment on heat capacity measurement and result interpretation						🟥	🟥		🟥						
4	Submission of Progress Report II									⬛						
5	Seminar										🟥	🟥	🟥			
6	Lab experiment on CO_2 solubility in DCIL									🟥	🟥	🟥	🟥			
7	Poster exhibition											⬛				
8	Submission of Dissertation (soft bound)													⬛		
9	Oral presentation														⬛	
10	Submission of Project Dissertation (Hard Bound)															⬛

⬛ Key Milestone

🟥 Progress

REFERENCES

1. Bradaric C. J, Downard A., Kennedy C, Robertson A. J., Zhou Y, 2003, *Green Chem.* (5)143

2. Kenneth R. Seddon, Robin D. Rogers, 2002, *Ionic Liquids Industrial Applications to Green Chemistry,* Washington, American Chemical Society

3. Chinn Daniel, Boudreau Laura, Michael S, Vu De Q, 2006, "CO_2 Removal from Gas using Ionic Liquid Absorbents", *FreePatentOnline.com*

4. Daniel W. Armstrong, Zachary S. Breitbach, 2008, "Characterization of Phosphonium Ionic Liquids through a Linear Solvation Energy Relationship and Their Use as GLC Stationary Phases", *Analytical and Bioanalytical Chemistry* 390(6): 1605-1617

5. Aleksandar Matic, Anna Martinelli, Fausto Croce, Jagath Pitawala, Per Jacobsson, Victor Koch, 2009, "Thermal Properties and Ionic Conductivity of Imidazolium Bis(trifluoromethanesulfonyl)imide Dicationic Ionic Liquids", *J. Phys. Chem B* 113: 10607-10610

6. Ning Sun, Suojiang Zhang, Xiangping Zhang, Xingmei Lu, Xuezhong He, 2006, "Physical Properties of Ionic Liquids: Database and Evaluation", *J Phys. Chem. Ref. Data* 35(4)

7. Chinn Daniel, Boudreau Laura, Michael S, Vu De Q, 2006, "CO_2 Removal from Gas using Ionic Liquid Absorbents", *FreePatentOnline.com*

8. Abu Bakr, Postgraduate student of Universiti Teknologi PETRONAS, Perak. Personal Interview. Sep. 10. 2009

9. Irza Hairani, 2009, *Carbon Dioxide Removal Using Ionic Liquid,* Final Year Project Thesis, Universiti Teknologi PETRONAS, Malaysia

10. Brian Smith, 1999, *Infrared Spectral Interpretation: A Systematic Approach,* New York, CRC Press

11. <http://science.jrank.org/pages/3265/Heat-Capacity.html>

12. Lee Ferguson, Paul Scovazzo, 2007, "Solubility, Diffusivity, and Permeability of Gases in Phosphonium-Based Room Temperature Ionic Liquids: Data and Correlations", *Ind. Eng. Chem. Res.* 46 (4): 1369–1374

13. International Union of Pure and Applied Chemistry, 1993, *Quantities, Units and Symbols in Physical Chemistry,* (2):50, Oxford: Blackwell Science

14. Jianmin Zhang, Rex X.-F. Ren, Suojiang Zhang, Xiangping Zhang, Yanqiang Zhang, Yuhuan Chen, 2005, "Solubility of CO_2 in Sulfonate Ionic Liquids at High Pressure", *J. Chem. Eng. Data* 50: 230-233

15. <http://www.chem.hope.edu/~polik/Chem345-2000/bombcalorimetry.htm>

16. Amir Shafeeq , Ayyaz Muhammad, C.D. Wilfred, M.I. Abdul Mutalib and T. Murugesan, 2008, "Thermophysical properties of 1-hexyl-3-methyl imidazolium based ionic liquids with tetrafluoroborate, hexafluorophosphate and bis(trifluoromethylsulfonyl)imide anions", *The Journal of Chemical Thermodynamics* 40(9): 1433-1438