REACTION MONITORING OF IONIC LIQUID SYNTHESIS USING RAMAN SPECTROSCOPY

By

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Dissertation submitted in partial fulfillment of the requirements for the Bachelor of Engineering (Hons)

(Chemical Engineering)

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CERTIFICATION OF APPROVAL

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A project dissertation submitted to the Chemical Engineering Programme
Universiti Teknologi PETRONAS
In Partial Fulfillment of the requirement for the
Bachelor of Engineering (Hons) Chemical Engineering

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UNIVERSITI TEKNOLOGI PETRONAS
TRONOH, PERAK
May 2012

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.

....
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ABSTRACT

In this project, the viability of Raman spectroscopy is studied during real-time reaction monitoring of synthesis of Ionic Liquid (IL). The vital IL for this project is 1-butyl-3-methylimidazolium tetrachloroferrate, [bmim] $FeCl_4$ which is synthesized from the reaction of 1-butyl-3-methylimidazolium chloride, [bmim] Cl^- and Iron (III) Chloride, $FeCl_3$. The characteristic of the Raman spectra throughout the reaction is studied by using a series of in-situ data to analyse the composition qualitatively in order to determine the individual reactant, intermediate, and product during the reaction. Raman spectroscopy is an influential instrument for researchers if it can be applied for the real-time monitoring synthesis of [bmim] $FeCl_4^-$. Undesired impurities such as 1-butyl-3-methylimidazolium, [bmim] $Fe_2Cl_7^-$ ions would form during the reaction when the ratio of [bmim] Cl^- to $FeCl_3$ is larger than 1 and Raman spectroscopic monitoring can help in determining it occurrence. These possible impurities has unknown properties and effect on the efficiency of [bmim] $FeCl_4^-$ in its application as a catalyst or a solvent extractor need to be studied. The project used Taguchi method as its design of experiment and 2 parameters is introduced. Reactant ratio from 1:1 to 1:2 and monitoring time from 1 to 4 hours is manipulated in L16 Taguchi Orthogonal Array. Standard room temperature and pressure of 25°C and 1 atm is assumed to be constant throughout the experiment. The result can be observed at the Raman excitation peak at the range of 50-500 cm^{-1}. From the data obtained, [bmim] $FeCl_4$ production in one-to-one ratio of synthesis does not contain any impurities while one-to-two synthesis ratio shows the difference in the spectral peak produced which indicates the additional formation of [bmim] $Fe_2Cl_7^-$. This finding concludes that Raman spectroscopy is proven to be a viable method in analysing the [bmim] $FeCl_4$ reaction monitoring.

ACKNOWLEDGEMENT

In the name of Allah, the Most Gracious, the Most Merciful. Praise to Him for blessing me with patience, strength, courage and perseverance to endure this Final Year Project.

A token of appreciation also goes to my supervisor, A.P. Dr Mohd Azmi Bin Bustam @ Khalil for his intelligences, persistent and endless encouragement to me throughout the whole project duration. Special thank and gratitude to Mrs. Naimah for her guidance, assistance and ideas which give me better understanding about the project. Another heartfelt gratitude is given to all PETRONAS Ionic Liquid Centre Research Officers and master students for their help throughout the laboratory experiment.

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1.0 INTRODUCTION

1.1 Background Studies

Reaction monitoring of chemical reaction is one of the fundamental chemical analysis method in the world of chemistry. It is very important for researcher to monitor a reaction so that any constituent involved in the reaction can be identified. There are several ways to monitor a reaction. Two distinct spectroscopy techniques commonly used are mass and light spectroscopy.

There are three main variations of light spectroscopy in use these days, namely absorption, emission, and scattering spectroscopy. Infrared (IR) and Ultraviolet (UV) spectroscopy processes the wavelength of absorbed light in a material, while fluorescence and laser spectroscopy measures the reflected light order of providing the information of its structure. In the other hand, scattering spectroscopy (Raman spectroscopy) is similar to emission spectroscopy but detects and evaluates all of the wavelengths that a substance reflects upon excitation.

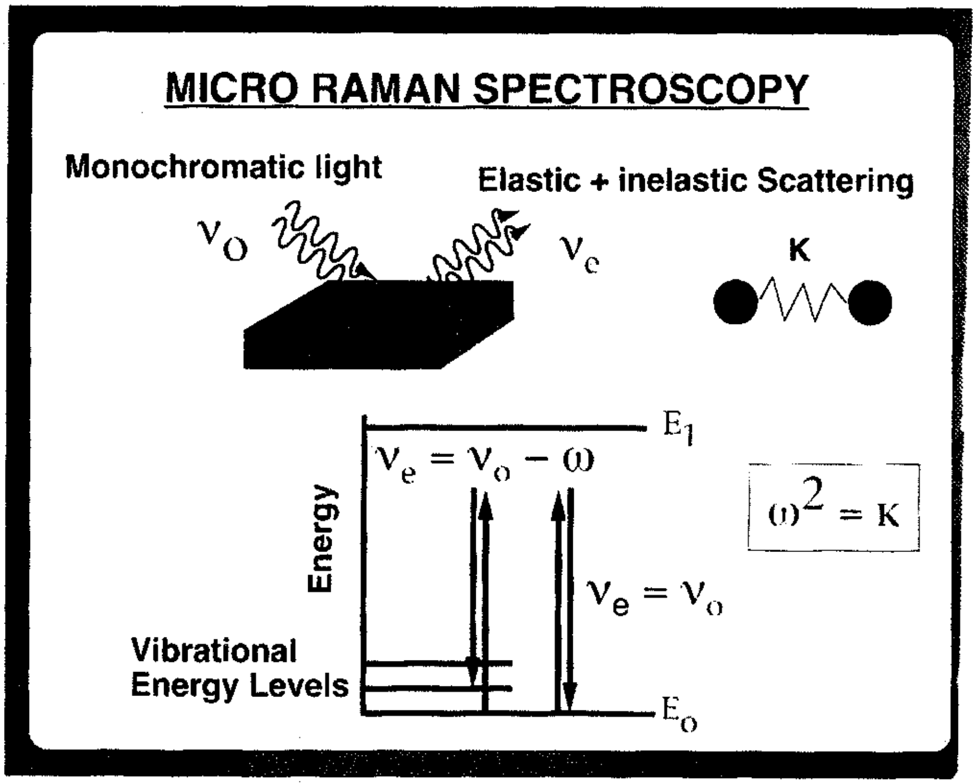


Figure 1: Raman Spectroscopy (Credit: Rensselaer Polytechnic Institute)

Raman spectroscopy is commonly used in chemical industry as the technique for identification and analysis of molecular species (Dennis, 2007). It studies vibrational, rotational, and other low frequency modes in a particular system and come out with a scatter plot, usually in a form of 2D or 3D topographic graph. Every chemical bond will emit different vibrational information which therefore provides a fingerprint in order to identify the molecule. This information is important for the identification of elements involved in a particular sample. Besides being non-destructive in most application, Raman instrument also provides fast result response which makes it suitable for real-time monitoring of chemical reaction (Perkin Elmer, 2007).

1-butyl-3-methylimidazolium tetrachloroferrate, [bmim] $FeCl_4^-$ is a new magnetic solvent in the world of ionic liquid. Being first synthesize at University of Tokyo in 2004, it has gained popularity due to its magnetic effect and its ability as solvent and extractor. However, detailed analysis of the synthesis of this ionic liquid by using Raman spectroscopy is still under study. The usage of Raman spectroscopy can provide more information about the synthesis reaction if it is deemed feasible from the experimental work.

1.2 Problem Statement

The synthesis of 1-butyl-3-methylimidazolium tetrachloroferrate, [bmim] $FeCl_4^-$ is done by adding up [bmim] Cl^- and $FeCl_3$. However, certain mixing ratio of both reactants might produce other product such as [bmim] $Fe_2Cl_7^-$. This compound, which often called as impurities for the [bmim] $FeCl_4^-$ is an undesirable product that can lower the efficiency of its application as catalyst or extractor. Controlling the formation of this impurity may be hard as the exact ratio of the reactant could vary. Studies have shown that the formation of bmim $FeCl_4^-$ alone can be done in a range of 0.53 to 1.7 molar ratios, which is a large for error. Raman monitoring should be able to detect this formation of bmim $FeCl_4^-$ and bmim $Fe_2Cl_7^-$ thus helping in getting the optimum ratio and reaction time of the process.

1.3 Objectives

An objective of this project is:

- To study the feasibility of using Raman spectroscopy in real-time monitoring of synthesis of 1-butyl-3-methylimidazolium tetrachloroferrate, [bmim] $FeCl_4^-$ from the reaction of 1-butyl-3-methylimidazolium Chloride and Iron (III) Chloride.

1.4 Scope of Work

The main focus of this project is to study the feasibility of Raman spectroscopy analysis on the reaction monitoring in synthesis of 1-butyl-3-methylimidazolium tetrachloroferrate from Iron (III) Chloride 98% (Merck) and 1-butyl-3-methylimidazolium Chloride 98% (Merck). Different stoichiometric ratio of the reactant was manipulated along with the stirring time which will act as the proposed Raman monitoring time. The experiment was done in room temperature and pressure and any changes of both conditions throughout the experiment are considered negligible. Excitation range from $100cm^{-1}$ to $3500cm^{-1}$ is chosen for the experiment as it is the maximum limitation for the equipment.

1.5 Relevancy of Project

This project aims to help in determining the feasibility of Raman spectroscopy in monitoring of [bmim] $FeCl_4^-$ ionic liquid. Further analysis of [bmim] $FeCl_4^-$ synthesis process can be determine if the Raman spectroscopy is proven to be viable for the process.

1.6 Feasibility of Project

The project's experiment is supervised by scheduled design of experiment which uses the Taguchi method. Numbers of experiments that was conducted throughout the two (2) semesters of Final Year Project and the weeks is pre-determined along with several weeks to spare in case of equipment failure or any other problems that might occur.

2.0 LITERATURE REVIEW

2.1 Raman Spectroscopy

With the advancement of modern technologies, Raman spectrometers have become small, portable, and easier to be used in research experiment. Raman spectroscopy was named by one of its first discoverer, Sir C. V. Raman, an Indian scientist who studied the sunlight in observing the inelastic scattering of the monochromatic light. While other spectroscopic techniques study the absorption or emission of the light, Raman spectroscopy relies on the scattering of light in determining the lower vibrational energy levels of molecules.

Raman scattering are generally used to offer information about chemical structures and its physical forms and classifying substance from its individual characteristic patterns (Smith & Dent, 2005). This structures identification can be applied to the spectra obtained later to cross check with existing spectral library in determining the molecular content of [bmim] $FeCl_4^-$ after the synthesis.

Raman spectroscopy works starting with the emission of a monochromatic light, usually from a laser beam. This light is focused on to a sample and the scattered light from the sample will be filtered, pass through a diffraction grating and straight onto a detector. Traditional Raman spectroscopy have this difficulty on reading the diffracted light as the detector is not very sensitive towards some of the wavelength. Through time, a more sensitive photomultiplier tube is developed to be the main detector of the lights, allowing data to be collected and handled electronically (Allman, 2010).

The reaction monitoring process needs its own reaction bench to equip the entire instrument. With a fibre optic probe, the bench can be set up easily as long as it is still in the reach of the probe length, which can be up to 10 meters or more. The use of fibre optic probe in combination with Charged Couple Device (CCD) detector allows Raman spectroscopy to monitor any reaction in hostile condition remotely (Svensson, Josefson, & Langkilde, 1999). The reason behind this detector choosing is that this modern Raman spectrometer combines the advantages of the previous detection techniques of being very sensitive, capable to read electronically, and can measure the entire spectrum at once. In addition, the portability of Raman spectroscopy in fact helps a lot in this project.

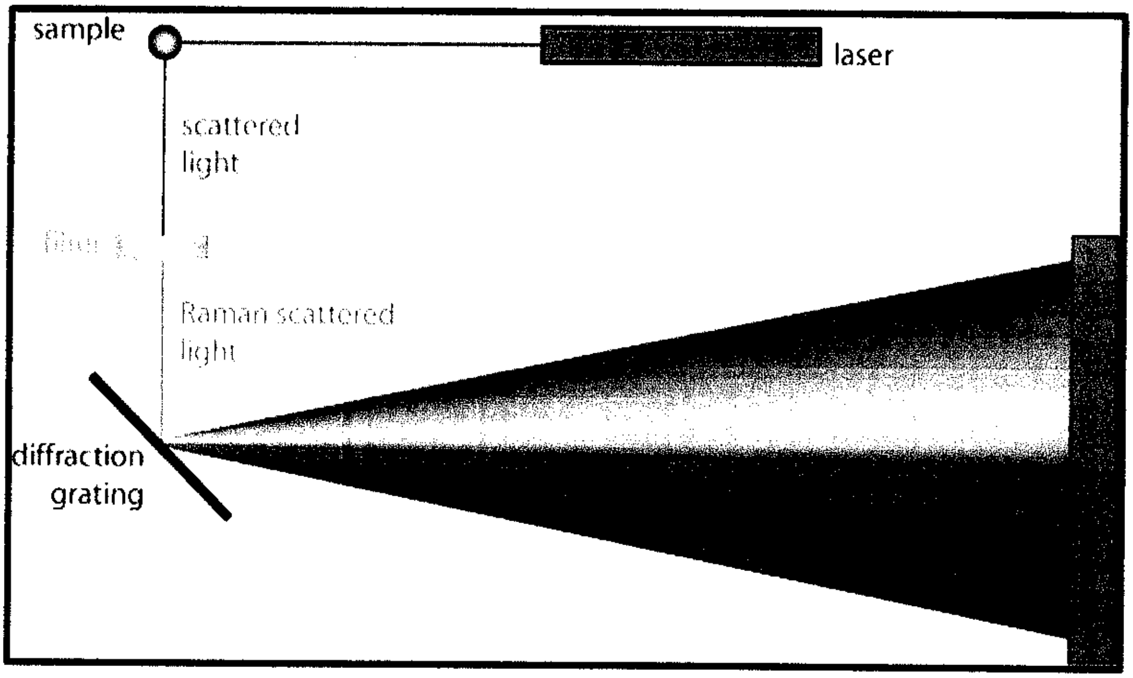


Figure 2: A simplified diagram of Raman spectrometer's operation (source: doitpoms.ac.uk)

Besides that, one of the main features of Raman monitoring is that it can produce a very quick result response (Perkin Elmer, 2007). This analysis technique is actually suitable to be used during manufacturing production as a means of obtaining real-time, high-quality chemical information at regular time interval and through a vast range of industrial applications (Gurden, Westerhuis, & Smilde, 2002). On-line Raman monitoring system is practically installed in more manufacturing companies around the world today, replacing off-line, slow, but accurate reading of chromatographic analysis.

Another amazing features or Raman spectroscopy is that it can be used without destroying the sample. Besides that, samples spectra in transparent containers, such as glass, can easily be obtained (Dennis, 2007). Both features helps in providing our [bmim] $FeCl_4^-$ support through the experiment while making it still usable for other test after this project is completed. The cost of pure solid reactant ([bmim] Cl^-) is still quite high as it is an engineered chemical so preserving the purity of the product is vital economically.

Raman spectroscopy can be combined with other analytical method to produce more accurate result. In term of qualitative analysis, the combination of Raman and Infra-red spectroscopy can gives out more information about the molecular compound involved in the sample. Strong infrared absorptions appear usually as weak Raman ones and vice versa (Hendra, 2004). So this complementary effect of both Raman and infrared can be used to determine the compound inside the synthesis product of [bmim] FeCl4- to identify any presence of any impurities.

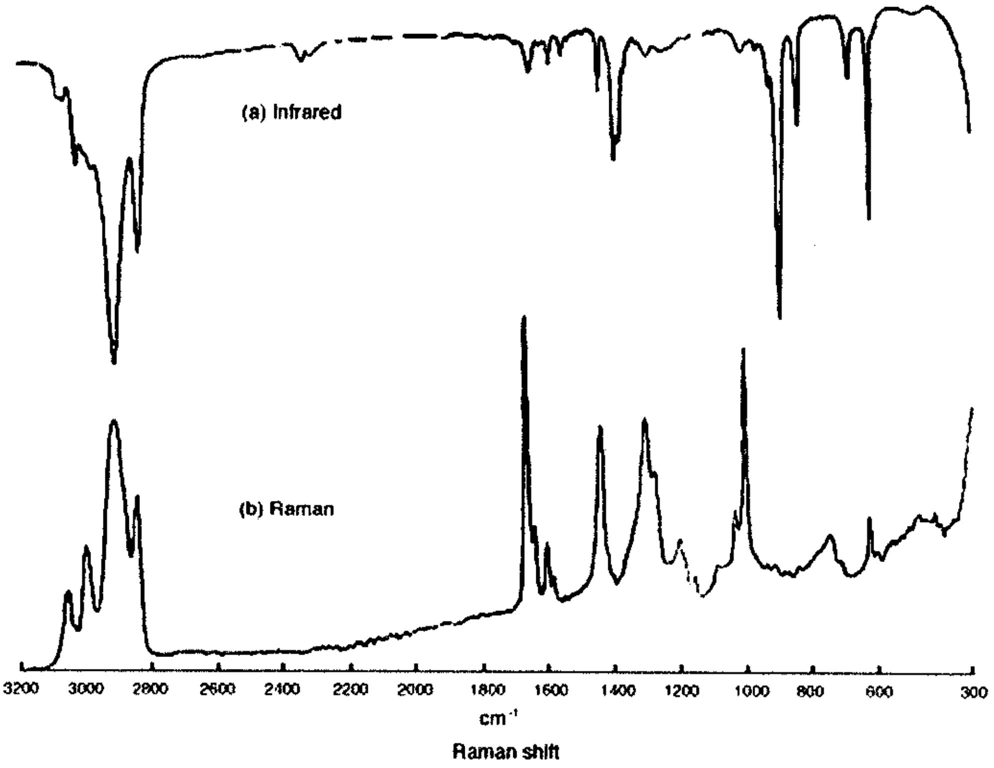


Figure 3: The Infrared and Raman Spectrum of Styrene/Butadiene Rubber (Hendra, 2004)

2.2 Ionic Liquids

Solvent is an important chemical in which most reactions are done in nowadays. For a long time, chemical engineers rely heavily on their knowledge of behaviour of molecules in solution phase of molecular solvent (Earle & Seddon, 2000). However, new type of solvent called ILs has recently emerged. An IL is a salt in liquid form while in mild temperature; generally below 100°C. This liquid property occurs due to the poorly coordinated ions and also the delocalised charge and organic component which in turns preventing the ions from forming crystal lattice. It is sometime called as the designers solvent as many of the ILs can be tailored according to specific synthetic problems (Organic Chemistry Portal).

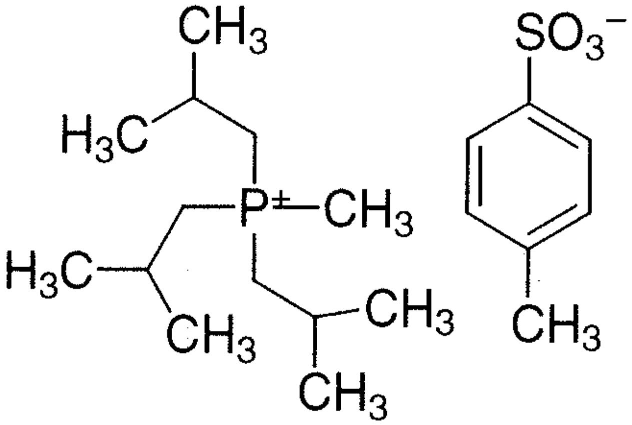


Figure 4: Example of ILs structure, tri-isobutyl (methyl) phosphonium p-toluenesulfonate(Nollert, 2009)

There are many advantages of ionic liquids. One of the main features is that the vapour pressure of the liquid is practically negligible, thus making so-called room temperature ionic liquids (RTILs) to be thermally and hydrolytically stable. Besides that, many of these RTILs have a wide liquid range along with flexible viscosity and electrochemical window. Because of the negligible vapour pressure and the nature of stability of the ILs, it is a very attractive source of new 'green solvent' in modern day usage. The use of ILs varies from solvent, to catalyst, to even as adsorbent of a specific gas in certain cases. For example, (Holbrey & Seddon, 1999) had done a study in which they summarised that classical transition-metal catalysed hydrogenation, hydroformylation, isomerisation, dimerization and coupling reactions can be conducted in IL solvents.

2.2.1 1-butyl-3-methylimidazolium tetrachloroferrate, [bmim] FeCl4

One of the notable room temperature ionic liquids (RTILs) is 1-butyl-3-methylimidazolium tetrachloroferrate, [bmim] $FeCl_4$. This particular IL acquired the unique magnetic properties that not many other ILs has. This finding of ferromagnetic behaviour on [bmim] $FeCl_4$ has opened an entirely new perspective for ionic liquids (Kogelnig, et al., 2010). The strong magnetic response of [bmim] $FeCl_4$ provides easier and more energy effective way to separate and recycle the solvent after each use (Lee, Ha, You, & Koo, 2006). The report also stated that a combination of magnetic field and conventional methods to recover magnetic ILs from reaction mixtures will be very useful.

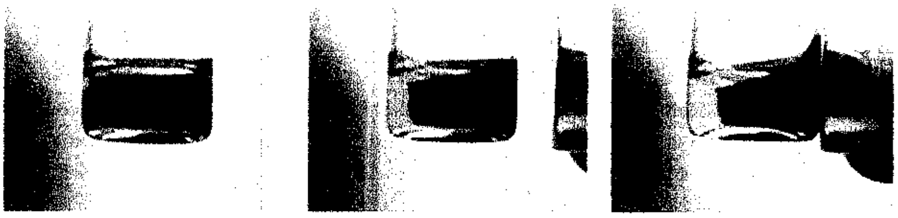


Figure 5: A Magnetic Ionic Liquid [bmim] $Fecl_4$(Hayashi & Hamaguchi, 2004)

Many studies had been done in terms of catalytic behaviour of [bmim] $FeCl_4$. For instance, (Wang, Yan, Li, Zhang, & Zhang, 2010) reported that higher catalytic activity is observed when [bmim] $FeCl_4$ is used in glycolysis of poly-(ethylene terephthalate) (PET). Compared to when $FeCl_3$ or [bmim] Cl is used separately as the catalyst, the study shows that the synergetic effect of anions and cations in [bmim] $FeCl_4$ helps in increasing the catalyst activity while reducing the onset reaction temperature of glycolysis process to only 140°C. This shows that [bmim] $FeCl_4$ may be suitable in replacing conventional catalyst in depolymerisation process of PET.

When talking about liquid mixture, it is often prone to problems when separation is in concern. The ionic liquids, known to act as catalyst in many reactions, have also faced with the same problem. In order to deal with the glitch, immobilized [bmim] $FeCl_4$ is introduced. The ions are attached to a supporter (silicon compound is usually used), making it to be as useful as any ILs, but in solid form thus creating it much easier to separate after a catalytic reaction is done. For example, (Wang, et al., 2008) had use this kind of immobilized chloroferrate ILs catalyst on the synthesis of diphenylmethane and proved that such ILs can be reused without any significant loss of catalytic activity. Besides being used as catalyst, many researches are still under study where they try to use immobilized [bmim] $FeCl_4$ in desulphurization of crude oil in industries.

2.3 Project-related Existing Research

There are several similar works which has been done in the field of reaction monitoring. One experiment done by (Lee, Kim, Rhee, & Choo, 2003) in Hanyang University, Korea recorded detailed monitoring of Imine synthesis using the similar method of this project. They concluded that Raman spectroscopy is a great tool for in-situ monitoring process which does not interfere with the reaction process at all. The fast result obtained from the process can also be reproduced accurately and the handling of the data is very straightforward. Moderate reaction rate and Raman spectrometers detection capability are some of the reasons why [bmim] $FeCl_4$ is considered to be a good model system for Raman study.

N-substitution heterocyclic compound such as imidazole does not only act as an important precursor to many ILs, but is also a key route to formulate essential bactericidal complexes and new medications (Casilda, Pérez-Mayoral, Banares, & Diz, 2010). In order to obtain highly accurate data, they had combine and cross reference other analysis such as NMR spectroscopy and gas chromatography with the Raman spectra that they acquired. They concluded that Raman spectroscopic monitoring can provides thorough molecular data on the reaction mechanism and potential intermediates while remains non-invasive. The methodology used can also be tuned and applied to various numbers of other processes.

Raman spectral result can be viewed in 2D or 3D graph. The combination of Raman shift (cm^{-1}) and Intensity (cps) axis with the real time data (minutes) can demonstrate a very good representation on what really happening during the synthesis reaction. In research done by Mikolajska, Calvino-Casilda, and Ba˜nares in 2012, they concluded that real-time Raman monitoring of liquid phase cyclohexane epoxidation can confirms the reaction mechanism and provides a mean to monitor the deactivation of catalysts.(Mikolajska, Calvino-Casilda, & Banares, 2012)

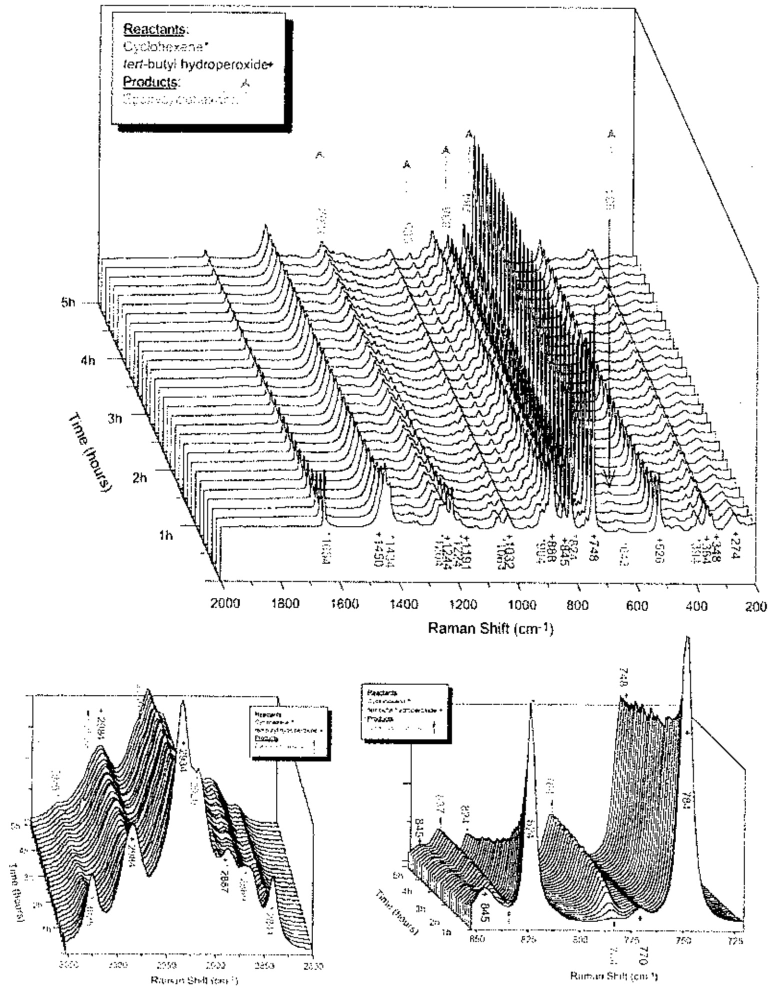


Figure 6: 3D view Raman spectra of cyclohexane epoxidation (Mikolajska, Calvino-Casilda, & Banares, 2012)

In research by Wang et. al. entitled 'Synthesis and Characterization of the Iron-Containing Magnetic Ionic Liquids' recently this year, they also use [bmim] $FeCl_4^-$ as one of their research subject. Although their research is not on real-time synthesis monitoring, but the result obtained for Raman spectra can be used and compared to this project's future result. They recorded the Raman spectra from 50 cm^{-1} to 1600 cm^{-1} with 785 nm laser as the excitation source. The finding shows that [bmim] $FeCl_4$ has its peak at the range of 50-500 cm^{-1} while Fe-Cl bond stretch vibration appears at two peaks which are 113.24 cm^{-1} and 333.20 cm^{-1} in the spectra. This finding can be very useful at the end of this project as it can be compared to show any existence of impurities at the end-product of the ratio parameter experiments.

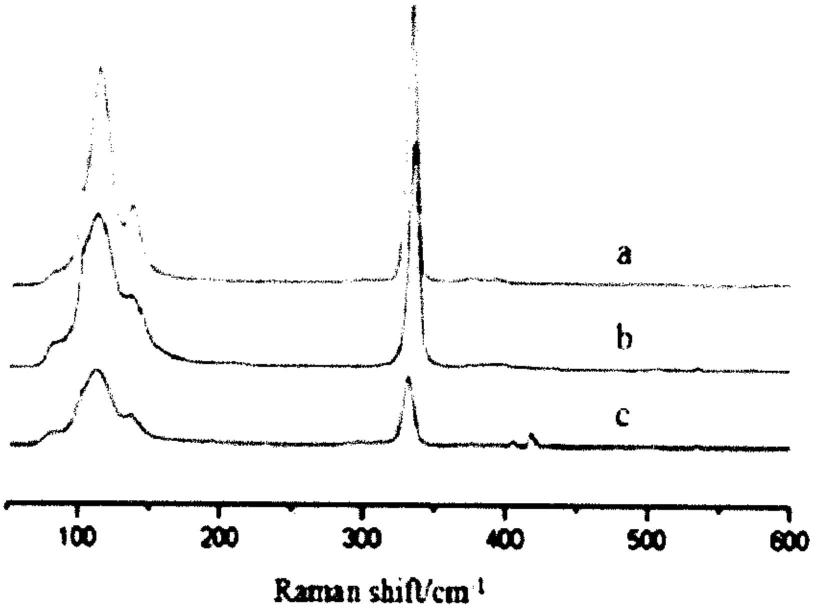


Figure 7: Raman spectra of [bmim] FeCl4 (a), [bPy] FeCl4 (b) and [bmP] FeCl4 (c) at room temperature (Wang, Yao, Nie, Zhang, & Li, 2012)

2.4 Taguchi Method

Design of experiment is the design of a well-planned set of experiment with variety of parameter over a specified range produced in order to obtain systematic data (Apte, 2008). There are many methods available to produce these sets of experiment such as The Design of Experiment by Ronald A. Fisher, Plackett-Burman designs, Taguchi method by Genichi Taguchi, and more recent frequentist interference and Bayesian approach.

In the early development of Taguchi method, it is designed to improve the quality of manufactured goods. However, lately more engineering, biotechnology, and business development field has also started to implement Taguchi design of experiment in their field of study (Apte, Introduction to Taguchi Method, 2008).

Taguchi uses the Orthogonal Array (OA) in proposing the experimental design that gives different combinations of parameters and their levels for each experiment (Kamaruddin, Khan, & Wan, 2004). This in turn reduces the number of experiment needed for each variation thus making it suitable for experiment with 2 or more variable parameter.

Taken from (Fraley, Oom, Terrien, & Zalewski, 2007), the general steps involved in the Taguchi Method are as follows:

1. Define the process objective, or more specifically, a target value for a performance measure of the process. This may be a flow rate, temperature, etc. The target of a process may also be a minimum or maximum. The deviation in the performance characteristic from the target value is used to define the loss function for the process.

2. Determine the design parameters affecting the process. Parameters are variables within the process that affect the performance measure such as temperatures, pressures, etc. that can be easily controlled. The number of levels that the parameters should be varied at must be specified.

3. Create orthogonal arrays for the parameter design indicating the number of and conditions for each experiment. The selection of orthogonal arrays is based on the number of parameters and the levels of variation for each parameter, and will be expounded below.
4. Conduct the experiments indicated in the completed array to collect data on the effect on the performance measure.
5. Complete data analysis to determine the effect of the different parameters on the performance measure.

3.0 METHODOLOGY

3.1 Experimental Schematic Diagram

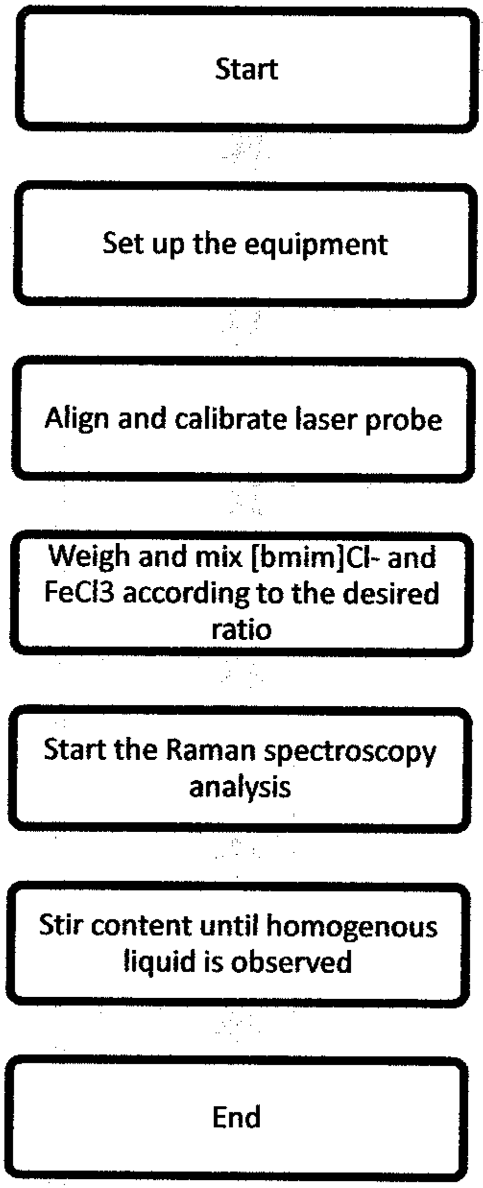


Figure 8: Experimental Flow Chart

3.2 Equipment Set Up Diagram

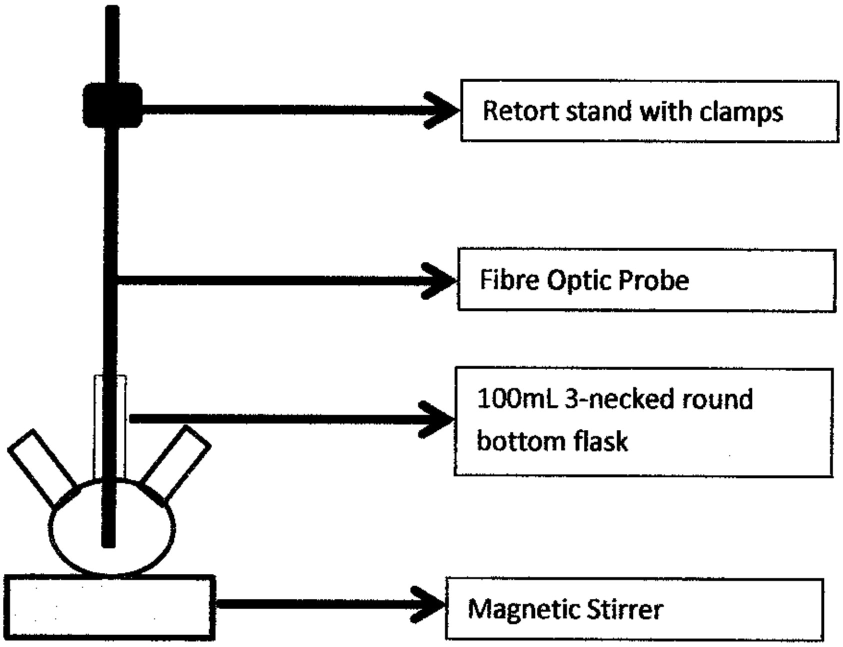


Figure 9: Setup Diagram

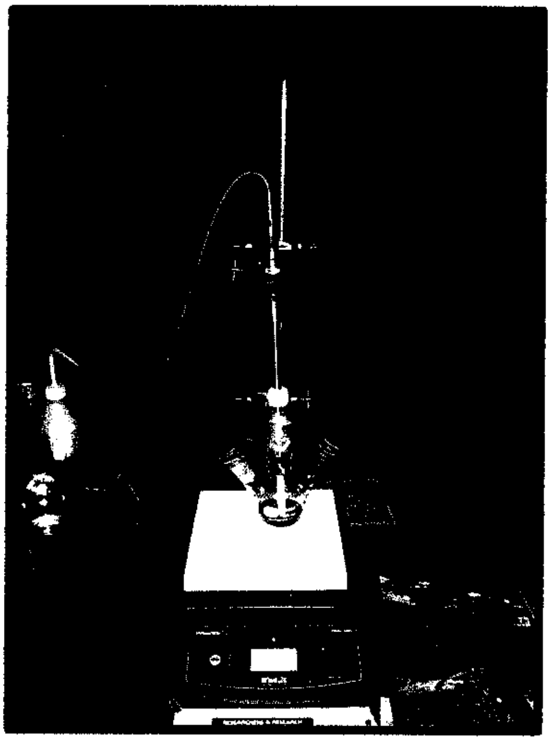


Figure 10: Standard equipment setup in dark chamber

3.3 Experimental Procedure

In order to synthesis one to one ratio of [bmim] $FeCl_4$, the general procedure is as follows. First, Raman spectrometer equipment is set up according to standard setting as in figure 9. Fibre optic probe is then aligned and calibrate with a standard PS accessory before starting the experiment. This is to ensure the wavelength, laser frequency, and white light emitted from the equipment is within the specification.

Then, 100ml round bottom flask along with a stirrer bar in it is tared. [bmim] Cl^- (Merck) 12.73 g (0.73 mol) is added into the flask. After that, the laser fibre optic probe of Raman spectroscope is properly immerse in to the chemicals. The monitoring process is started with the spectra capture is set to 30 seconds. 11.85 g (0.73 mol) of Iron (III) Chloride (Merck) is then slowly added into the round bottom flask. The stirring speed of 500rpm is set.

The flask is then sealed with Parafilm and the stirring and capturing process is continued for 4 hours. The reaction is completed when a dark brown homogenous liquid is observed in the flask. The experiment is then repeated accordingly with the ratio and time different. All this steps are done in a dark chamber to prevent interference from the cosmic rays in surrounding.

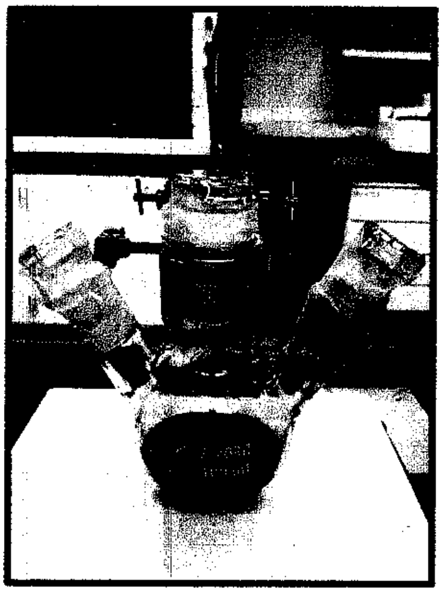


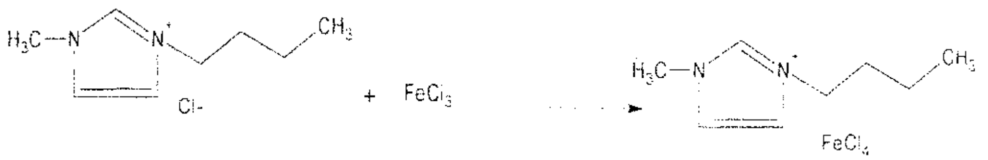
Figure 11: Sealed round bottom flask

Thermoscientific DXR Smart Raman 780nm filter equipment is used for the experiment along with immersion laser probe to help collecting data in real time. Room temperature (25°C) and atmospheric pressure (1atm) are selected as the operating condition and any changes on either are assumed to be negligible. Laser power is set to 150 watt while the wavelength collection spectrum is ranged between 100 cm^{-1} to 3200 cm^{-1}. 100ml three necks round bottom flask along with a magnetic stirrer are used as the reaction medium to ease the addition process of $FeCl_3^-$ into the reactant.

Running time for the experiment is set to 5 hours and will be shorten according to result accordingly. The result from the Raman spectroscopy will be analysed using the 2D and 3D graph analysis and the entire outcome will be recorded. Further analysis such as FTIR and NMR analysis still can be carried out if needed and deemed possible during the time frame.

3.4 Chemicals Involved

1. 1-butyl-3-methylimidazolium Chloride([bmim] Cl) 98% Merck
2. Iron (III) Chloride ($FeCl_{3)}$anhydrous 98% Merck
3. 1-butyl-3-methylimidazolium tetrachloroferrate([bmim] $FeCl_4$(Synthesized Product)



[Bmim] Cl^- + $FeCl_3$→ [Bmim] $FeCl_4^-$

Figure 12: Reaction Mechanism

3.5 Design of Experiment

In this project, Taguchi method is selected as the design approach for the experimental schedule. The varying parameter conducted for this project is the ratio and stirring time only. Due to this small variable value, Taguchi method is chosen as it reduces the number of experiment needed to be done for the whole process.

In this project, two (2) parameters are defined which are the reactant ratio and monitoring time. L16 table array is selected according to the Taguchi method approach for two parameters. The first parameter will vary the mixing ratio of 1:1, 1:1.5, 1:1.75, and 1:2. This is selected specifically to determine the ratio of when the production of [bmim] $Fe_2Cl_7^-$ will occur. The second parameter is the variance of monitoring time from 1 to 4 hour. This is essential in determining the time needed for the reaction to finish. The experimental design according to Taguchi method for this project is as in Table 1.

Table 1: Experiment Design Using L16 Table Array

Experiment	Ratio	Stirring Time (hour)
1	1:1	1
2	1:1	2
3	1:1	3
4	1:1	4
5	1:1.5	1
6	1:1.5	2
7	1:1.5	3
8	1:1.5	4
9	1:1.75	1
10	1:1.75	2
11	1:1.75	3
12	1:1.75	4
13	1:2	1
14	1:2	2
15	1:2	3
16	1:2	4

3.6 Final Year Project Timeline (Gantt Chart)

	Details/Week	1	2	3	4	5	6	7	8	9	10	11	12	13	14	■	1	2	3	4	5	6	7	8	9	10	11	12	13	14
		Final Year Project I														■	Final year Project II													
1	Briefing on Final Year Research Project Background	■						MID-SMESTER BREAK								SEMESTER BREAK							MID-SMESTER BREAK							
2	Preliminary Research Work/Literature survey		■	■	■	■	■																							
3	FYP seminar "Research Methodology"			■																										
4	Preparation of Extended Proposal Defence				■	■																								
5	Sample Preparation				■	■																								
6	Raman Spectrometer Introduction					■	■																							
7	Experiment 1-2								■	■																				
8	Experiment 3-4									■	■																			
9	Experiment 5-7										■	■	■																	
10	Result Analysis								■	■	■	■	■	■																
11	Submission of Interim Report													■	■															
12	Experiment 8-14																■	■	■	■	■	■								
13	Progress report submission																							■						
14	Experiment 15-16																							■	■					
15	Spare Weeks For Safety and Correction of Data																								■	■	■	■		
16	Pre-EDX																											■		
17	Submission of Dissertation																												■	
18	Submission of Technical Paper																												■	
19	Oral Presentation																													■
20	Submission of Project Dissertation																													■

4.0 RESULT AND DISCUSSION

4.1 Raman Spectra

Raman spectra can be a great tool in generating an accurate spectral fingerprint that is unique to a specific molecular structure. From the comparison of existing library database provided by the software manufacturer, along with the laboratory in-house record, the peaks at 2500 cm^{-1} to 3000 cm^{-1}, 1400cm-1, and at 1000 cm^{-1} can all be associated to represent the signature of imidazolium cations, which in this case is 1-methyl-3-methylimidazolium, [bmim].

Figure 13 shows the different Raman spectra of [bmim] Cl$^-$ before the mixing process is started. The product, [bmim] FeCl$_4^-$ is shown in Figure 14. The important peaks which can be analysed are the one at the 2500 cm$^-$ to 3000 cm$^-$ and peak from 100 cm$^-$ to 500 cm$^-$. The most significant peak observed throughout the reaction monitoring is the peak at 333 cm$^-$ which can be seen clearly at Figure 16.

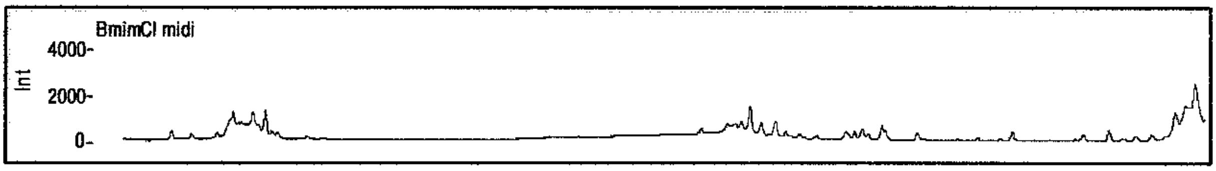


Figure 13: [bmim] Cl$^-$

Pure [bmim] FeCl$_4^-$ produces spectra as follow:

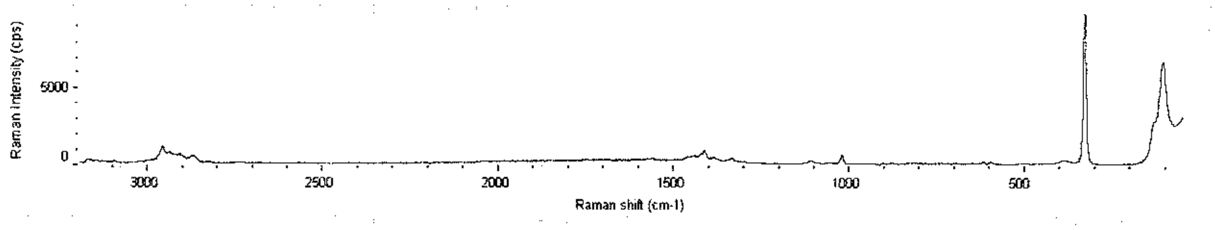


Figure 14: [bmim] FeCl$_4^-$

The distinctive peak at 333cm^{-} was reported to be the symmetric Fe-Cl Bond stretch vibration of $[FeCl_4]^-$ according to the study of characterization of magnetic ionic liquid done by (Wang, Yao, Nie, Zhang, & Li, 2012). The increase in the intensity of this peak represents the magnitude of formation of $FeCl_4^-$ ions in the product. The totally symmetric stretching of $FeCl_4^-$ bonds helps in producing clear intensity of Raman scattering to be captured by the detector.

Figure 15 shows the comparison between the final synthesis products with commercial library data. The similar peaks created at the wavenumber clearly indicate that the synthesis is successful and no impurities are produced in the 1:1 molar ratio synthesis.

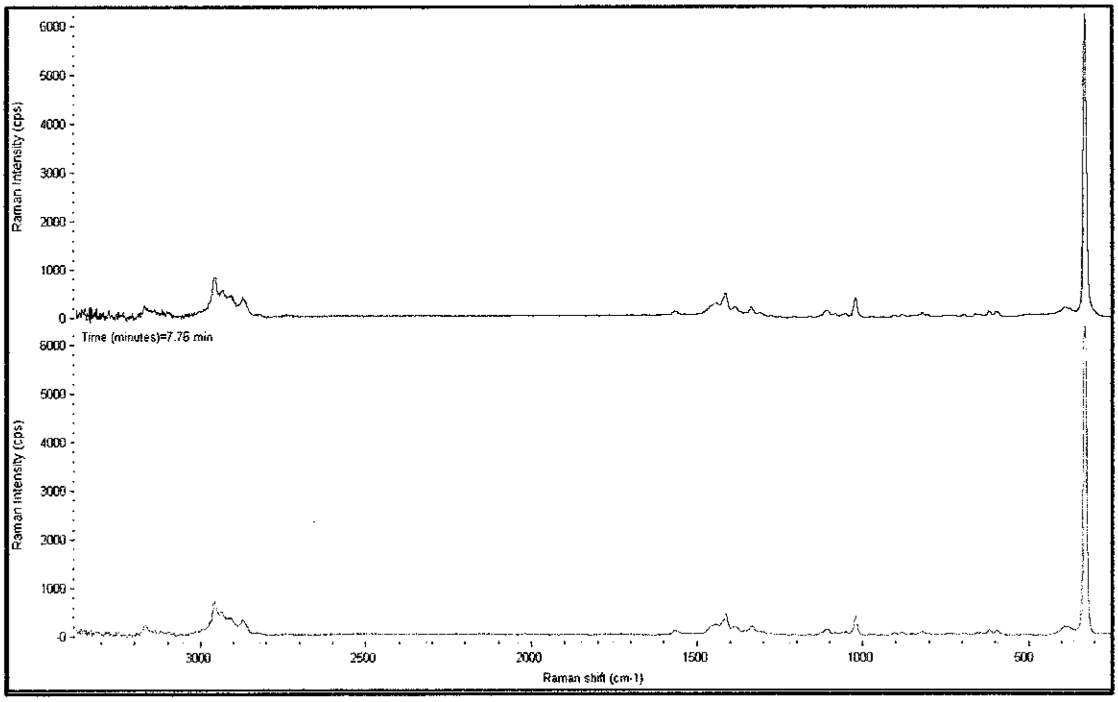


Figure 15: Comparison between final synthesis product with existing library

The monitoring process is started when Iron (III) Chloride, $FeCl_3$ was added into the original [bmim] Cl. The synthesis is then captured by Raman instrument and the production of $FeCl_4^-$ ion can be seen clearly at different points in Figure 14. These selected points were taken at the starting point of mixing at point 21 (5 minute) and at the end of point 30 (8 minute), the intensity of 333 cm-1 peak started to flatten out till the rest of the stirring time. This concludes that the synthesis process has a fast reaction process. Further detailed quantitative analysis of the reaction can be studied to determine the reaction rate of this mechanism. The point separating each spectral reading is taken at 30 seconds apart.

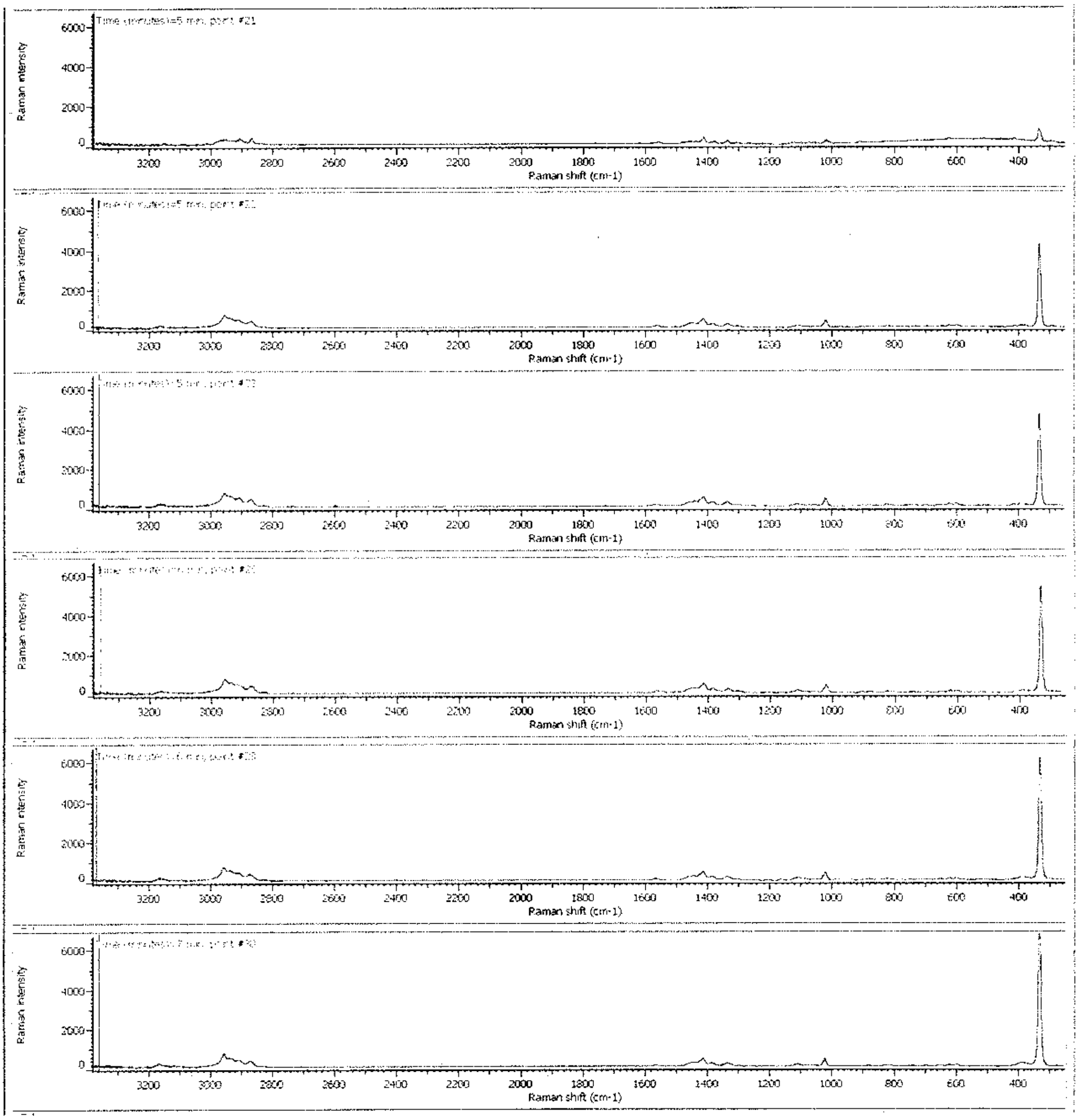


Figure 16: Raman spectra throughout the monitoring process

The regions at 1050 cm^-, 1300 cm^- to 1500 cm^-, and 2800 cm^- to 3000 cm^- shows no significant changes indicating that it is the region of the imidazole molecular stretches. The reaction process of combining the $FeCl_3$ and Cl^- anions in producing $FeCl_4^-$ does not affect the $[bmim]^+$ cations in any ways.

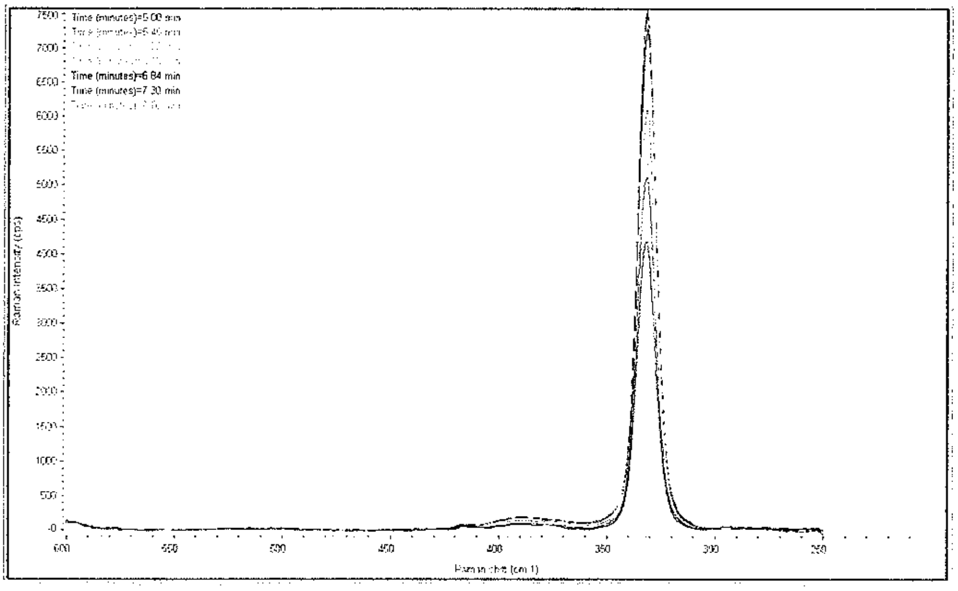


Figure 17: Region that indicates the formation of $FeCl_4^-$ ions at 333 cm^{-1}

The 3-dimensional model of the reaction monitoring is as follows. Here, the point of adding the iron chloride can be seen at around minute 2 thus producing slight disturbance on the model. After all the reactant has been added, the stable fast reaction starts to take place. The production of $[FeCl_4]^-$ ion can be seen indicated by red region which shows high intensity in the Raman spectrum.

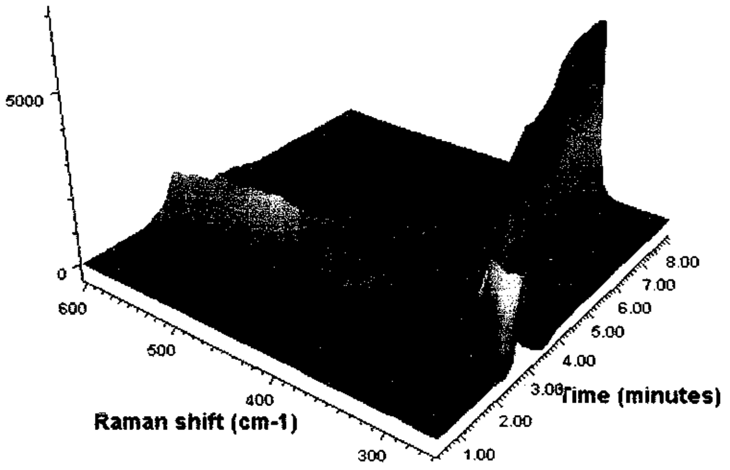


Figure 18: 3-dimentional model of reaction monitoring

The data produced by the spectrum confirms the ability of Raman spectroscopy in monitoring the synthesis of [bmim] $FeCl_4^-$.

4.2 [1:2] Reactant Ratio and Its Effect on Raman Spectra

The monitoring process of [bmim] $FeCl_4^-$ synthesis is then continued by adding another mole of iron chloride in the produced sample. In this case, we want to see the changes it made on the final product itself. Figure 16 shows the change in 100 cm^- to 500cm^- spectral region.

Shifting occurred in the region mainly because of the formation of [bmim] $Fe_2Cl_7^-$ ion. This ion formation is due to the abundance of iron chloride in the reactant. It has been confirmed that the new peaks at 370cm^- and 430cm^- are belonged to $Fe_2Cl_7^-$ ion by the research done (Sitze, Schreiter, Patterson, & Freeman, 2001).

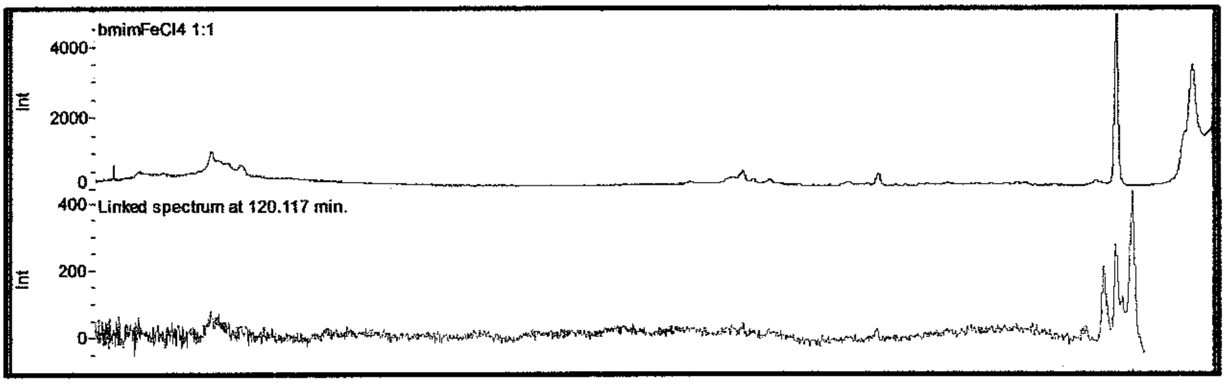


Figure 19: Comparison between [1:1] and [1:2] reactant ratio

The peak at 333 cm^{-1} is still visible but there are new features at around 370 cm^{-1} and 420 cm^{-1} that can be associated with $Fe_2Cl_7^-$. The same literature calculated the prediction of A-symmetry vibration to be visible at frequency 375 cm^{-1}. Another A-type $Fe_2Cl_7^-$ vibration predicted at 240 cm^{-1} is also visible here at around 250 cm^{-1} peak where both peaks now surrounding the initial 333 cm^{-1} $FeCl_4^-$ peak. The emergence of these new peaks supports the initial hypothesis of the formation of $Fe_2Cl_7^-$ at higher mixing ratio.

5.0 CONCLUSION AND RECOMMENDATION

5.0 Conclusion

The objective of determining the feasibility of using Raman spectroscopic technique in monitoring the IL synthesis is achieved. At the end of the project, Raman spectroscopy gives out much information on the reaction process and also about the $Fe_2Cl_7^-$ ions formation when the mixing ratio is more than 1. The molecular stretching analysed at 333 cm^{-1} is determined as the symmetric FeCl4 bonds while the production of $Fe_2Cl_7^-$ produces extra peaks at 250 cm^{-1} and 375 cm^{-1}. The minimum time needed for the monitoring process to end can be determine with further analysis but a fast reaction rate is already known.

5.1 Recommendation

Several suggestion that can be made for the future work of expansion and continuation of this project are as follows:

1. The result of Raman spectroscope should be compared with many other analytical equipment such as FTIR and NMR spectroscopy.
2. More parameter can be added for the monitoring experiment such as different temperature or more ratio composition to be examined.
3. The exact ratio and time of the starting formation of [bmim] $Fe_2Cl_7^-$ need to be search and calculated along with its effect on [bmim] $FeCl_4^-$ application behavior change.

REFERENCES

1. Apte, P. R. (2008, Disember 14). *Introduction to Taguchi Method.* Retrieved April 20, 2012, from Indian Institute of Technology, Mumbai: Apte's Web-Page: http://www.ee.iitb.ac.in/~apte/CV_PRA_TAGUCHI_INTRO.htm

2. biology-online.org. (2006, November 27). *A brief history on spectroscopy.* Retrieved February 15, 2012, from Biology Online: http://www.biology-online.org/articles/raman_spectroscopy_gateway_tomorrows/brief_history_spectroscopy.html

3. Casilda, V. C., Pérez-Mayoral, E., Banares, M. A., & Diz, E. L. (2010). Real-time Raman monitoring of dry media heterogeneous alkylation of imidazole with acidic and basic catalysts. *Chemical Engineering Journal*, 371-375.

4. Dennis, A. (2007). What is Raman Spectroscopy? Belfast, Northern Ireland.

5. Earle, M. J., & Seddon, K. R. (2000). Ionic liquids. Green solvents for the future. *Pure Appl. Chem.*, pp. 1391-1398.

6. Fraley, S., Oom, M., Terrien, B., & Zalewski, J. (2007, November 27). *Design of experiments via taguchi methods: orthogonal arrays.* Retrieved February 18, 2012, from The Michigan Chemical Process Dynamic and Controls Open Text Book: https://controls.engin.umich.edu/wiki/index.php/Design_of_experiments_via_taguchi_methods:_orthogonal_arrays

7. Gurden, S. P., Westerhuis, J. A., & Smilde, A. K. (2002, October). Monitoring of Batch Processes Using Spectroscopy. *AIChE Journal*, pp. 2283-2297.

8. Hayashi, S., & Hamaguchi, H.-o. (2004). Discovery of a Magnetic Ionic Liquid [bmim]FeCl4. *Chemistry Letters*, 1590.

9. Hendra, P. (2004). *What is Raman Spectroscopy?* Retrieved February 27, 2012, from The Internet Journal of Vibrational Spectroscopy: http://www.ijvs.com/volume1/edition5/section1.html

10. Holbrey, J., & Seddon, K. (1999). Ionic Liquids. *Clean Products and Processes 1*, 223-236.

11. Kamaruddin, S., Khan, Z. A., & Wan, K. S. (2004). THE USE OF THE TAGUCHI METHOD IN DETERMINING THE OPTIMUM PLASTIC INJECTION MOULDING PARAMETER. *Jurnal Mekanikal*, 98 - 110.

12. Kogelnig, D., Stojanovic, A., Kammer, F. v., Terzieff, P., Galanskia, M., Jirsaa, F., et al. (2010). Tetrachloroferrate containing ionic liquids: Magnetic- and aggregation behavior. *Inorganic Chemistry Communications*, 1485-1488.

13. Lee, M., Kim, H., Rhee, H., & Choo, J. (2003). Reaction Monitoring of Imine Synthesis Using Raman Spectroscopy. *Bull. Korean Chem. Society*, pp. 205-208.

14. Lee, S. H., Ha, S. H., You, C.-Y., & Koo, Y.-M. (2006). Recovery of magnetic ionic liquid [bmim]FeCl4 using electromagnet. *Korean J. Chem. Eng*, 436 - 437.

15. Mikolajska, E., Calvino-Casilda, V., & Banares, M. (2012). Real-time Raman monitoring of liquid-phase cyclohexane epoxidation over alumina-supported vanadium and phosphorus catalysts. *Applied Catalysis A: General*, 164-171.

16. Nollert, P. (2009, November 6). *Ionic Liquid for Protein Crystallization*. Retrieved March 13, 2012, from Emerald Bio: http://www.emeraldbiosystems.com/blog/post/ionic-liquids-for-protein-crystallization.aspx

17. Organic Chemistry Portal. (n.d.). *Ionic Liquids*. Retrieved February 9, 2012, from Organic Chemistry Portal : http://www.organic-chemistry.org/topics/ionic-liquids.shtm

18. Perkin Elmer. (2007). Introduction to Raman Spectroscopy. Waltham, MA, USA.

19. Perkin Elmer. (2007). Introduction to Raman Spectroscopy: Top 20 Questions Answered. Waltham, MA, USA.

20. Sitze, M. S., Schreiter, E. R., Patterson, E. V., & Freeman, R. G. (2001). Ionic Liquids Based on FeCl3 and FeCl2. Raman Scattering and ab Initio Calculations. *Inorg. Chem.*, 2298-2304.

21. Smith, E., & Dent, G. (2005). *Modern Raman Spectroscopy A Practical Approach.* West Sussex, England: Wiley.

22. Svensson, O., Josefson, M., & Langkilde, F. W. (1999). Reaction monitoring using Raman spectroscopy and chemometrics. *Chemometrics and Intelligent Laboratory Systems*, 49-66.

23. Wang, G., Yu, N., Peng, L., Tan, R., Zhao, H., Yin, D., et al. (2008). Immobilized Chloroferrate Ionic Liquid: An Efficientand Reusable Catalyst for Synthesis of Diphenylmethane and its Derivatives. *Springer Science*, 252-258.

24. Wang, H., Yan, R., Li, Z., Zhang, X., & Zhang, S. (2010). Fe-containing magnetic ionic liquid as an effective catalyst for the glycolysis of poly(ethylene terephthalate). *Elsevier: Catalysis Communications*, 763-767.

25. Wang, J., Yao, H., Nie, Y., Zhang, X., & Li, J. (2012). Synthesis and Characterization of the Iron-Containing Magnetic Ionic Liquids. *Journal of Molecular Liquids*, 152-155.