Crystallisation Study of Ionic Liquids

by

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CERTIFICATION OF APPROVAL

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A project dissertation submitted to the
Chemical Engineering Programme
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Approved by ,

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(Dr. Lukman Ismail)

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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 acknowledgements , and the original work contained herein have not been undertaken or done by unspecified sources or persons.

(NURUL SYAFIQAH BINTI AB RAHMAN)

ABSTRACT

Ionic liquids have attracted much attention at late due to their unique properties as functional liquids in a wide variety application such as electrochemical material and chemical reaction media. Ionic liquid is an ionic salt that melts below 100°C and has characteristics of non volatile environmental friendly solvents as compared to traditional organic solvents. Therefore, this project will present the study on crystallization of ionic liquid as it is important as one of possible methods to recycle and regenerate ionic liquids. The objective of this project is to study the kinetic of ionic liquids by crystallizations. Avrami analysis was utilized to study the crystallization kinetics of ionic liquid. Different parameters that influence the crystallization of ionic liquid will be explored such as effects of initial temperature, effect of crystallization temperature and effects on ratio of water content.

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First and foremost, praise be to Allah for providing me with the opportunity to complete my final year project and having opportunity to conduct an experiment entitle Crystallisation of Ionic Liquids.

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CHAPTER 1

INTRODUCTION

1.1 Background

An ionic liquids (ILs) is a salt that are comprising of cation and anion and have a melting point below 100°C (Wilkes, 2002).It is also known as molten salts and has high thermal stability. There are several common of ILs which are ammonium, phosphonium, sulfonium, guanidium, pyridinium, imidazolium, and pyrrolidinium cations (Koel, 2008). ILs has significantly lower symmetry and the charge of the cation and anion distributed over a larger volume of the molecule by resonance. As a result, the solidification of the ILs will take place at lower temperatures. In another conditions, if long aliphatic side chains are involved, a glass transition is observed instead of a melting point. Next, the properties of ILs and its stability are depending on the choice of cation whereas the choice of anion will be define the chemistry and functionality of the ILs.

Ionic liquids are capable in acting as solvents. But, it is essentially important to know the physical and chemical properties of ILs before we design the desirable ILs and optimize the use of ILs .A fundamental understanding of the chemical and physical properties should be known before industrial applications. Therefore, it has been used as functional liquids in a wide variety of applications such as electrochemical materials, and chemical reaction media. Some applications of ionic liquids are electrolytes in batteries, lubricants, fertilizers, etc. Moreover, due to the unique properties of ILs, it has received a great increase in attention in the field of engineering during the last decades. Realization of the potential advantages of chemical processes based on ILs has been limited by the high cost of ILs. Therefore, it is economic if the ILs that has been used can be recycle or reuse.

A separation technique is an important method to remove impurities because after the reaction chemical takes place in the ionic liquid, this industrial solvent of ILs might be contaminated. On the other hand, distillation technique can be used to separate any impurities from ILs. Another technique for purification also can be used such as extraction, membrane technologies and crystallization. But ionic liquids are different from the others organic solvent because it is cannot be simply purified by distillation directly, due to its non-volatile character. Therefore, crystallization is the dominant method to purify non-volatile chemical.

1.2 Problem Statement

ILs has become an increasingly popular class of solvent in the last decade as the potential application of these materials become more diverse. As a result, most ionic liquids will be used in chemical process and most of them are in the form of solution. The application of ILs in industry can improve efficiency in the chemical process. ILs that has been used in any chemical process can be purified and recycled by using separation techniques such as crystallization based on their impurities. Crystallization of ionic liquid is important as by using crystallization process, ionic liquid can be regenerate and recycle so that it is not being wasted after used in any chemical processes. Moreover, the products of crystallization successfully retain the molecular ion of ILs as the molecular structure is related to the ILs properties. Other method of purify IL such as drying, it is not recommended as it may decompose the molecular ion of ILs. Therefore, crystallization is one of the possible methods seeking means for their purification. Insufficient data available nowadays make it difficult to know the best condition for them to crystallize effectively. Therefore, the main focus for this paper is to study crystallization of ILs and investigate the kinetics using Avrami theory.

1.3 Aim And Objective

The aim of this project is to study the kinetic of ionic liquids by crystallizations under different operating parameters and conditions. The kinetics of crystallization will be analyzed by using Avrami approach.

i) To study the effect of initial temperature on the crystallization of ionic liquids.
ii) To study the effect of crystallization temperature on the crystallization of ionic liquids.
iii) To study the effects on ratio of water content.

1.4 Scope of Study

In order to complete this project, several scope of study is in need to achieve. The experiment on crystallization process of ionic liquid is conducted in the laboratory. Prior to that, understandings of the physical and chemical properties of ILs allow the proper selection of ILs for a crystallization process. Thus, by choosing the right ionic component, it can control solubility critical to crystallization process. Furthermore, suitable method and approach will be designed and applied to conduct the experiment. The parameters that will be used in this project are initial temperature, crystallization temperature, and water content. The preferable choice of ILs is 1-Butyl-3-methylimidazolium chloride, [BMIM]Cl because it has desired crystallization properties, structurally comparable, and widely used in industries. Apart from that, this project also covers the analysis on the findings of the experiments. Avrami equation is used to perform analysis on crystallization kinetics.

1.5 Relevancy and Feasibility of the Project

Ionic liquids is a molten salts consisting cations and anions and in the form of liquid at room temperature. It has a good solubility characteristics and suitable for multiphase catalysis. These ionic liquids, which in some cases can serve as both catalyst and solvent, are attracting increasing attention from industry because they promise significant environmental benefits, according to British and French researchers. According to Seddon (1999), ionic liquids is a conventional solvents that is used in the industrial syntheses of organic chemicals, they are nonvolatile and therefore do not emit vapors. ILs that has been used in any chemical process can be purified and recycled by using separation techniques such as crystallization based on their impurities. Therefore, it is important to understand the formation of crystallization as it can contribute and motivate to further explore the regenerating and recycling process of ionic liquid. It will be beneficial for the chemical process industries as its will help to reduce the cost. This project is considered as feasible as all the equipment and material are available at the laboratory in Petronas Ionic Liquids Centre (PILC). The time provided for the research is sufficient for the experiments and research to be conducted and shall be completed within the time specified in the project Gantt chart.

CHAPTER 2

LITERATURE REVIEW

2.1 Ionic Liquids

The history of ILs began in 1914 with an observation by Paul Waden who reported the physical properties of ethylammonium nitrate [EtNH3][NO3], (Plechkova and Seddon, 2008).The term ionic liquid refers to a class of liquids that are composed solely of ions. It is synonym of molten salt. Although molten salt implicitly means a high-temperature liquid that is prepared by melting a crystalline salt, ionic liquid includes a new class of ionic compound that are liquids at the ambient temperature. Thus, ionic liquids in a narrow sense often stands for room-temperature ionic liquid (RTIL), also known as molten salts, are liquids composed entirely of ions with melting points under 100 °C. They are generally organic salts where one or both of the counterions can be customized for specific applications. Below are the chemical structures of some common cations and anions used to form ILs.

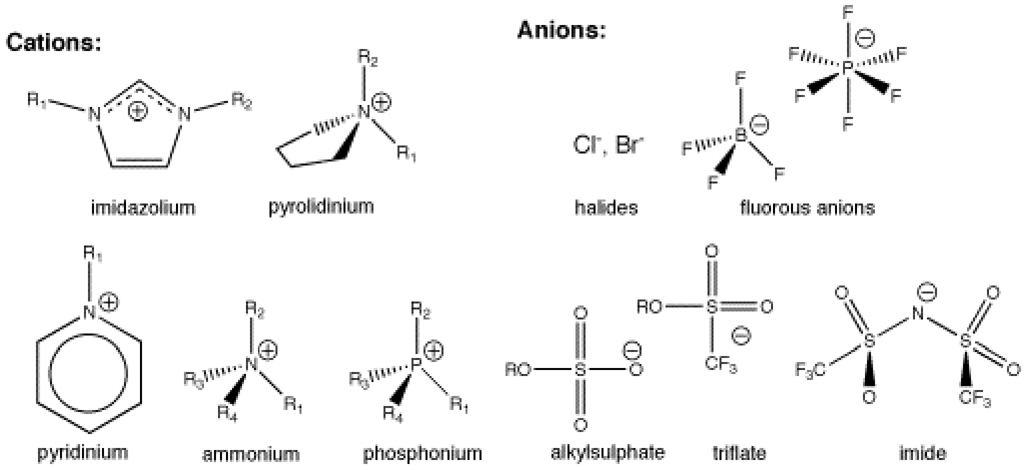

Figure 2.1: Some chemical structure of cations and anions (Welton, 1999)

Liquids, such as ethylammonium nitrate consist almost of cations and anions with only a small amount of molecular species as ionic liquids (Wasserscheid and Welton, 2003). In general, they are thermally stable, non flammable and exhibit very low vapor pressure. Ionic liquids can dissolve a wide range of organic and inorganic compounds and can be water miscible. Because of these properties, ionic liquids have been used as solvents for conducting a wide range of chemical reactions, in some cases replacing more toxic solvents, earning them the reputation of being environmentally friendly solvents. The most common application of ionic liquids has been use as chemical reaction solvents. ILs have also been used for electrochemical processes, removal of metal ions, purification of gases, generation of high conductivity materials, extraction solvents stationary phases in chromatography, thermal fluids, lubricants, and propellants.

2.2 Crystallization

Crystallization is a technique for purifying solid organic compounds. It is a mass transfer of solute from the liquid phase to the solid phase. Crystallization can also refer to the solid-liquid separation and purification technique in which mass transfer occurs from the liquid solution to a pure solid crystalline phase

According to Allan S. Myerson (2011), crystallization from solution can be divided into two step process. The first step is the phase of separation of a new crystal and the second step is the growth of crystal into larger size. These two step is known as nucleation and crystal growth, respectively. Nucleation is the beginning process of phase separation where the solute molecules have formed the smallest sizes particles under the conditions present. Then, the next stage of crystallization is the process of nuclei growth by addition of solutes molecules from supersaturated solutions. Crystal growth along with the nucleation will controls final particle size distribution of crystals. Generally, the rate of crystal growth has a significant impact on the product purity and crystal behavior. The action of crystal growth yields a crystalline solid whose atoms or molecules are typically close packed, with fixed positions in pace relative to each other. Many ionic liquids tend to form glasses on cooling presenting, as a consequence, practical challenges for their recovery and recycling (Choudry and Winterton , 2006).The low melting points exhibited by ILs result from decreased lattice energies, frustration of crystallinity caused by reduced symmetry, inhibition of crystallization through provision of a large number of similarly stabilized solid-state structures (polymorphism) which can also lead to plasticity and glass formation in the solid state, and low energy melting transitions, *via* ‘weaknesses’ in the crystal lattice (Holbrey, 2003).The shape of growing crystal can be affected by the fact that different crystal faces have different growth rate. Crystals are grown in many shapes, dependent upon downstream processing or final product. This can include cubic, tetragonal, hexagonal and trigonal. Therefore, an understanding of the crystal growth theory and experimental techniques for examining crystal growth from solution are important and very useful in the development of industrial crystallization processes (Allan, 2011).It is frequently mentioned that ionic liquids do not form crystalline phases. IL has high degree of asymmetry which hinders ordered packing and thus inhibits crystallization (Welton, 2004). They tend to undergo some cooling and frequently form amorphous structures in the solid state. Studies on solid phase transition performed on imidazolium-based ILs have shown that, although crystallization can in principle be successfully achieved, this also depends to a certain extent on the cooling rate among other factors; in fact, most of these molten ILs are very good glass-formers, that is, they actually present a weak tendency to crystallize.

2.3 Usage of Ionic Liquid in Chemical Process

Lately, ionic liquids had been used in chemical process. Ionic liquids (ILs) have been used as reaction media, for separations in gas and liquid phases (Olivier, 1999, and Wasserscheid and Welton, 2003, Welton, 2004 and extraction processes (Meindersma *et al.*, 2005). Furthermore, these seem suitable for being used as a solvent in gas absorption (Anthony et al., 2003, and Davis, 2005).It is due to solvent properties of ionic liquid that can affect the reactions. As an example, L.M Galan Sanchez, G.W Meindersma amd A.B de Haan had done researches on properties of fuctionalized ionic liquids can be used as carbon dioxide absorption and the results showed that CO_2 absorption behaviour was influenced by the functionalized chains appended to the RTILs cation.

Others than that,according to Cserjési Petra and Bélafi-Bakó Katalin (2011), Ionic liquid can be used in membrane separation process. Due to the special features of ionic liquids, such as high thermal and chemical stability, low vapour pressure, non flammability, tunable physicochemical properties, etc. make them perfect candidates for the substitution of organic membrane phase in liquid membranes, to Cserjési Petra and

Bélafi-Bakó Katalin (2011).The special properties of ionic liquids, i.e. high thermal and chemical stability, low vapour pressure (Endres et al., 2008), non-flammability (Wasserschied & Welton, 2007) and tuneable physicochemical properties, make them the ideal candidates for the replacement of organic solvents in liquid membranes and hence for the realization of environmentally sound and economical membrane separation processes (Koel, 2008).

2.4 Avrami Kinetic

Crystallisation of ionic liquids has been investigated in the test tube and by referring to Lukman et al (2008), the degree of crystallinity is measured by the relative crystallization δr, defined as the mass fraction of the liquid that are not crystallized divided by the initial mass of the crystal and water mixture liquid. Thus,

$$\delta\mathrm{r} = \frac{\delta t - \delta\mathrm{o}}{\delta\infty - \delta\mathrm{o}} \text{ ………………… Equation 1}$$

δt – extent of crystallization at time t

δ∞ - maximum asymptotic crystallization from Avrami plot

δ0 - initial mass of crystallized content content in liquid (g)

After that, the Kolmogorov-Johnson-Mehl-Avrami (KJMA) is applied in order to describe the kinetic in crystallization
by Equation 2:

$$1 - X = e^{-Kt^n} \text{ ……………………. Equation 2}$$

X - volume fraction of crystalline material

K – growth rate

n – Avrami exponent related to the nucleation growth

Replacing the X in Equation 2 with δr from Equation 1 and taking log twice for Equation 2 it can be written as:

$$\log [-\ln (1 - \delta\mathrm{r}) = \log K + n \ \log (t)]$$

Referring to the Equation 2, the graph can be plotted using the left side as y-axis versus log (t). Then, the slope of the graph equal to Avrami's exponent (n) and the intersection of y-axis represent the growth rate (K) .

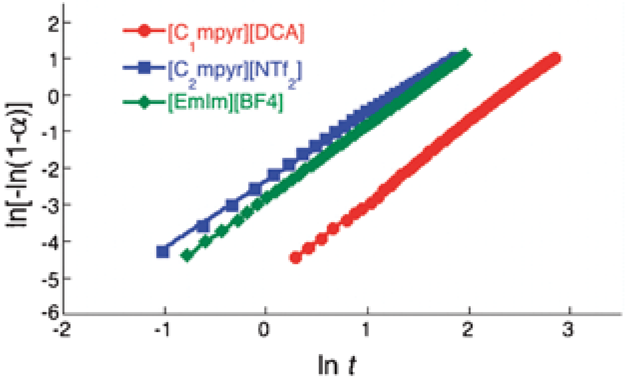

Figure 2.2 : Avrami analysis (Macfarlane, 2011)

CHAPTER 3

METHODOLOGY

The experimental work is conducted at Petronas Ionic Liquid centre (PILC). The main purpose of this research is to study about the kinetics crystallization of ionic liquids by using Avrami approach and it will involve several parameters. There are 3 parameters used which are initial temperature, crystallization temperature and water content. In this research, imidazolium-based ILs is used due to the fact that it has desired crystallization properties, structurally comparable and widely used in industry.

3.1 Sample Preparation

The imidazolium-based ILs, 1-Butyl-3-Methylimidazolium Chloride [BMIM]Cl, was prepared and to be mix with water(solvent).Water is chosen as it is miscible with [BMIM]Cl ,non flammable and non toxic. ILs was purchased from Merck Chemical Malaysia and was in the form of crystals.

3.2 Equipment

Test tube and weighing balance were used in the experiment. Test tube was used for the process of crystallization occurred whereas weighing balance was used to weigh the non crystallized liquid. Next, without refrigerator the process of crystallization might be incomplete. Therefore, refrigerator JULABO F-32 Refrigerated and Heating Circulator was used to cool down the sample until crystal formed. The JULABO F-32 Refrigerated and Heating Circulator used ethylene glycol as a refrigerant because it has an ability to reach temperature below 0^{o}C. Water cannot be used as refrigerant for chiller because it cannot reach low temperature in order to make ionic liquids crystallized. Other than that, hot plate is required to supply heat during experiment.

Figure 3.1: Weighing balance

Figure 3.2: JULABO F-32 Refrigerated Heating Circulator

Figure 3.3 Test tube

3.3 Measurement of Crystallization

Gravimetric analysis method was used in order to quantify the amount of crystallization. Prior to the experiment, the sample solution was weight to get initial weigh. At the end of experiment, non crystallized liquid was drain out of test tube to a beaker and weigh. Then, the crystallized ILs can be measured by initial weight of solution minus the weight of non crystallized liquid. The percentage weight of crystals can be calculated as shown below:

$$\%\text{ weight of crystal} = \frac{Weight\ of\ crystal}{Total\ weight\ of\ sample\ \ solution\ \ (initial\ \ weight\ of\ sample\ )} \times 100\%$$

3.4 Crystallization

3.4.1 Effects on initial temperature

In this experiment, different degree of initial temperature is used to heat up the IL. The objective of this experiment was mainly to study the Avrami kinetic theory at different temperature.2 sample of solution was prepared with the degrees of temperature used was 50^{o}C and 60^{o}C.Firstly, the ILs liquid was mixed with water that acts as a solvent. Then the solution was heat up to the desired temperature. After that, the solution was cooled down by using JULABO F-32 Refrigerated and Heating Circulator (chiller) that used ethylene glycol as its refrigerant. The crystallized temperature used in this experiment was -15 ^{o}C and it is a constant parameters. The IL was undergoing crystallization process for certain period of time and in every 10 minutes; the non crystallized ILs is measured. Then, the liquid is put back into the test tubes. The process was stopped only when there is no significant change regarding the weight of non crystallized ILs. The data obtained from the experiment will be analyzed and plotted by using Avrami kinetics.

3.4.2 Effects on crystallization temperature

For this experiment, different degree of crystallization temperature is used to cool down the IL. Two sample of solution was prepared with the degrees of initial temperature was fixed which is 60^{o}C.Therefore, the ILs solution required to heat up until 60^{o}C. After that, the solution was cooled down by using chiller with the degree of crystallization temperature is -15 ^{o}C and the sample with the degree of -20 ^{o}C. The IL was undergoing crystallization process for certain period of time and in every 10 minutes; the non crystallized ILs is measured. Then, the liquid is put back into the test tubes. The process was stopped only when there is no significant change regarding the weight of non crystallized ILs. The data obtained from the experiment will be analyzed and plotted by using Avrami kinetics.

3.4.3 Effects on ratio of water content

For this experiment, different ratio of water content to ILs was used in preparing sample of solution. The ratios of water content to ILs are 1:1 and 2:1 was prepared. Then each of the ILs solution required to heat up until 60^{o}C. After that, the solution was cooled down by using chiller with the degree of crystallization temperature is -15 ^{o}C. The IL was undergoing crystallization process for certain period of time and in every 10 minutes; the non crystallized ILs is measured. Then, the liquid is put back into the test tubes. The process was stopped only when there is no significant change regarding the weight of non crystallized ILs. The data obtained from the experiment will be analyzed and plotted by using Avrami kinetics.

CHAPTER 4

RESULT AND DISCUSSION

4.1 Effects of Initial Temperature

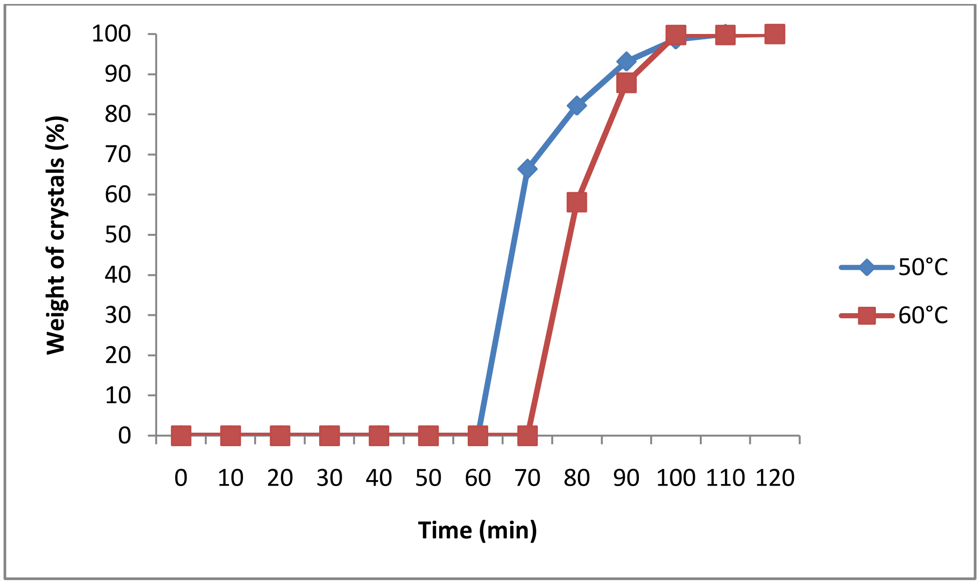

Figure 4.1: Degree of crystallinity for various initial temperature

The above figure shows the effect of initial temperature on the crystallization for the experimental duration almost of 2 hours. The rate of crystallization increased with time and 100% crystallization was achieved. Generally the graph shows the crystallization time was reduced as the initial temperature decreased. It can be proved by the time used for 60 ^oC of ionic liquid to achieve greater mass of crystallization is at minute of 80 whereas for 50 ^oC of ionic liquid the time taken to achieve greater mass crystallization is at minute of 60.Therefore, the increased in initial temperature of ionic liquids, will have slower crystallization response . As a conclusion, the reduction time for crystallization can be achieved by using appropriate initial temperature.

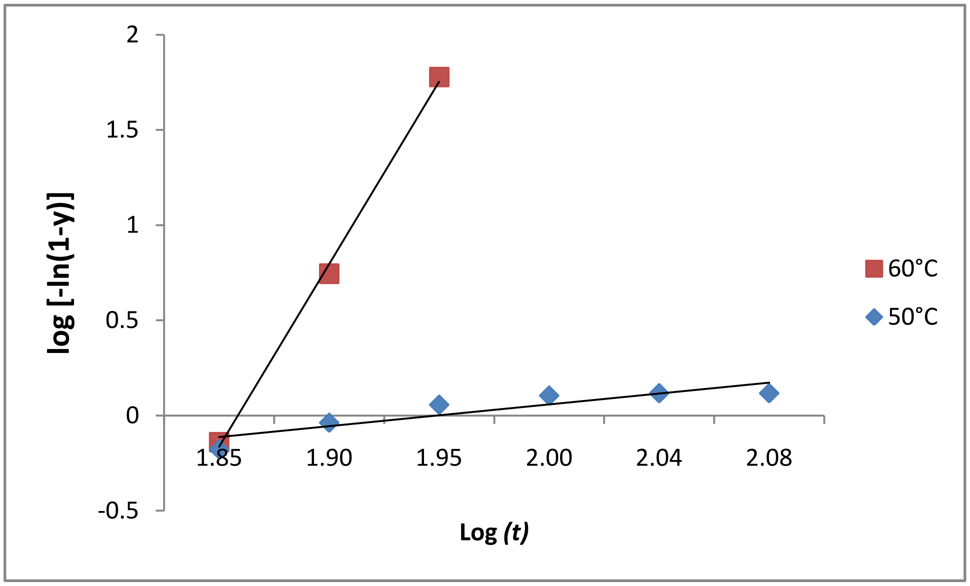

Figure 4.2: Plot of Log [-ln(1-y)] vs Log (t) to obtain linear format of Avrami Equation

The Avrami kinetic analyses were conducted by plotting the graph using the linearize equation of Avrami .The Avrami exponent, *n* can be determine through the slope of straight line whereas and the rate constant *k* can be determine through the intersection of the straight line with y-axis. The value of *n* will indicate the structure of crystal as well as on the nature of nucleation and the value of *k* indicate the crystal growth rate over the entire duration.

Table 4.1: Extracted Avrami parameters

Temp (^{o}C)	***n***	***k***
50	0.57	0.845
60	0.958	0.325

Based on table 4.1 it can be seen that the value of the Avrami exponent, *n* increase as the temperature increase. Generally, the increasing in Avrami exponent contributed to the change of crystal nucleation. The graph shows that the transformation of [BMIM]Cl takes places by nucleation at 50^{o}C based on the value of *n*. It takes more time for the nuclei to start gather into cluster before it grow into stable crystal size. From the table

4.1 , at initial temperature of 60°C, the Avrami exponent value (*n*) was 0.958 indicating that ionic liquid crystals produced were of one-dimensional , rod like or needle-like type as shown in Figure 3 below.

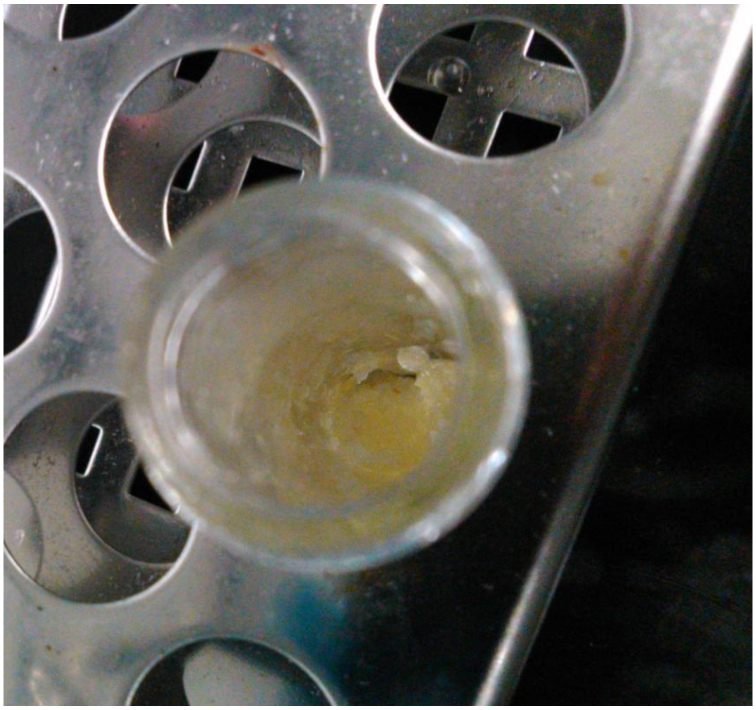

Figure 4.1 Image of ILs crystal (needle shape)

4.2 Effects of Crystallisation Temperature

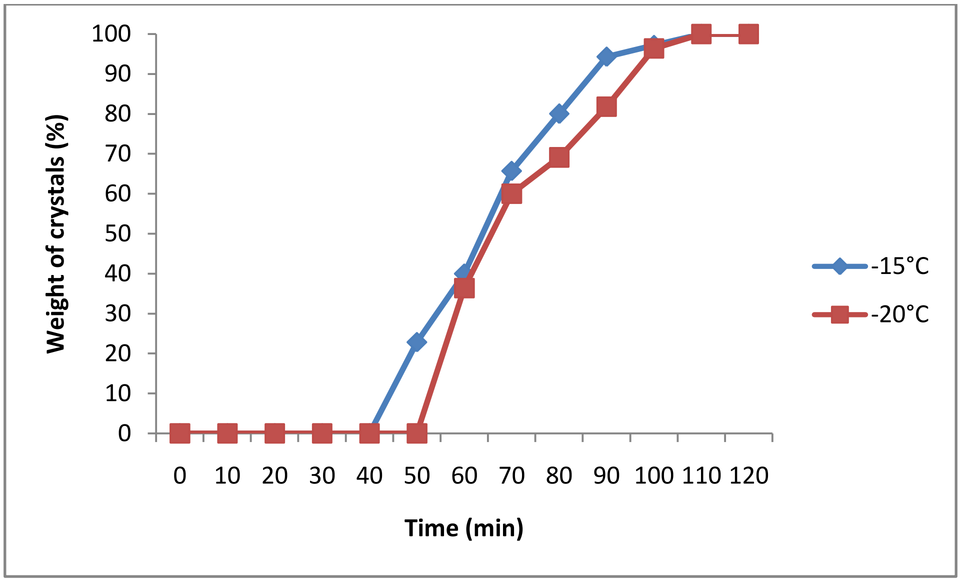

Figure 4.1: Degree of crystallinity for various of crystallisation temperature

In order to assess the effect of crystallization temperature, control experiment was carried out with initial temperature of 60 ^oC. The crystallization temperature used was -15 ^oC and -20 ^oC. Observations from the experiment were that the ionic liquids crystal was in the form of solid-liquid. When 100% crystallization has been reached, the solid-liquid ionic liquid filled the whole bottom of test tube and became solidified. Figure 4.4 show the percentage of crystallization for different crystallization temperature where the y-axis corresponds to the percentage of ionic liquids crystallized. From the graph, it can be clearly observed that crystallization shifts to longer times with an increasing of the crystallization temperature**.** Consequences, it gives slower rate of crystallization and have longer time taken to reaches 100% crystallization.

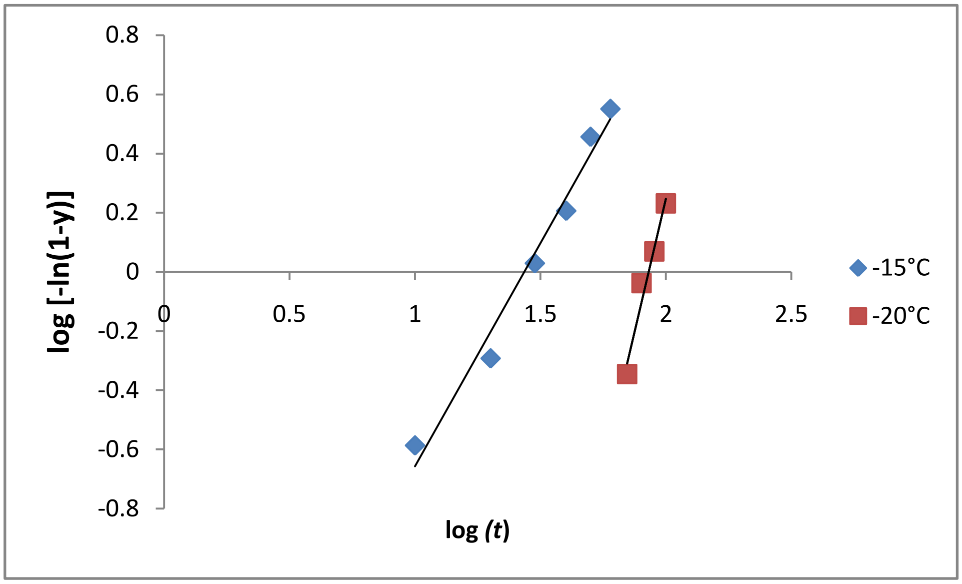

Figure 4.2: Plot of Log[-ln(1-y/)] vs Log (t) to obtain linear format of Avrami equation

Table 4.2 : Extracted Avrami Parameters from figure 4.4

Temp (^oC)	***n***	***k***
-15	1.507	0.115
-20	3.586	9.82E-4

Figure 4.4 shows the corresponding Avrami plots for various crystallization temperatures. The straight line fit through the curves yield the 2 important Avrami parameters, *k* and *n.* Based on table 4.2 the value of n decreased as the temperature decreased. Both Avrami exponent *n* and the rate constant *k* are dependent on the crystallization temperature. Consequently, the nucleation and crystal growth mechanisms and rates are expected to be effected by crystallization temperature and degree of supersaturation. Avrami Exponent reflects the nucleation mechanism and growth dimension of the crystals. The different *n* values as crystallization temperature changes mean that a different nucleation and/or crystal growth would take place at different temperatures, thus suggesting the existence of different crystallization mechanism depending on the degree of supersaturation. At higher supersaturation (low temperature, -20 °C), sporadic nucleation have important role with Avrami exponent of 3.58. At low supersaturation,-15 °C the Avrami exponent indicate one dimensional growth (needle/rod) mechanism with the value of 1.507.

Figure 4.2 Image of solid-liquid crystals

4.3 Effects on Ratio of Water Content

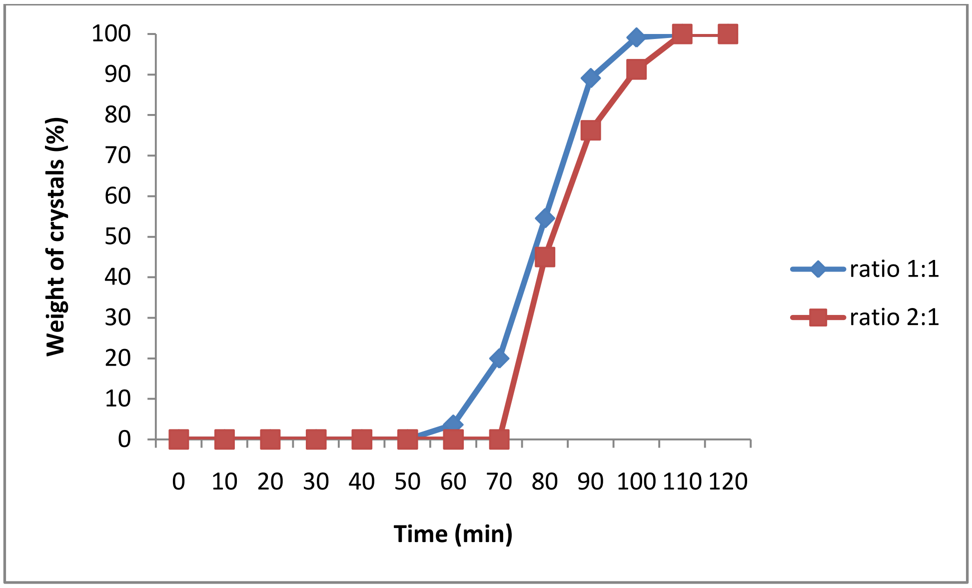

Figure 4.3: Degree of crystallinity for various of water content in ionic liquid

Figure 4.7 show the graph for the weight of crystal formed as a function of time for different ratio of water content. From the visual observations during experiments, the ionic liquids crystals were form of solid-liquid that adhered to the wall of the test tube. Based on the figure above, the rate of crystallization is increase as the concentration of ionic liquid increase .(i.e 1:1 is more concentration than 2:1 based on ratio water to ionic liquids) Time used for the ionic liquid at ratio 1:1 concentration to totally crystallize is less than the ratio 2:1. The increased growth rates at larger supersaturation contribute to a faster crystallization response and this would be reflected in the higher values of *n* obtained at higher concentration of ionic liquid in the solution.

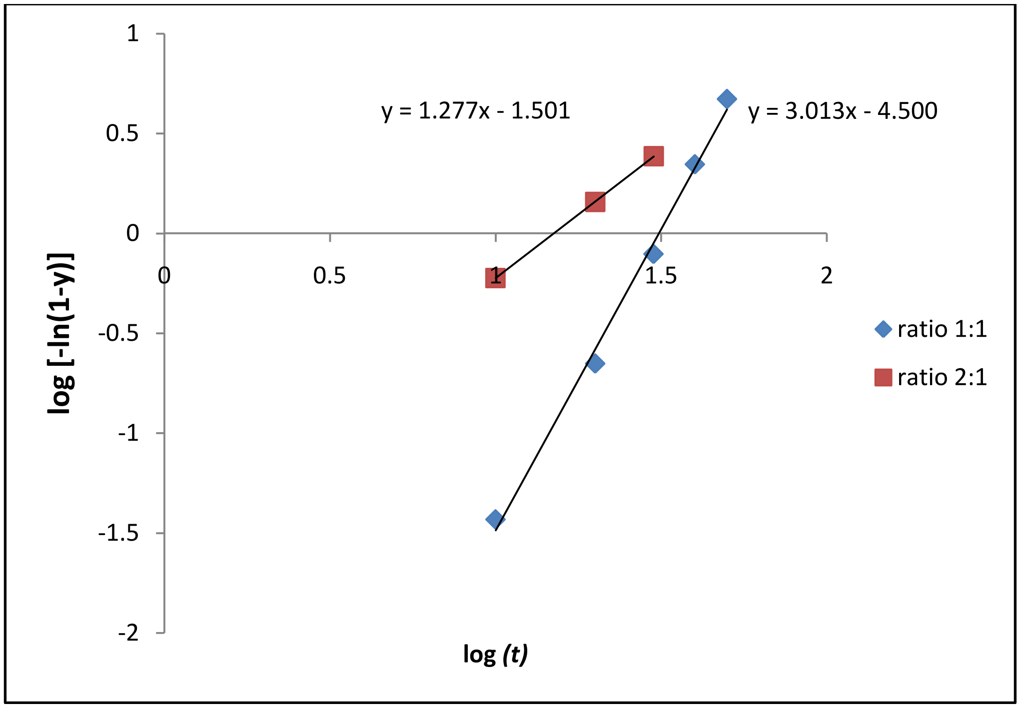

Figure 4.4: Plot of Log[-ln(1-y/)] vs Log (t) to obtain linear format of Avrami equation

Table 4.2 Avrami parameters extracted from figure 4.6

Ratio	*n*	*k*
1:1	3.013	0.011
2:1	1.277	0.223

Based on the Avrami plot in Figure 4.8, the transformation of [BMIM]Cl is dominated by nucleation for the first phase. The driving force is required for the nucleation and crystal growth is the level of supersaturation the solution. Therefore, based on the table 4.2 it can be seen the Avrami exponent for ratio 1:1 is 3.013 indicating that the ionic liquids crystals produced is 2-dimensional, cluster plate type shape. When higher water content is used, a step change in the value of *n* can be observed leading to smaller *n* values. The step increase in the Avrami exponent is contributed to by the change in the type of nucleation , from slightly instantaneous to more sporadic. Crystallization can only occur at solution compositions where the amount of solute exceeds the solubility limit. Driving force for crystallization is increase with increasing supersaturation. Lower concentration of ionic liquid in the solution will lower the level of supersaturation. The crystal growth rate also decreases and crystal yield only be reach in the limit of infinite time.

CHAPTER 5

CONCLUSION AND RECOMMENDATION

The finding in study of crystallization ionic liquid will contribute to a better understanding of the crystallization behavior. From the experimental data, degree of crystallinity of ionic liquid can be determined. Apart from that, the Avrami exponent, *n* and growth constant, *k* can be calculated and then analyzed. The completion of this project will enable us to know the kinetics of the crystallization process of ionic liquid and its crystallization behavior. Lastly, this study will contribute to development in efficient recycle and re-use of ionic liquid. Therefore, it can be concluded that,

i) The decrease in crystallization temperature led to an increase in the value of Avrami exponent while the value of parameter k dropped significantly.
ii) Increasing in initial temperature cause the rate of crystallization at a slower rate.
iii) Crystal growth mechanism and rates are dependent on the degree of saturation ionic liquids.

There is some recommendation to improve the result of the project. Kinetic study of ionic liquids can be studied by Differential Scanning Calorimetry. DSC is a thermodynamical tool for direct assessment of the heat energy uptake, which occurs in a sample within a regulated increase or decrease in temperature. The calorimetry is particularly applied to monitor the changes of phase transitions .Other recommendation is use different type of cation of ionic liquids such as pyridinium in order to get wide range and meaningful data.

CHAPTER 6

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