Crystallisation of Ionic Liquid by Using Avrami Kinetic Theory

by

Muhammad 'Imran Bin Ishak

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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,

(Dr. Lukman Bin Ismail)

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

MUHAMMAD ‘IMRAN BIN ISHAK

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ABSTRACT

Ionic liquids have received an immense increase in interest in the fields of engineering during the last decade due to their distinctive properties. Ionic liquids (ILs) are molten salts having by definition melting points below 100°C and a very important new class of non-volatile environmentally friendly solvents as compared to traditional organic solvents. This study is focused on crystallisation of ionic liquid which is one of the possible techniques to purify ionic liquids. Different factors that influencing will be explored such as: effects of temperature variations, effects of cooling rate, effects of seeding procedure (addition of crystals as solid) and effects of ionic liquid content. Analyses will be conducted to evaluate and characterize the ionic liquid crystallisation are: the percentage of ionic liquid crystallisation (δ, wt.%); the Avrami exponent (n) which correspond to the type of crystals; and the half time of crystallisation ($t_{1/2}$) which is associated with the rate of crystallisation. On the study of the effect of temperature deviations, it was found that increasing the initial temperature (T_1) reduced the overall crystallisation; increase of the initial temperature (T_1) altered the type of ionic liquid crystal from needle type to clustered plate-like shapes; and decreased the rates of crystallisation. On the effect of cooling rate, it was observed that decreasing the cooling rate reduced the crystallisation, increased n and $t_{1/2}$ values hence reduced the crystallisation rates. The study on the effect of seeding procedure revealed that crystallisation increased with seeding procedure, increased n value, decreased $t_{1/2}$ and caused lower crystallisation rate. Lastly in the effect of ionic liquid content, it was found that the higher the ionic liquid content, the longer times were taken to produce ionic liquid crystals, increased n and $t_{1/2}$. Since the use of ionic liquid in industrial applications is relatively a new technology, perhaps the results of this study will provide useful information for understanding of the crystallisation behaviour of this new class of materials.

TABLE OF CONTENTS

LIST OF FIGURES

LIST OF TABLES

CHAPTER 1

INTRODUCTION

1.1 Background of Study

Ionic liquids (ILs) are a promising set of materials with a various and astonishing set of properties. Ionic liquids are molten salts having by definition melting points below 100°C, evolved from traditional high temperature molten salts (Wilkes, 2002). the Ionic liquids relatively are not new materials; some of them have known for many years, for instance [$EtNH_3$]-[NO_3], which has melting point of 12°C, was first described in 1914 (Welton, 1999). Reichert *et al.* (2006), point out that ionic liquids are materials that have been known for over 100 years but renewal of interest arose from a new way of thinking about these low melting salts as solvents, specifically for VOC (Volatile Organic Compound) replacements.

Current usage is to call salts with melting temperatures below 100°C as ionic liquids. A large number of ionic liquids melt well below ambient temperatures, with typical glass transition temperatures in the range from 180 to 220 K (Castner and Wishart, 2010). The exact reason that these salts have such low melting points is not well understood, although the asymmetry of the cation is assumed to be the best explanation (Larsen *et al.*, 2000). Most ionic liquids are formed from cations that do not contain acidic protons. There are two sections that ionic liquids can be synthesized of which are the formation of the desired cation, and anion exchange where necessary to form the desired product (Wasserscheid and Welton, 2003). Room-temperature ionic liquids (RTILs), which are composed of large organic cations and weakly coordinating anions, are regarded as environmentally benign solvents offering a wide range of applications as solvents, in catalysis, electrochemistry, and separation (Im *et al.*, 2011).

Many ionic liquids display a liquid phase at room temperature are non-volatile, not-flammable and thermally stable solvents that are very useful as compared to the traditional volatile organic solvents used in chemical manufacturing industries and chemistry research laboratories (König *et al.*, 2008). However, ionic liquids are relatively expensive that until recently many of them have not been readily available commercially (Pusey *et al.*, 2007). Alkyl-Imidazolium and Alkyl-Pyridinium salts as Chlorides or Ethylsulfates are common ionic liquids (König and Wasserscheid, 2006).

Ionic liquid is a different product as compared to traditional organic solvents because it is a non-volatile material and it cannot be purified directly by distillation process. On the other hands, any volatile impurity can be separated from ionic liquid by distillation. Other unit operations that can be used for purification of ionic liquids are extraction, membrane technologies as well as crystallization. In addition, ionic liquids have low vapor pressure which permits the extracted product to be separated from the ionic liquid by low-pressure distillation with the potential for energy savings (Marsh *et al.*, 2002). BASF Company is claiming all kinds of industrial and laboratory crystallisation techniques for purification of ionic liquids (König *et al.*, 2008). Reichert *et al.* (2006), point out that hundreds of ionic liquids are commercially available from major sources, such as BASF, Merck KGaA/EMD Chemicals, Aldrich, Solvent Innovations, and many more.

Recently, there has been an increasing amount of research concerning the application of ionic liquids (organic salts that are liquid at room temperature) as additives or new reaction media in crystallisation processes (Kowacz *et al.*, 2010). Schmeisser and Eldik (2009), point out that ionic liquids as alternative solvents for various applications because of their different tunable properties such as density, viscosity, polarity, melting point, and solubility, they enable the use of perfectly adapted reaction media and are even considered to be "designer solvents" of the future. However, our understanding toward their fundamental nature is still far from complete. Among the basic questions yet to be answered are why their melting points are so low despite their ionic characters and why they are not readily crystallised upon cooling (Nishikawa *et al.*, 2008). Therefore, further understanding in respect to crystallisation of ionic liquids presents a wide array of challenges and opportunities to the chemical physics and physical chemistry community to explore the purification and recovery of ionic liquid.

1.2 Problem Statement

Ionic liquids (ILs) may be observed as a latest and extraordinary set of solvents, or as a type of materials that have contribute to the advancement of chemical industry throughout history. However, there are still very few studies relating to the crystallisation process of ionic liquid ever been discovered. One of the reasons is that many ionic liquids display non-volatility and are not conducive to crystallisation studies from many practitioners point of view that use evaporation of solvents (slow or fast) to purify reaction products. Perhaps more challenging reasons for the limited study of ionic liquid as crystallisation solvents is that the complexity of ionic liquid solvents makes it difficult to predict how crystallisation will behave (*e.g.*, predicting the resulting crystal structure). Ionic liquid that have been used in any chemical process can be recycled and regenerated by using the separation process known as crystallisation process, with the techniques used based on the impurities to be removed. This process is one of the possible methods seeking means for their purification. The purification of ionic liquid can be done by partially crystallise the melt of the ionic liquid and to separate the crystal formed during the crystallisation from the residual melt. Thus, crystallisation of ionic liquid is a vital process in chemical industry.

1.3 Aim and Objectives

The aim of the project is to study and analyze the kinetics of ionic liquid crystallisation by using the Avrami's kinetic theory.

The project objectives can be drawn as:

i. To study the effects of temperature variations.
ii. To investigate the effects of cooling rate.
iii. To examine the effects of seeding procedure.
iv. To study the effects of ionic liquid content.

1.4 Scope of Study

Several scopes of studies need to be emphasized in order to carry out the project. The experiment on crystallisation process of ionic liquid is to be conducted in the laboratory throughout the project lifespan. Prior to that, the understanding of crystallisation phenomena is extremely important in dealing with the mechanism of crystallisation in ionic liquids. Furthermore, the experiment is to be conducted carefully so as to gain valuable information regarding the kinetics of ionic liquid crystallisation by using the Avrami kinetic theory. Several parameters affecting the crystallisation process need to be considered and analyzed prior to run the experiment. The preferable choice of ionic liquid is within the range of 100°C to -20°C of its melting point as the experiment is to be conducted in the lab. The imidazolium-based ionic liquid (*i.e* 1-Butyl-3-methylimidazolium chloride) was prepared due to the fact that it has the desired crystallisation properties, structurally comparable and is widely used in the industries. Table 1.1 below shows the concise information regarding the parameters used as shown below:

Table 1.1 The general information of modern ionic liquids (Johnson, 2007)

Properties	Descriptions
Molten salt	Cation and or anion quite large
Freezing point	Preferably below 100°C
Liquidus range	Often > 200°C
Thermal stability	Usually high
Viscosity	Normally < 100 cP, workable
Dielectric constant	Implied ≤ 30
Polarity	Moderate
Specific conductivity	Usually < $10 mScm^{-1}$, "Good"
Molar conductivity	< $10\ Scm^{2}\ mol^{-1}$
Electrochemical window	> 2V, even 4.5 V, except for Brønsted acidic system
Solvent and/or catalyst	Excellent for many organic reactions
Vapor pressure	Usually negligible

CHAPTER 2

LITERATURE REVIEW

This chapter reviews the background literature that is relevant to purification, recycle and reuse of ionic liquids, (ILs) hence to their technological utility and is divided into two main sections. Section 2.1 introduces background information including physical and chemical properties as well as impurities of ionic liquids. Section 2.2 covers the background studies of crystallisation and crystallisation of ionic liquid.

2.1 Ionic Liquid

2.1.1 Background

Most salts identified in the literature as ionic liquids (ILs) are liquid at room temperature, and often to substantially lower temperatures. One fairly general feature of ionic liquids that is not part of the definition is the most have organic cations and inorganic anions (Wilkes, 2002). While high temperatures molten salts are usually metal halides, popular ionic liquids often comprise organic cations paired with organic or inorganic anions (Castner and Wishart, 2010). It is expected that there may be in excess of 10^6 possible ionic liquids if all currently known ionic liquid cations and anions were to be paired, and as many as 10^{18} if all ternary systems were to be investigated (Plechkova and Seddon, 2008).

The history of ionic liquids can be traced back even the early report by Paul Walden of which the room temperature ionic liquid ethylammonium nitrate ($[EtNH_3][NO_3]$; mp 13-14°C), which was formed by the neutralisation of ethylamine with concentrated nitric acid in 1914 (Plechkova and Seddon, 2008). Cations and anions that are commonly used in recent generations of ionic liquids are shown in Figure 2.1. Their distinctive properties like a large liquidus range, a very low vapor pressure and high thermal, chemical and electrochemical stability guarantee a broad acceptability (Nockemann *et al.*, 2005). The choice of ionic liquid cation and anion to be studied should be based upon the type of process one is to employ and the specific interactions desired, and not based on what is in popular stage (Reichert *et al.*, 2006). Many of ionic liquids study that has been done until now has made use of a small group of salts. In large section these are quaternary ammonium, phosphonium, imidazolium, or pyridinium cations with large, charge-diffuse inorganic counterions. (Davis, 2004). The chronological summary on the crystallization of ionic liquids are shown in Table 2.1.

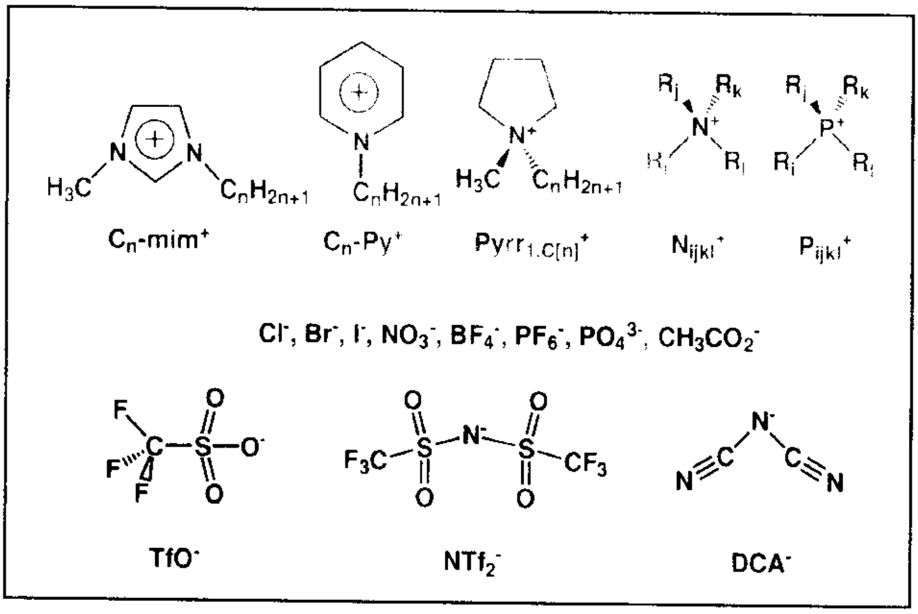

Figure 2.1 Chemical structures for common IL cations (red) and anions (blue) (Castner and Wishart, 2010)

Table 2.1 Chronological summary on the crystallisation of ionic liquids (from 2005 to 2011)

Year	References	Title	Findings
2005	Fiene *et al.*	Purification of ILs	Process of purifying an IL comprises the steps (a) partial crystallization of the IL from its melt and (b) separation of the crystals from the residual melt
2006	Choudhury *et al.*	In situ crystallization of ILs with melting points below -25°C	[emim]OTF and [emim]NTf$_2$ form single crystals.
2006	Reichert *et al.*	Approaches to crystallization from ILs: complex solvents-complex results, or, strategy for controlled of new supramolecular architectures?	ILs as crystallization solvents. Both the utility and complexity of these novel solvents are highlighted.
2008	König *et al.*	Ultra purification of ILs by melt crystallization	Melt crystallization is an efficient technique for purification and ultra purification.
2008	Nishikawa *et al.*	Rhythmic melting and crystallizing of IL 1-butyl-3-methylimidazolium bromide	The phenomena of rhythmic phase transition found in this study.

Year	References	Title	Findings
2010	Kowacz *et al.*	On the use of ILs to tune crystallization	Precipitation of barium sulfate in IL containing solutions provides further insights into the fundamentals of nucleation phenomena in aqueous ionic solutions.
2011	Tang and Mudring	ILs as crystallization media: weakly-coordinating anions do coordinate in $^{1}_{\infty}$[Eu (OTf)$_3$ (CH$_3$CN)$_3$]	Lanthanide triflate can be easily isolated from ILs by simply adding appropriate amount of acetonitrile to the system.
2011	Pas *et al.*	Crystallisation kinetics of some archetypal ILs: isothermal and non-isothermal determination of the Avrami exponent	Nothing unusual about the crystallisation mechanism of the ILs studied.
2011	König *et al.*	Method of purifying ILs	The effectiveness of the purification can be increased through the addition of entrainer substances.
2011	Im *et al.*	Anomalous thermal transition and crystallization of ILs confined in graphene multilayers	Thermal transition and crystallisation behaviours of bulk RTILs are dramatically changed when confined in graphenes.

2.1.2 Physical and Chemical Properties

Welton (1999), listed some simple physical properties of the ionic liquids that make them interesting as potential solvents for synthesis that are of the following: (1) They are good solvents for a wide range of both inorganic and organic materials, and unusual combinations of reagents can be brought into the same phase. (2) They are often composed of poorly coordinating ions, so they have the potential to be highly polar yet non-coordinating solvents. (3) They are immiscible with a number of organic solvents and provide a non-aqueous, polar alternative for two phase systems. Hydrophobic ionic liquids can also be used as immiscible polar phases with water. (4) Ionic liquids are non-volatile, hence they may be used in high-vacuum systems and eliminate many containment problems and also do not evaporate.

Ionic liquids can be further used and not only restricted to just an alternative "green solvents". They vary from molecular solvents by their distinctive ionic character and structure organisation which in turns may lead to particular effects (Oliver-Bourbigou *et al.*, 2010). Reichert *et al.* (2006), refers that one of the attributes of ionic liquids is the ability to fine-tune their physical (*e.g.*, density, viscosity, melting point) and chemical (*e.g.*, solvent) properties by selection of the appropriate cations and anions. For instance, increasing the length of an alkyl chain has a propensity to decrease water solubility by increasing the hydrophobicity of the cation (Brennecke and Maginn, 2001). Furthermore, it is vital to understand the basic thermophysical properties of ionic liquids for design and evaluation (*e.g.*, melting points, glass-transition temperatures, and thermal decomposition temperatures are required to set the practical temperature operating range for a particular fluid.) (Fredlake *et al.*, 2004). Oliver-Bourbigou *et al.*, (2010), listed a list of critical remarks in order to describe some of the physico-chemical properties of the ionic liquids. The list of critical remarks is given in Table 2.2.

Table 2.2 Physico-chemical properties of ionic liquid

Properties	**Descriptions**
Melting point	Data must be considered with caution as the melting point of many ILs may be uncertain as they can undergo supercooling and because of the potential occurrence of impurities.
Volatility	ILs can be distilled at 200-300°C but under considerably reduced pressure and at very low distillation rate (<0.01 g h^{-1}).
Non flammability	ILs always known as "green" alternatives to volatile organic solvents because ILs are considered as non-volatile and consequently non-flammable at ambient and higher temperatures. In contrast, it is not because they are non-flammable that ILs can be used near a heat source, ILs are combustible. They can be fine-tuned for energetic content and replace hydrazine and its derivatives.
Thermal and chemical stability	The onset of thermal decomposition calculated from fast thermogravimetric analysis (TGA) signifies high thermal stability for many ILs, generally >350°C.
Conductivity and electrochemical window	ILs display broad range of conductivities ranging from 0.1 to 20 mS cm^{-1}. Generally higher conductivities are found for imidazolium-based ILs in comparison with the ammonium ones.
Density	In general ILs are denser than either organic solvents or water, with typical density values ranging from 1 to 1.6 g cm^{-3}.
Viscosity	The viscosity of many ILs is relatively high compared to conventional solvents, one to three orders of magnitude higher. It has been reported for a variety of ILs to range from 66 to 1110 cP at 20-25°C.
Polarity	There is no single parameter and direct measurement that can characterise IL polarity.
Toxicity and biodegradability	According to the early reports, ILs have low toxicity and biodegradability whereas it has been confirmed that commonly ILs are not easily biodegradable.
Surface tension	ILs have fairly moderate surface tensions compared to organic solvents.

2.1.3 Effects of Impurities on Ionic Liquids

The physical and chemical properties of ionic liquids can be influenced significantly by small amounts of impurities (König *et al.*, 2008). As for most ionic liquids, it is well known that a little impurity, especially adventitious water, excessively affects their physical and chemical properties and sometimes prevents the liquids from crystallizing (Nishikawa *et al.*, 2008). However, the miscibility of ionic liquids with water is mainly fascinating. All ionic liquids explained until now are hygroscopic. Some will mix with water in any compositions, whereas others in the end saturate and then form two layers. This behaviour can be described when strong hydrogen bonds that may form between the water and the anion of the ionic liquid (Welton, 2004). When ionic liquids are used for carrying of chemical reactions, the purity of the ionic liquids used is of great importance (Fiene *et al.*, 2005). Although perhaps challenging at times, ionic liquids are in fact recyclable, with the techniques used based on the impurities to be removed. Two such techniques under current exploration comprise use of supercritical CO_2 and "salting out" other than the use of ion exchange resins, pervaporation (for volatile impurities), solvent extraction, and *etc.* (Reichert *et al.*, 2006).

The quality of ionic liquids became an important consideration (König and Wasserscheid, 2006). Their catalytic activity and their electrochemical behaviour highly depend on the purity level of the ionic liquid. In addition, commercial producers try to make ionic liquids in the highest quality that can be achieve at reasonable cost. The common grades of purity are greater than 95% "for synthesis", greater than 99% "high pure" and greater than 99.9% "ultra pure". Moreover, typical impurities that can be found are colours, organic starting materials and othe volatiles, halide impurities, protic impurities, other ionic impurities from incomplete metathesis reactions and water (König *et al.*, 2008). Fiene *et al.* (2005), point out that impurities can, for example, have a generally adverse effect on the course of chemical reactions. There is therefore a need for ionic liquids having a high purity.

2.2 Crystallisation

2.2.1 Background

Crystallisation by definition means a solid-fluid operation in which crystalline particles are formed from a homogeneous fluid phase. The crystals are a pure chemical that can be obtained in a high yield with a desirable shape and a practically uniform and desirable size. In general, crystallisation is one of the oldest separation techniques, with the recovery of sodium chloride as salt crystals from water dating back to ancient times. Currently, the most common applications are the crystallisation from aqueous solution of various inorganic salts. (Seader and Henley, 2006). Besides, crystallisation is applied for improving product recovery to increase yield, to refine intermediates and to remove undesired salts (König and Schreiner, 2001).

2.2.2 Crystallisation of Ionic Liquid

A known problem of ionic liquids is that they are reluctant to crystallize. Brennecke and Maginn, (2001), characterize ionic liquids as organic salts which have a high degree of asymmetry which hinders ordered packing and thus inhibits crystallisation. It has been realized that ionic liquids and ionic liquid-cosolvent mixtures allow crystallizing compounds which are otherwise not accessible or only with great difficulty (Tang and Mudring, 2011). Wasserscheid and Welton, (2003), point out that typical ionic liquids form glass-like structures on cooling. Many ionic liquids tend to form glasses on cooling presenting, as a consequence, practical challenges for their recovery and recycling (as traditional methods, such as distillation, are not options) (Choudhury *et al.*, 2006). Huddleston *et al.*, (2001), point out that ionic liquids tend to undergo some cooling and frequently form amorphous structures in the solid state. Solidification of ionic liquids often results in glass formation (Choudhury *et al.*, 2005). The solid phase after crystallisation includes a lot of mother liqueur (König *et al.*, 2008).

There are several properties of ionic liquids that currently studied may be advantageous in a crystallisation process. Ionic liquids have a tendency to supercool, which gives many of them fairly wide liquidus operating ranges (in some cases as large as 200-300 °C and provide thermal operating windows not possible with conventional solvents. Thus, ionic liquids may provide unique opportunities to use much higher and much lower temperatures for a process in a single solvent. In addition, ionic liquids typically possess higher viscosities than traditional organic solvents. The increase in viscosity is relatively important in crystal engineering where slow crystal growth from diffusing solvents is an advantage although it is not attractive for bulk crystallisations. Furthermore, ionic liquid solvent properties can also be tuned to suit particular crystallisation process by adjusting intermolecular and interionic interactions that take place in the solvent. Moreover, one solvent property important for crystallisation is the ionic liquids' hydrogen bonding ability. Thus, solvent properties can also be modified based on the choices of cation and anion components (Reichert *et al.*, 2006). An advantage of the use of ionic liquids as solvents which emphasized is that ionic liquids have virtually no measurable vapor pressure and, for this reason, solvent losses due to evaporation do not occur when they are used as solvents. The advantage of ionic liquids having no measurable vapor pressure becomes a disadvantage when they are used as solvents in a process in which high-boiling byproducts which cannot be separated off again by distillation or extraction are formed (Fiene *et al.*, 2005).

Crystallisation of low-melting ionic liquids is one of the possible methods seeking means for their purification (Choudhury *et al.*, 2006). Fiene *et al.*, (2005), point out that it has surprisingly been found that ionic liquids can be crystallised from their melt with good purifying action. There are several techniques for purification including zone melting, layer crystallsation and dry melting in lab scale whereas layer crystallisation for static and dynamic crystallisation conditions in pilot scale (König *et al.*, 2008). Figure 2.2 shows the purification technique by using zone melting.

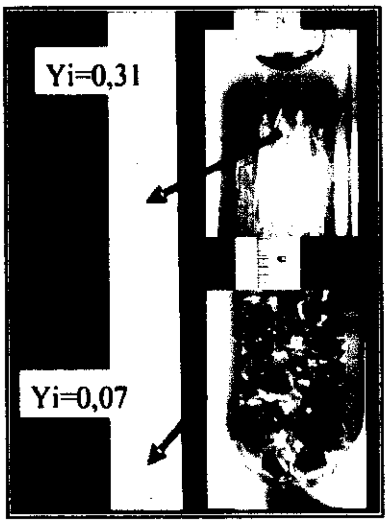

Figure 2.2 Zone melting of EMIM-Cl (König et al., 2008)

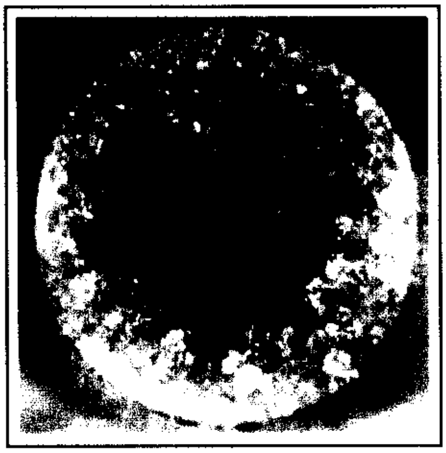

Figure 2.3 Top view of the crystal layer after liquid draining (König et al., 2008)

The crystallisation can be carried out dynamically or statically and all types of known ionic liquids can be purified by means of partial crystallization as shown in Figures 2.4 and 2.5 (König *et al.*, 2011). The partial crystallisation according to the invention of the ionic liquids and the separation of the crystals from the residual melt can be carried out without restriction by means of known melt crystallisation processes (Fiene *et al.*, 2005). Guardani *et al.* (2001), describe that melt crystallisation is one of the most appealing process alternative due to some favourable characteristics such as lower energy consumption, prevention from degradation of thermally sensitive substances as well as no need to introduce extraction solvents. Melt crystallisation is a technique suited for purification of organic chemicals as well as ionic liquids and is also a very efficient method to produce in different scales from 0.5 g up to 1000 kg ultra pure ionic liquids $w_{IL} > 99.99\%$ (König *et al.*, 2008). The principle of this technique is to cool a melt in a controlled way in order to crystallize a fraction of the melt (König and Wasserscheid, 2006). In general, the ionic liquid is allowed to crystallize until at least 5% by weight, preferably at least 10% by weight and particularly preferably at least 20% by weight, of the ionic liquid has crystallised out (Fiene *et al.*, 2005).

Figure 2.4 Static layer crystallisation of EMIM-Cl, $m_{Feed} = 50$ g (König et al., 2008)

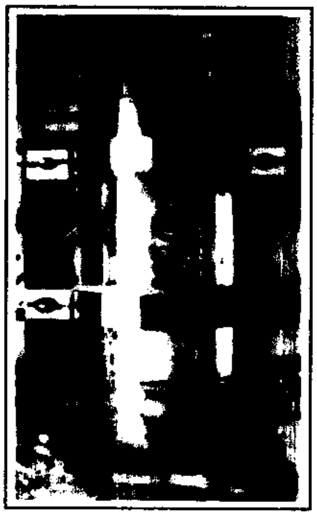

Figure 2.5 Dynamic layer crystallisation of EMIM-Cl (König et al., 2008)

2.3 Avrami Kinetic Theory

Isothermal crystallization is a popular method for attaining kinetics data. It is based on rapidly cooling the sample from the melt to the crystallization temperature (Foreman and Blaine, 1995). Avrami theory is generally used for analyzing the primary stage for isothermal crystallisation kinetics (Saengsuwan *et al.*, 2010). Ismail *et al.* (2008), in the study of the mechanism and kinetics of the paraffin wax crystallization, point out the importance of Avrami crystallisation kinetics in polymer context regarding the principle of imagining raindrops falling in a puddle, where expanding circles of waves produced by the raindrops which intersect and cover the whole surface. Either sporadically or all at once are the mechanisms of the drops may fall respectively. Consequently, whichever the case, they must strike the puddle surface at random points. The expanding circles of waves are the growth front of the spherulites, and the points of impact are the crystallite nuclei. The volume fraction of crystalline material, X, which represents as the degree of crystallinity, through probability derivations can be written as

$$1 - X = exp(-E) \tag{2.1}$$

where E represents the average number of fronts of all points in the system. For low degrees of crystallinity a useful approximation is $X \approx E$. In the case of bulk crystallisation of polymers, X in the exponent may be referred as the volume or volume fraction of crystalline materials, V_t. Thus,

$$1 - X = exp(-V_t) \tag{2.2}$$

This formula is broadly used in the study of crystallisation (Caze *et al.*, 1997; El-Oyoun, 2000; Toro-Vazquez *et al.*, 2002; Bhattacharyya *et al.*, 2003; Pal and Nandi, 2005; Nandi and Ghosh, 2007; Durmus *et al.*, 2008; Su *et al.*, 2009; Wang and Run, 2009; Zhang *et al.*, 2009; Ma *et al.*, 2010; Patial *et al.*, 2010; Saengsuwan *et al.*, 2010; Jiang et *al.*, 2011; Martins *et al.*, 2011; Qiu *et al.*, 2011). Ismail *et al.* (2008), further point out that equation (2.3) can be written as

$$1 - X = exp(-K_t^n) \tag{2.3}$$

for either instantaneous or sporadic nucleation where K represents the growth rate, and n is the Avrami exponent, which depends on the nature of the nucleation and growth geometry of the crystals. Equation (2.3) can be applied only when the nucleation and growth conditions do not change during the crystallisation process (Martins *et al.*, 2011). Different mechanisms of crystallisation can be differentiated by using the Avrami exponent, n which is the phenomenological index of crystallisation. Toro-Vazquez *et al.* (2002), in his study of TAG crystallisation in oil blends of palm stearin in sesame oil, characterize that in homogenous nucleation a crystallisation process with $n = 4$ follows a 3-D crystal growth mechanism, a value of $n = 3$ a 2-D mechanism, and $n = 2$, 1-D crystal growth. In addition, non-integer values of n are associated with heterogeneous and secondary nucleation. In the context of ionic liquid, a recent yet breakthrough study by Pas *et al.*, (2011), they point out that crystallisation of the ionic liquids is a thermal or mass diffusion-controlled process. The decreasing values of $n = 1.8 - 2.2$ indicate that growth occurs from all three different ionic liquids with three different anions and cations.

CHAPTER 3

METHODOLOGY

This chapter presents the preparation of ionic liquids and solvent as well as the measurement considerations; experimental and the analytical procedures.

3.1 Preparation of Ionic Liquid and Solvent

In this project, similar types of ionic liquid were considered of which all are imidazolium-based ionic liquids due to the fact that all have the desired crystallisation properties, structurally comparable and are widely used in the industries. In addition, the experiment can be conducted for lab scales due to the fact that their melting points are not too low. The melting point shows the affinity to decrease with increasing alkyl chain lengths and reaches a minimum for alkyl chains of about eight carbon atoms. Further increase of the chain length leads again to an increase of the melting point (Binnemans, 2005). The imidazolium-based ionic liquid (*i.e* 1-Butyl-3-methylimidazolium chloride ($BmimCl_2$) was prepared and to be mix with water (solvent). Ionic liquid were purchased from Merck Chemicals Malaysia, and were in the form of crystals.

3.2 Equipment

Test tube was used to in the experiment where the crystallisation process occurred. Prior to the experiment, the test tube is connected to the refrigerator, JULABO F-32 Refrigerated and Heating Circulator as shown in Figure 3.1 that used R-134a as its refrigerant. R-134a also known as 1, 1, 1, 2-Tetrafluoroethane in terms of IUPAC name is a haloalkane refrigerant. Water cannot be used as refrigerant for chiller instead of R-134a because it cannot reach low temperatures in order to make the ionic liquid crystallised.

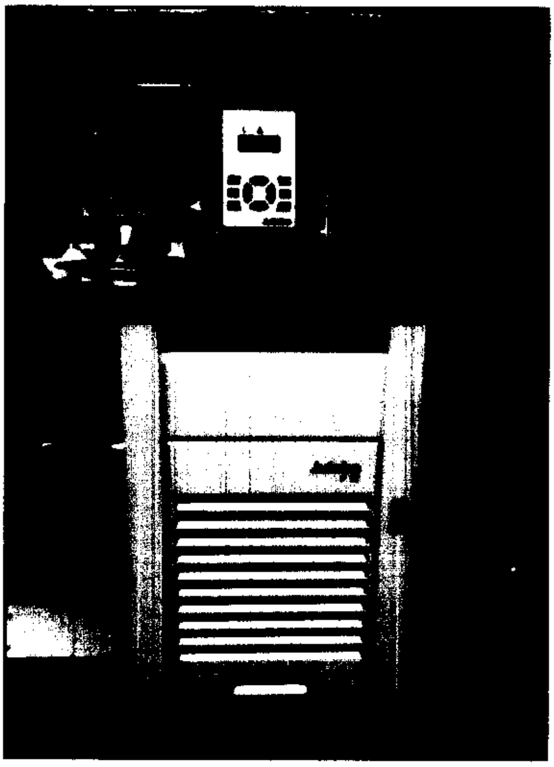

Figure 3.1 JULABO F-32 Refrigerated and Heating Circulator

3.3 Measurement of the Crystallisation

In order to quantify the amount of crystallisation, the gravimetric method was chosen. At the end of each experiment, the test tube was taken out and put upside down. The non-crystallised liquid and water mixture was drained out of the test tube through gravity to a beaker and then weighed. The crystallised ionic liquid is then qualified by weighing the whole beaker minus the weight of empty beaker. The ionic liquid crystal was then calculated as a weight percentage of the total ionic liquid and water mixture solution used as shown below:

$$\text{Crystal, } \delta = \frac{\text{weight of crystal on beaker}}{\text{total weight of ionic liquid and water solution in beaker}} \times 100\% \qquad (3.1)$$

3.4 Crystallisation

3.4.1 Effects of Temperature Variations

Samples of 10 wt.% of 1-Butyl-3-methylimidazolium chloride ($BmimCl_2$) were mixed with distilled water (solvent) to form a solution. A solution at 25°C (room temperature) is prepared. Another two samples of solution are then to be heated to 35°C and 45°C respectively. The solutions are then measured during isothermal crystallisation at -20°C until complete crystallisation to study the influence of temperature. The constant parameters are cooling rate, the type of ionic liquid being used and the process is to be conducted without seeding procedure. The liquid that was not crystallised will be taken out in every 5 minutes time. The liquid then was weighed and put back into the test tube. The process was stopped only when there was no significant change regarding the weight of the liquid that was not crystallised. The data obtained from the experiment will be plotted and analyzed by using the Avrami kinetics.

3.4.2 Effects of Cooling Rate

Samples of 10 wt.% of 1-Butyl-3-methylimidazolium chloride ($BmimCl_2$) were mixed with distilled water (solvent) to form solutions. The solution was measured by cooling down from room temperature to -20°C until complete crystallisation to study the influence of cooling rate. The constant parameters are temperature, the type of ionic liquid being used and the process is to be conducted without seeding procedure. The time to crystallize at respective temperatures was taken once the cooling process starts. The liquid that was not crystallised will be taken out in every 5 minutes time. The liquid then was weighed and put back into the test tube. The process was stopped only when there was no significant change regarding the weight of the liquid that was not crystallised. The data obtained from the experiment will be plotted and analyzed by using the Avrami kinetics.

3.4.3 Effects of Seeding Procedure

Samples of 10 wt.% of 1-Butyl-3-methylimidazolium ($BmimCl_2$) were mixed with distilled water (solvent) to form a solution. The solution was measured by cooling down from room temperature to -20°C until complete crystallisation to study the influence of seeding procedure. Seeding can be achieved by addition of 0.1g of 1-Butyl-3-methylimidazolium ($BmimCl_2$) crystals as solids or as suspension to the melt of the respective ionic liquid. The constant parameters are temperature, the type of ionic liquid being used and cooling rate. The time to crystallize at respective temperatures was taken once the cooling process starts. The liquid that was not crystallised will be taken out in every 5 minutes time. The liquid then was weighed and put back into the test tube. The process was stopped only when there was no significant change regarding the weight of the liquid that was not crystallised. The data obtained from the experiment will be plotted and analyzed by using the Avrami kinetics.

3.4.4 Effects of Ionic Liquid Content

Samples of 10 wt.% , 12.5 wt.% and 16.7 wt.% of 1-Butyl-3-methylimidazolium chloride ($BmimCl_2$) were mixed with distilled water (solvent) to form solutions. The solution was measured by cooling down from room temperature to -20°C until complete crystallisation to study the influence of ionic liquid content. The constant parameters are temperature, cooling rate and the process is to be conducted without seeding procedure. The time to crystallize at respective temperatures was taken once the cooling process starts. The liquid that was not crystallised will be taken out in every 5 minutes time. The liquid then was weighed and put back into the test tube. The process was stopped only when there was no significant change regarding the weight of the liquid that was not crystallised. The data obtained from the experiment will be plotted and analyzed by using the Avrami kinetics.

3.5 Avrami Methodology

In this study, crystallisation of ionic liquids has been investigated in the test tube, and by referring both (Ismail *et al.*, 2008) and (Martins *et al.*, 2011), the degree of crystallinity is measured by the relative crystallisation, δ_r, defined as the mass fraction of the liquid that are not crystallised divided by the initial mass of the crystal and water mixture liquid, Thus,

$$\delta_r = \frac{\delta_t - \delta_0}{\delta_{\infty} - \delta_0} \tag{3.2}$$

where, δ_t is the extent of crystallisation at time t (g), δ_{∞} the maximum asymptotic crystallisation obtained from the Avrami plots when the asymptotic condition or quasi-steady state has been achieve (g); δ_0 the initial mass of the crystallised content in liquid. By replacing X with δ_r and taking log twice in equation (2.3) resulting,

$$\mathrm{Log}[-\ln(1-\delta_r)] = \mathrm{Log}\,K + n\mathrm{Log}(t) \tag{3.3}$$

By plotting the left side in the equation (3.3) vs. Log(t), the slope of the straight line n and the intersection K, the kinetic coefficient can be obtained.

The crystallisation half-time, $t_{1/2}$, defined as the time at which the extent of crystallisation, δ_t is 50% and can be calculated from the measured kinetic parameters,

$$t_{1/2} = \left(\frac{\ln 2}{K}\right)^{1/n} \tag{3.4}$$

The crystallisation half-time is a parameter for understanding the rate of crystallisation. Both the Avrami exponent and the crystallisation half-time will be used to evaluate the crystallisation process of ionic liquids.

CHAPTER 4

RESULTS AND DISCUSSION

Chapter 4 presents the experimental results and discussions of the crystallisation of ionic liquid and is divided into four main sections. The effects of operating parameters such as the temperature variations on the crystallisation of ionic liquid are discussed in Section 4.1. The effects of cooling rate are given in Section 4.2. Section 4.3 presents the effects of seeding procedure on the crystallisation of ionic liquids. Lastly, section 4.4 investigates the effects of ionic liquid content on the crystallisation of ionic liquid.

4.1 Effects of Temperature Variations on the Crystallisation

This section reports and discusses the results obtained from the experiments on the investigation of the effects of the temperature on the crystallisation. In the experiments, three initial temperatures, T_1, were tested, *i.e.* 25°C, 35°C and 45°C and the final temperature (T_2) was selected at -20°C. 1-Butyl-3-methylimidazolium chloride ($BmimCl_2$) content (w) was set at 10 wt.% and dissolved in distilled water as the solvent and with no seeding procedure. The cooling rate, q_C, of JULABO F-32 Refrigerated and Heating Circulator was set at 0.45°C/min. When carrying out measurements of ionic crystal, the experiment was not stopped; the non-crystallised ionic liquid was drained out of the test tube to a beaker and weighed. The crystallised ionic liquid inside the test tube was determined by the difference between the weight of the empty test tube and the weight of the test tube with the crystal. The crystal was then calculated as percentage from the total ionic liquid and distilled water mixture solution used. Results are presented in terms of the crystallisation as a function of time and the Avrami kinetic studies focusing on the Avrami exponent, n, and the crystallisation half time ($t_{1/2}$).

4.1.1 Crystallisation Study

Figure 4.1 shows the effect of temperature on the crystallisation, δ_t (wt.%), for the experimental durations of 3 hours. The crystallisation of ionic liquid increased with time and 100% crystallisation was always achieved. Generally the graphs show that the crystallisation time was reduced and the asymptotic crystallisation, i.e. the final maximum crystallisation, was achieved at later times as the initial temperature, T_1 increased. In spite of scattering in the data, the important message from the results is that significant reduction of the crystallisation time can be achieved using appropriate temperature.

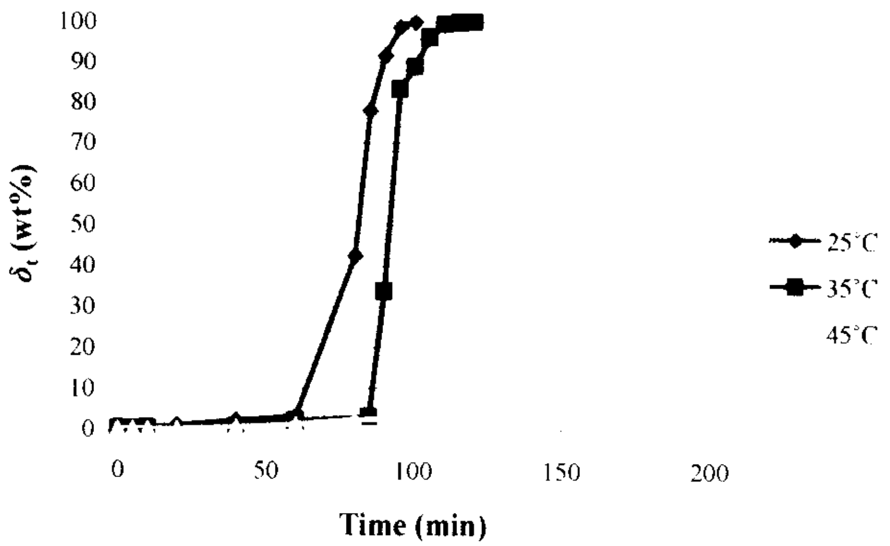

Figure 4.1 Effect of temperature on the crystallisation as a function of time.

4.1.2 Avrami Kinetic Analysis

Avrami kinetic analyses were conducted by plotting a graph using equation (3.6), as explained in Section 3.5 as well as Appendix A, and Figure 4.2 is the Avrami plot for temperature tested in this study. From the straight lines, the slopes can be obtained and give the Avrami exponents (n). The intersections of the straight lines with y-axis are the Avrami rate constant (K (min^{-n})). The Avrami exponent, n, provides information on the structure of the crystal as well as on the nature of nucleation and can be used as the phenomenological index of crystallisation to distinguish between different mechanism of crystallisation; while the Avrami rate constant, K, represents the growth rate over the entire duration and is used to calculate the half time of crystallisation as $t_{1/2} = (\ln 2/K)^{1/n}$. Based on Figure 4.2, the Avrami plot has two different kinetics for each temperature of which defines two growth phases. The respective growth phases can be separated and shown in the Figures 4.3 and 4.4. However, it is not fully understood as to why the changes in the growth phase would affect the crystallisation. From the crystallisation profiles in Figure 4.1, significant kinetics information is embedded in the period of time up to 50% crystallisation has been reached, *i.e.* the half time of crystallisation. It is for this reason that $t_{1/2}$ is a useful tool for evaluation of the rate of crystallisation. The extracted data from the plots are summarised in Table 4.1.

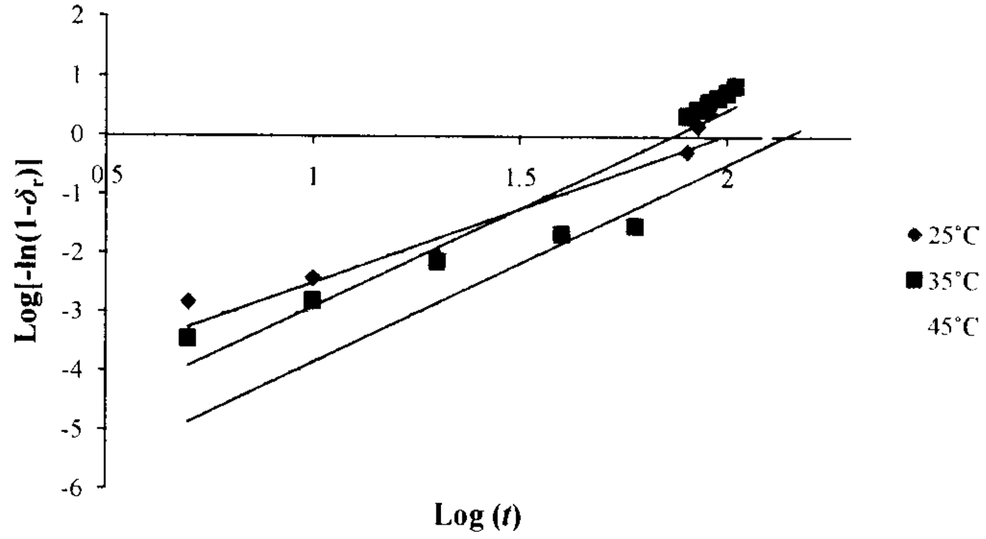

Figure 4.2 Plot of Log[-ln(1-δ_r)] vs. Log (*t*) to obtain the Avrami parameters

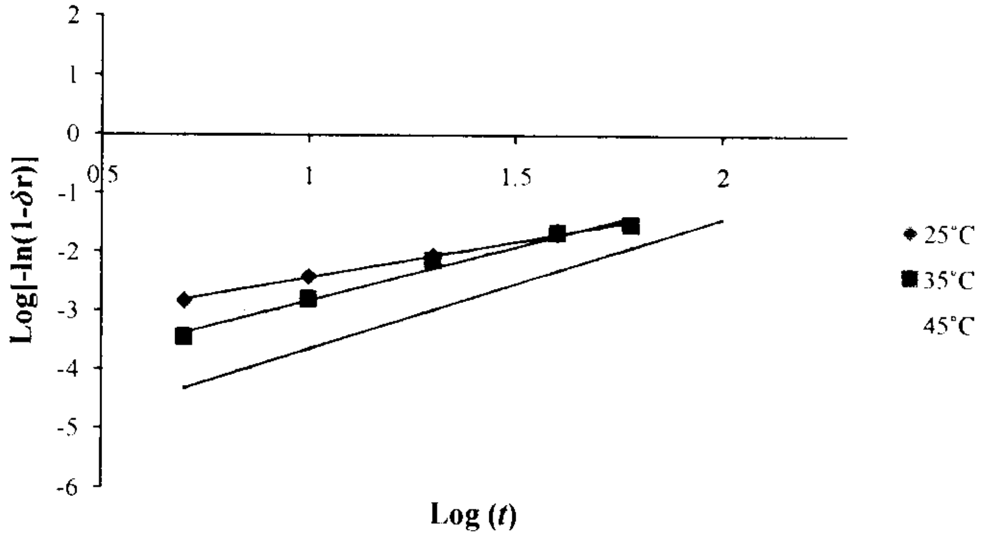

Figure 4.3 Plot of Log[-ln(1-δ_r)] vs. Log (*t*) of the first kinetic from Figure 4.2

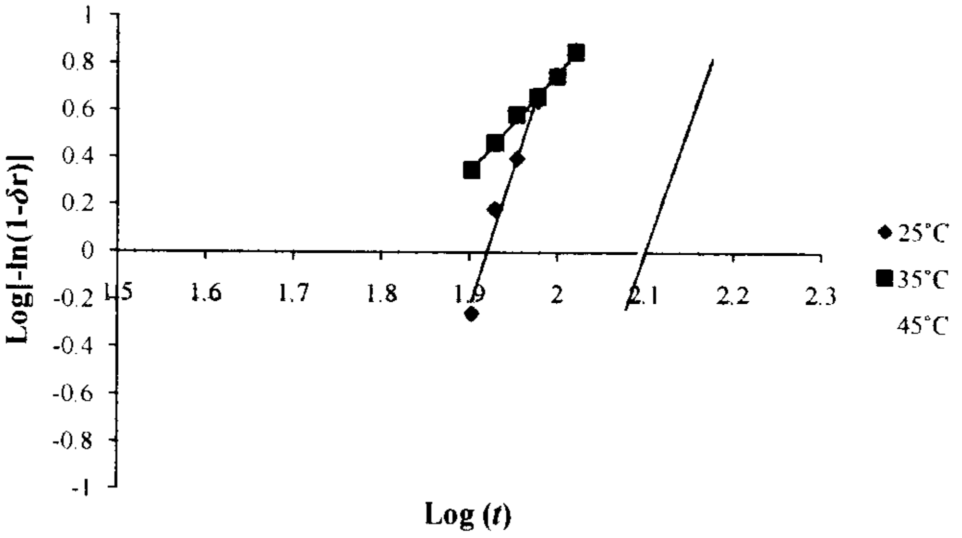

Figure 4.4 Plot of Log[-ln(1-δ_r)] vs. Log (t) of the second kinetic from Figure 4.2

Table 4.1 Extracted Avrami parameters from Figure 4.2

T_1 (°C)	n	K (min^{-n})	$t_{1/2}$ (min)
25	2.525	9.527x10^{-6}	84.23
35	2.938	1.169x10^{-6}	92.23
45	3.378	5.943x10^{-8}	123.6

From Table 4.1 it can be seen that in the experiment at the initial temperature, T_1 = 25°C, the Avrami exponent value (n) was 2.525 indicating that ionic liquid crystals produced were of one-dimensional, rod-like or needle-like type (Figure 4.5) as suggested by Toro-Vazquez *et al.* (2002). Figure 4.5 shows the image of crystals from the control experiments at the initial temperature of T_1 = 25°C and needle type crystals are clearly seen. When higher initial temperatures were used, a step change in the n values can then be observed leading to larger n values. This would suggest that the growth mechanism of crystals under these conditions changed from a one-to a multi-dimensional event and crystals are of clustered-plate-like shapes (Figure 4.6). The step increase in the Avrami exponent is contributed to by the change in the type of nucleation, from slightly instantaneous to more sporadic.

From the half time of crystallisation data in Table 4.1, it can be observed that the highest $t_{1/2}$ of 123.6 minutes was obtained when the initial temperature at T_1 = 45°C. Increasing the initial temperature generally increased the half time of crystallisation, $t_{1/2}$, suggesting that increasing the initial temperature decreased the rate of crystallisation, as the larger the $t_{1/2}$, the slower the rate of crystallisation. However it is worth mentioning that increasing the initial temperature had a significant impact in decreasing the overall crystallisation.

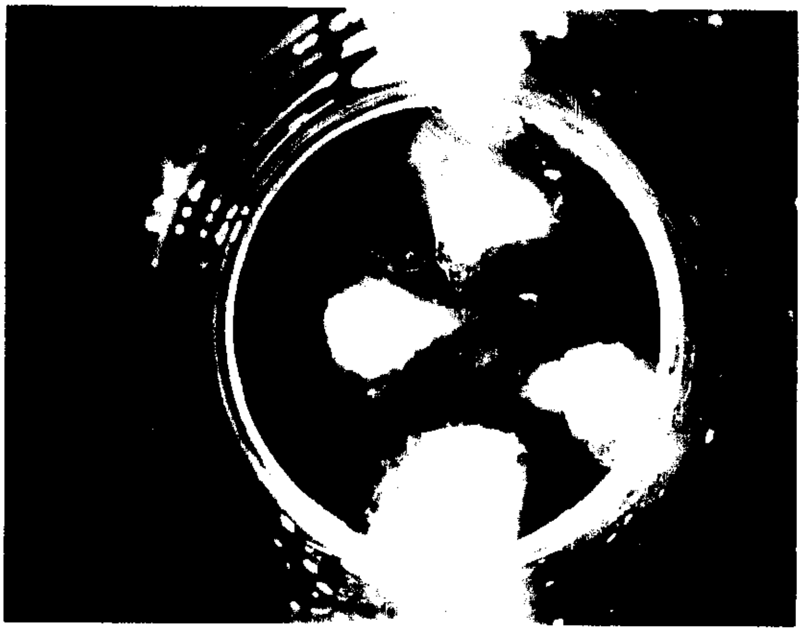

Figure 4.5 Image of ionic liquid crystals from the control experiment with T_1 = 25°C

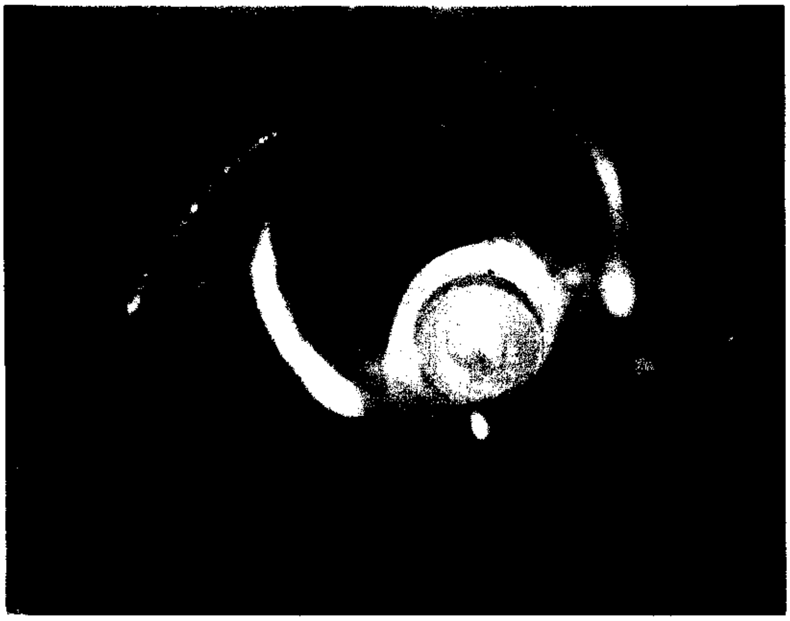

Figure 4.6 Image of ionic liquid crystals from the experiment with T_1 = 45°C

4.2 Effects of Cooling Rate on the Crystallisation

In these experiments the values for the cooling rates (q_C) examined were 0.45, 0.39 and 0.23°C/min. 1-Butyl-3-methylimidazolium chloride ($BmimCl_2$) content (w) was set at 10 wt.% and dissolved in distilled water as the solvent. In the experiments, three initial temperatures, T_1, were tested, *i.e.* 25°C, 15°C and 5°C and the final temperature (T_2) was selected at -20°C. The typical experimental duration was 3 hours and with no seeding procedure. When carrying out measurements of ionic crystal, the experiment was not stopped; the non-crystallised ionic liquid was drained out of the test tube to a beaker and weighed. The crystallised ionic liquid inside the test tube was determined by the difference between the weight of the empty test tube and the weight of the test tube with the crystal. The crystal was then calculated as percentage from the total ionic liquid and distilled water mixture solution used. The experimental results are divided into two main sections: a) the crystallisation study; and b) the Avrami kinetic analysis.

4.2.1 Crystallisation Study

In order to assess the effect of cooling rate on the crystallisation, control experiment was carried out with the cooling rate of 0.45°C/min. Observations from the experiment were that the ionic liquid crystal was in the form of solid-liquid. When 100% crystallisation has been reached, the solid-liquid ionic liquid filled the whole test tube and became solidified. Figure 4.7 shows the percentage of the crystallisation for different cooling rates in the control runs, where the *y*-axis corresponds to the percentage of ionic liquid crystallised.

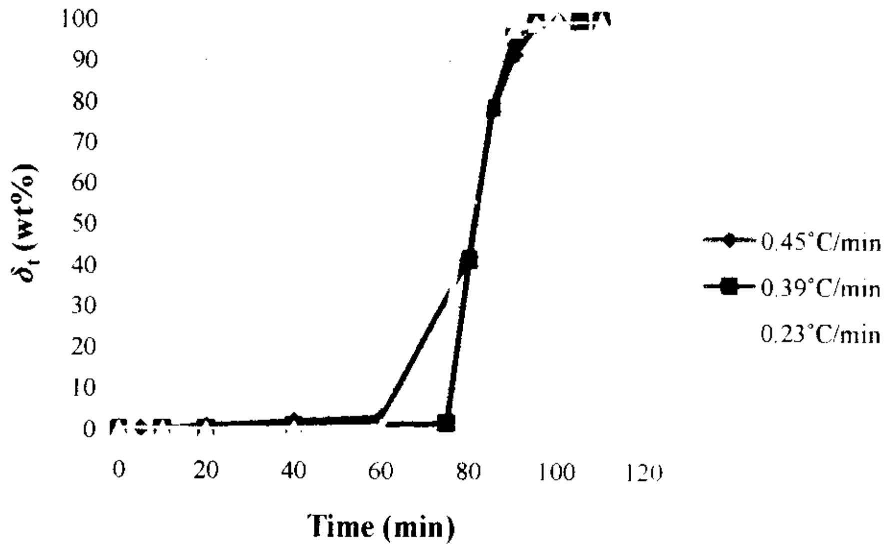

Figure 4.7 Effect of cooling rate on the crystallisation as a function of time.

From the graph it can clearly be observed that the higher the cooling rate, the more ionic liquid crystal produced at any given time; the faster the crystallisation rates; and the quicker it reaches 100% crystallisation. The results are expected: with the increase of cooling rate, the faster the rate formation of ionic liquid molecules to produce ionic liquid crystals.

4.2.2 Avrami Kinetic Analysis

From the crystallisation profiles presented earlier, ionic liquid formation can generally be divided into three main sections: the nucleation phase, the growth phase and the quasi-steady (or the asymptotic) state. As nucleation is too fast to measure, the first and second sections are combined as a single step in most related studies. By analysing the growth phase curves using the Avrami theory as explained in Section 3.5 and Appendix A, some crystallisation kinetics can be extracted. Figure 4.8 plot Log[-ln(1-δ_r)] vs. Log (t) for the effect of cooling rate. Based on Figure 4.8, the Avrami plot has two different kinetics for each cooling rate of which defines two growth phases. The respective growth phases can be separated and shown in the Figures 4.9 and 4.10. However, it is not fully understood as to why the changes in the growth phase would affect the crystallisation. From the figures, good linearity can be seen, indicating the effectiveness of the Avrami methodology. The Avrami exponent (n), and the half time of the crystallisation ($t_{1/2}$) are extracted from the plots and summarised in Table 4.2.

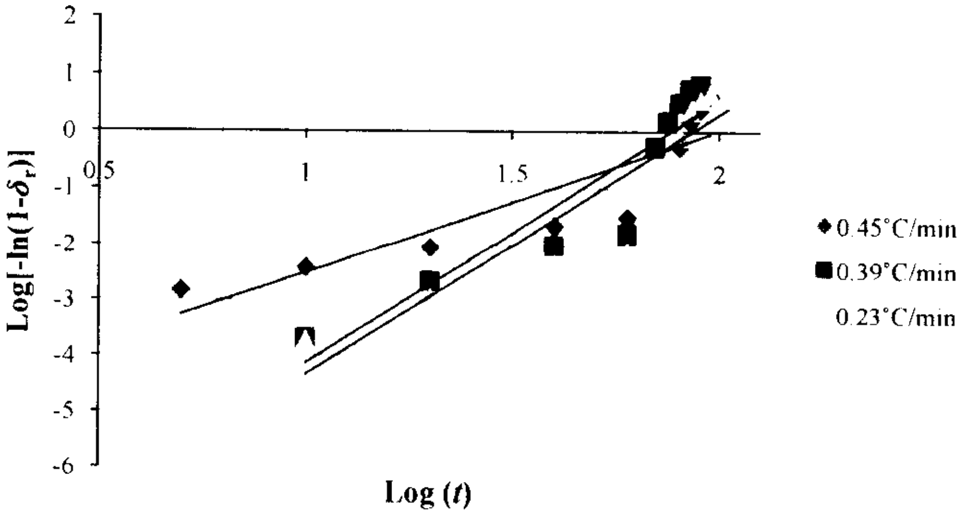

Figure 4.8 Plot of Log[-ln(1-δ_r)] vs. Log (t) to obtain the Avrami parameters

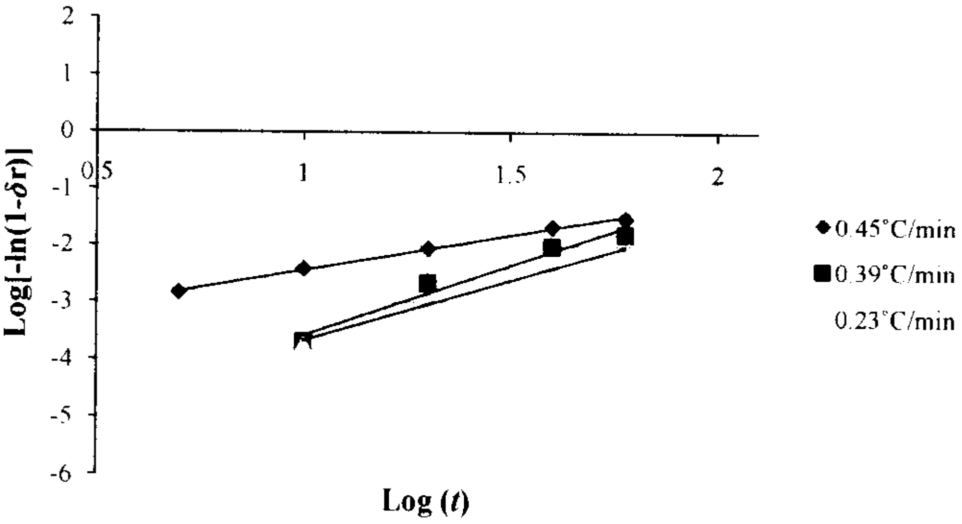

Figure 4.9 Plot of Log[-ln(1-δ_r)] vs. Log (t) of the first kinetic from Figure 4.8

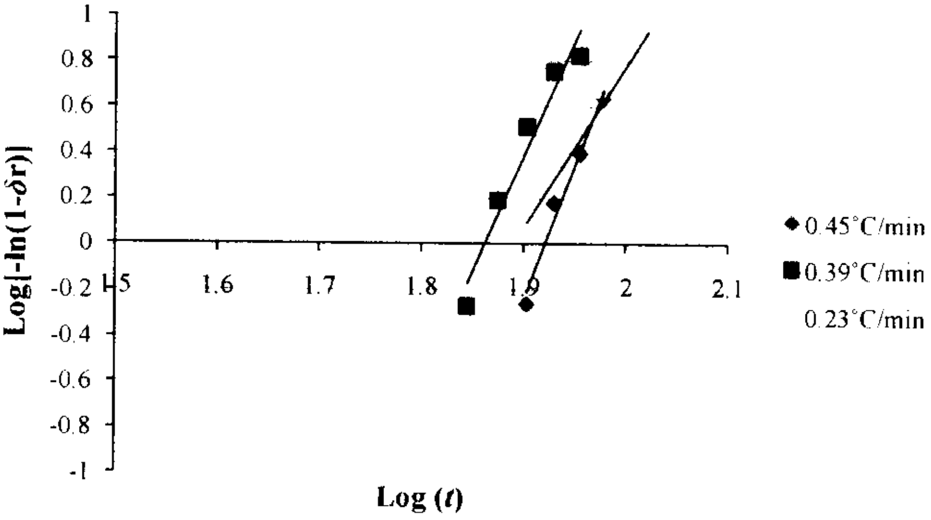

Figure 4.10 Plot of Log[-ln(1-δ_r)] vs. Log (t) of the second kinetic from Figure 4.8

Table 4.2 Extracted Avrami parameters from Figure 4.8

q_C (°C/min)	n	K (min^{-n})	$t_{1/2}$ (min)
0.45	2.525	$9.527\text{x}10^{-6}$	84.23
0.39	4.274	$5.070\text{x}10^{-9}$	80.09
0.23	4.658	$1.035\text{x}10^{-9}$	78.48

From Table 4.2, some general trends can be observed. Firstly, the half time of crystallisation, $t_{1/2}$, generally decreases with lower cooling rate indicating that the growth rate generally increases. Secondly, the Avrami exponent increases with the decrease of the cooling rate. The most noticeable increase in n in Table 4.2 can be seen where a step change is clearly visible with increasing cooling rate. Using both n and $t_{1/2}$ as the diagnostic tool of crystallisation mechanism, Toro-Vazquez *et al.* (2002) derived that in homogenous nucleation a crystallisation process with $n = 4$ follows a 3-D crystal growth mechanism, a value of $n = 3$ a 2-D mechanism, and $n = 2$, 1-D crystal growth. The results may underline the transition mechanism for the beneficial effect of cooling rate on the reduction of the crystallisation. With control experiment, the ionic crystals would be of rod-like shape in one-dimensional growth; these rods would spread to the walls of the test tube, resulting in solid-liquid formation and crystals precipitated out of solution.

When decreasing cooling rates, the Avrami exponents were beyond 4 suggesting sporadic nucleation, and the net result is to change the rod-like crystals (Figure 4.11) into clustered, sphere-like crystals (Figure 4.12). Clearly the shapes of the crystals shown in Figures 4.11 and 4.12 are matched well with the kinetic evaluations. However, it is not fully understood as to why the changes in the crystallisation mechanism would increase the crystallisation.

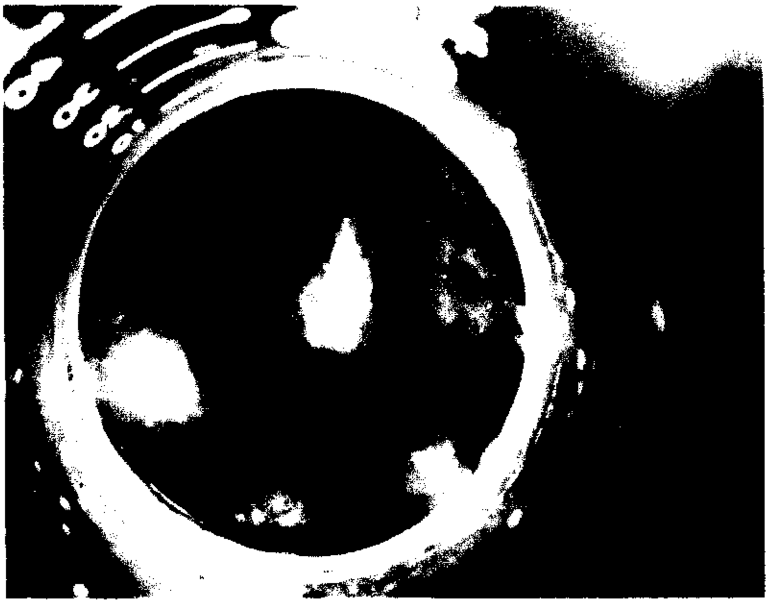

Figure 4.11 Image of ionic liquid crystals from the control experiment with q_C = 0.45°C/min

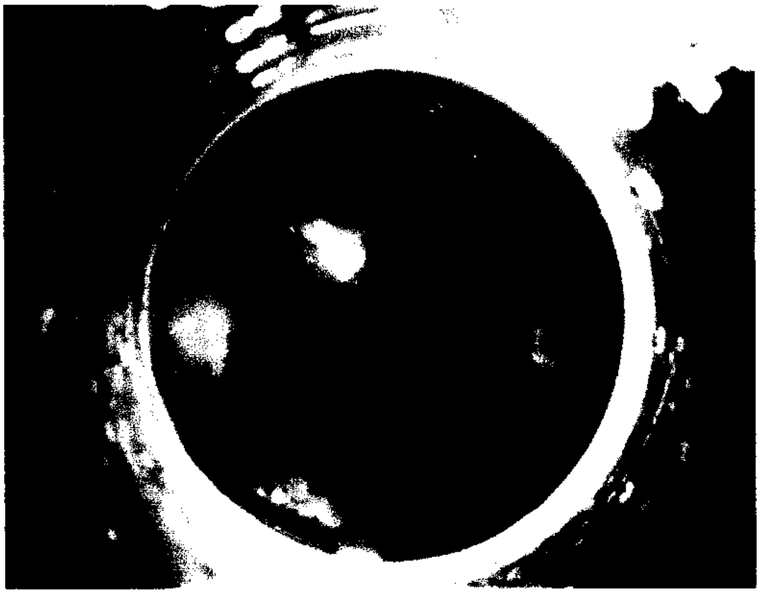

Figure 4.12 Image of ionic liquid crystals from the experiment with q_C = 0.23°C/min

4.3 Effects of Seeding Procedure on the Crystallisation

In this section, results are discussed on the systematic investigation of the effects of seeding procedure. The main objective of this work is to examine the impact of seeding crystals of 1-Butyl-3-methylimidazolium chloride ($BmimCl_2$) on the mechanism of crystallisation. The ionic liquid content was fixed at 10% for all experiments. The initial temperature (T_1) was set at 25°C and the final temperature (T_2) was selected at -20°C. The cooling rate, q_C, was set at 0.45°C/min and the typical experimental duration was 3 hours. When carrying out measurements of ionic crystal, the experiment was not stopped; the non-crystallised ionic liquid was drained out of the test tube to a beaker and weighed. The crystallised ionic liquid inside the test tube was determined by the difference between the weight of the empty test tube and the weight of the test tube with the crystal. The crystal was then calculated as percentage from the total ionic liquid and distilled water mixture solution used. Results are presented in terms of crystallisation studies and the Avrami kinetic analysis.

4.3.1 Crystallisation Study

The effects of seeding procedure on the crystallisation are examined by comparing with control experiments carried out with no seeding procedure and the cooling rate of 0.45°C/min. From the visual observations during experiments, the ionic liquid crystals were in the form of solid-liquid that adhered to the wall of the test tube. After reaching final crystallisation, the ionic liquid and distilled water mixture became solidified and filled the whole test tube. Figure 4.13 show the percentage of the crystallisation for seeding and non-seeding process, where the *y*-axis corresponds to the percentage of ionic liquid crystallised.

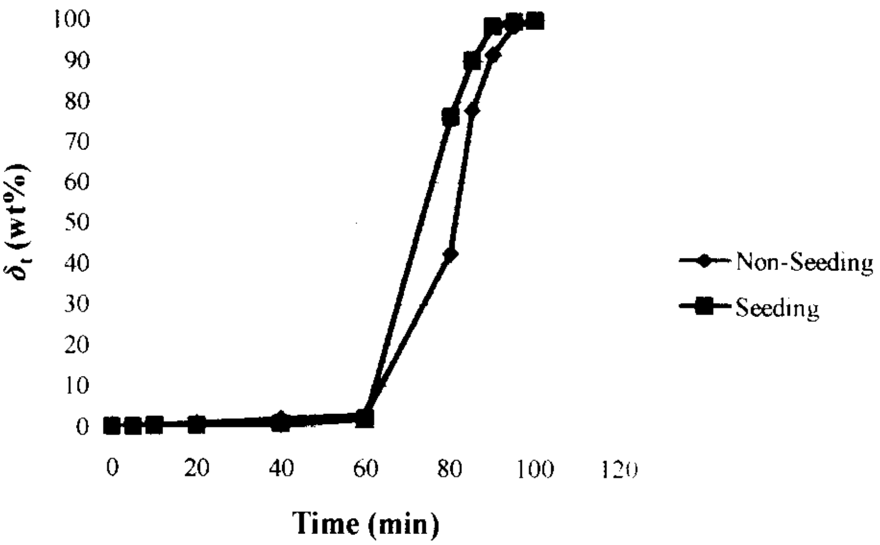

Figure 4.13 Effect of seeding on the crystallisation as a function of time.

From Figure 4.13, it can be observed that with seeding procedure, the more ionic liquid crystallised at any given time and the faster the crystallisation rates. These results are related to the fact that the suspension crystallisation is preferably induced by means of seeding procedure in the presence of the seed crystals (Fiene *et al.*, 2005). Hence ionic liquid molecules were more readily to be precipitated out with seeding process.

4.3.2 Avrami Kinetic Analysis

By examining the growth phase curves in Figure 4.14 using the Avrami theory, some crystallisation kinetics can be extracted as explained in Section 3.5 and Appendix A. Based on Figure 4.14, the Avrami plot has two different kinetics for both seeding and non-seeding procedures of which defines two growth phases. The respective growth phases can be separated and shown in the Figures 4.15 and 4.16. However, it is not fully understood as to why the changes in the growth phase would affect the crystallisation. From the figures, fine linearity can be observed, indicating the effectiveness and significance of the Avrami methodology. The Avrami exponent (*n*) and the half time of crystallisation $t_{1/2}$ are extracted from the plots and presented in Table 4.3.

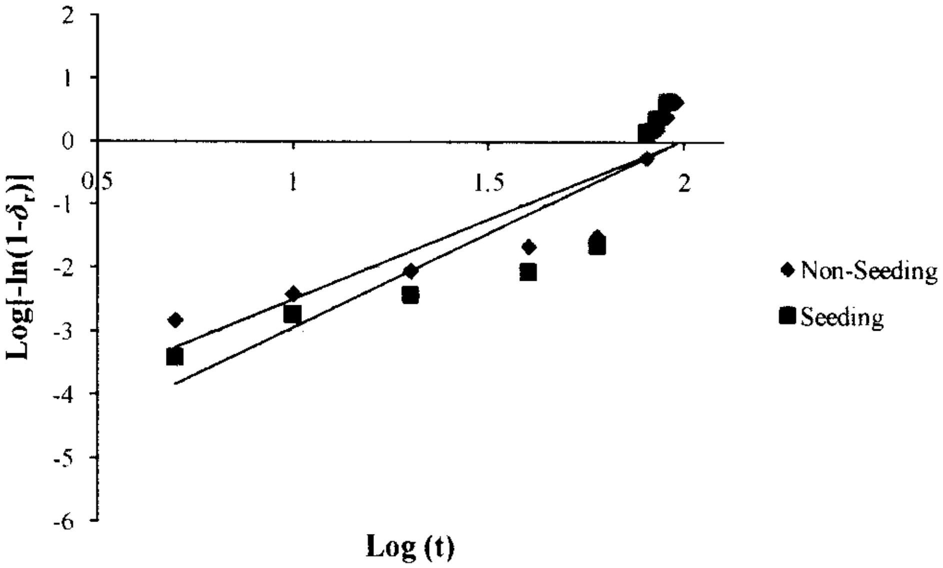

Figure 4.14 Plot of Log[-ln(1-δ_r)] vs. Log (t) to obtain the Avrami parameters

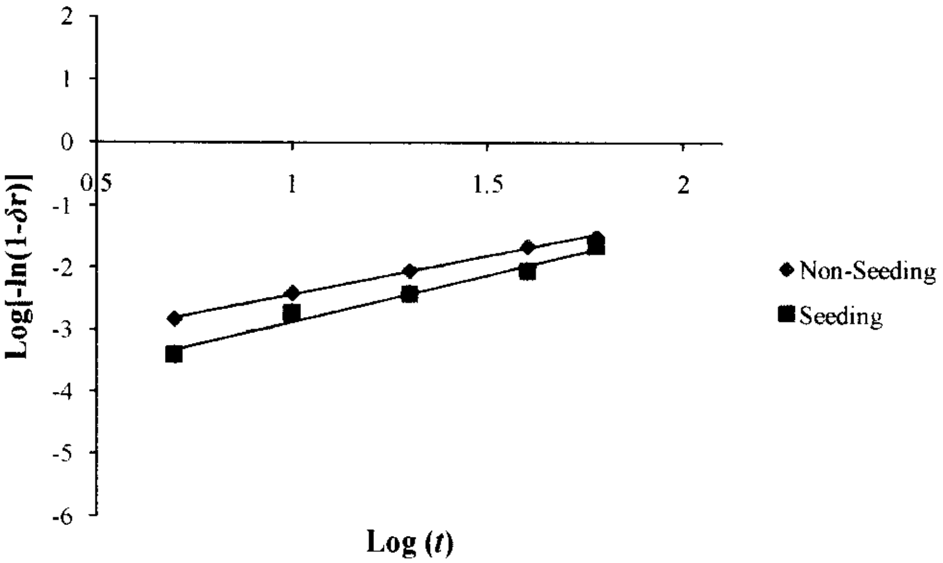

Figure 4.15 Plot of Log[-ln(1-δ_r)] vs. Log (t) of the first kinetic from Figure 4.14

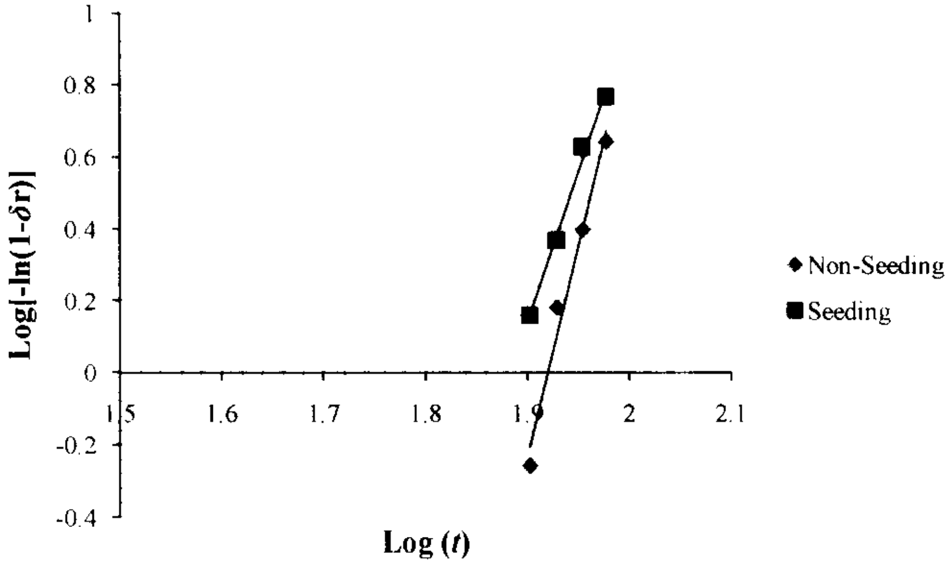

Figure 4.16 Plot of Log[-ln(1-δ_r)] vs. Log (t) of the second kinetic from Figure 4.14

Table 4.3 Extracted Avrami parameters from Figure 4.14

Procedure	***n***	***K* (min^{-n})**	***$t_{1/2}$* (min)**
Non-Seeding	2.525	9.527x10^{-6}	84.23
Seeding	3.147	8.017x10^{-7}	77.00

In Table 4.3, it can be seen that with seeding procedure the Avrami exponent value of 3.147 was higher than the non-seeding procedure with the Avrami exponent value of 2.525, suggesting that with non-seeding procedure, the crystal growth was one-dimensional (Toro-Vazquez *et al.*, 2002). This is also confirmed with the image presented in Figure 4.17, which show rod or needle-like shapes for non-seeding procedure. As the seeding procedure was applied, the *n* value was shifted dramatically to 3.147; indicating a different mechanism crystal growth. The image taken with seeding procedure (Figure 4.18) verifies the multi-dimensional structures of the ionic crystals obtained.

The half time of crystallisation, $t_{1/2}$, presented in Table 4.3 can be used as a tool to evaluate the crystallisation rates. It can be observed that in control experiments with no seeding procedure, the value of $t_{1/2}$ was larger, indicating lower crystallisation rate. Therefore, it can be assumed that ionic liquid crystals were more rapidly precipitated with seeding procedure.

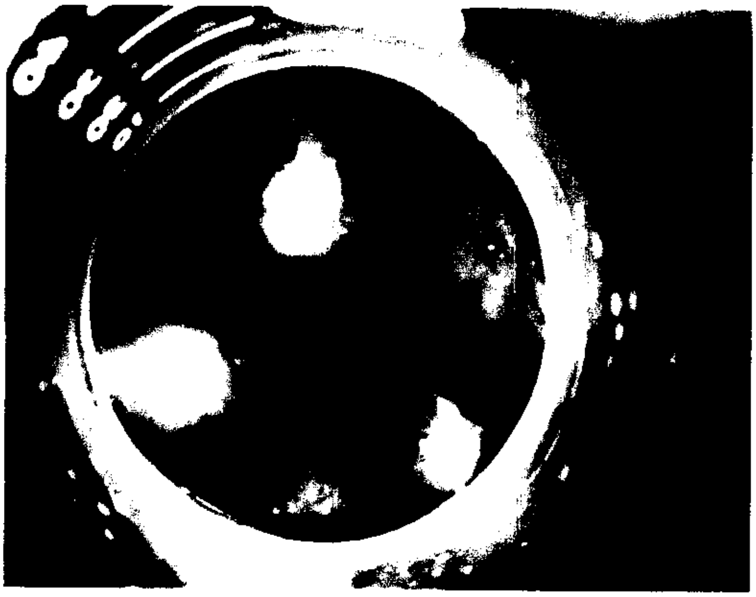

Figure 4.17 Image of ionic liquid crystals from the control experiment without seeding procedure

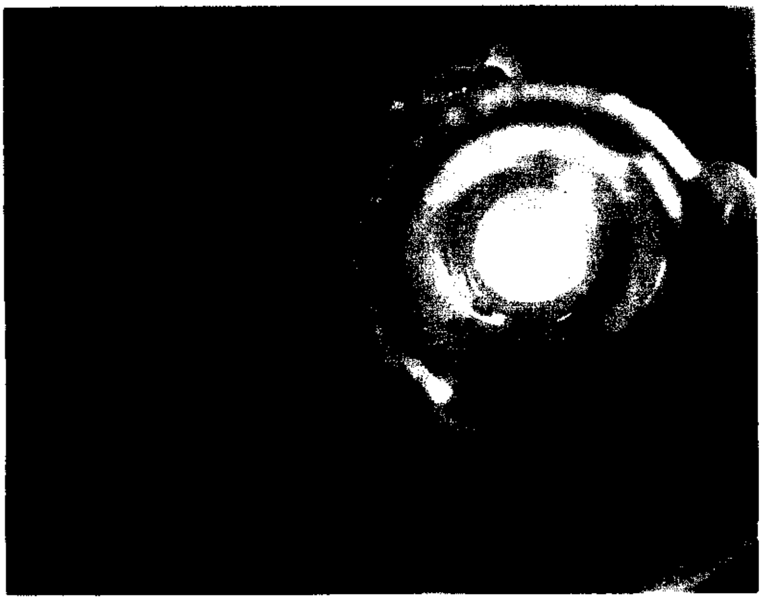

Figure 4.18 Image of ionic liquid crystals from the control experiment with seeding procedure

4.4 Effects of Ionic Liquid Content

The main focus of this investigation was on the effect of ionic liquid content of the 1-Butyl-3-methylimidazolium chloride ($BmimCl_2$)-distilled water solution. Three $BmimCl_2$ contents have been tested, *i.e.* 10, 12.5 and 16.7 percent by weight, represent three different supersaturation levels in terms of the crystallisation process. The initial temperature (T_1) was set at 25°C and the final temperature (T_2) was selected at -20°C and with no seeding procedure. $BmimCl_2$ contents higher than 16.7 wt.% were tried but observed to cause that ionic liquid crystals did not appeared when the final temperature (T_2) of -20°C is reached; hence the maximum $BmimCl_2$ content was taken as 16.7 percent by weight. The cooling rate, q_C, was set at 0.45°C/min and the typical experimental duration was 3 hours. When carrying out measurements of ionic crystal, the experiment was not stopped; the non-crystallised ionic liquid was drained out of the test tube to a beaker and weighed. The crystallised ionic liquid inside the test tube was determined by the difference between the weight of the empty test tube and the weight of the test tube with the crystal. The crystal was then calculated as percentage from the total ionic liquid and distilled water mixture solution used. As usual, results and analyses are presented in terms of crystallisation and the Avrami kinetic analyses.

4.4.1 Crystallisation Study

In order to assess the effect of cooling rate on the crystallisation, control experiment was carried out with 10% ionic liquid content, no seeding procedure and the cooling rate of 0.45°C/min. Observations from the experiment were that the ionic liquid crystal was in the form of solid-liquid. When 100% crystallisation has been reached, the solid-liquid ionic liquid filled the whole test tube and became solidified. Figure 4.19 shows the percentage of the crystallisation for different cooling rates in the control runs, where the *y*-axis corresponds to the percentage of ionic liquid crystallised.

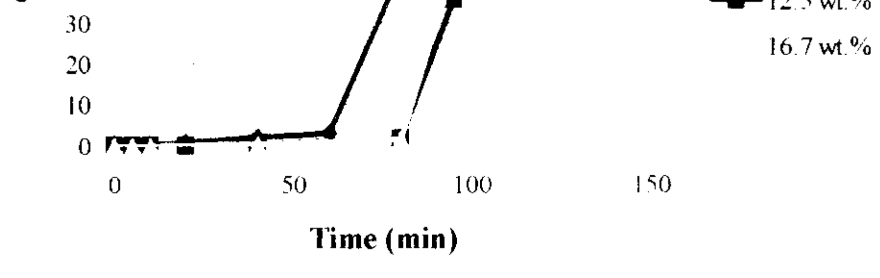

Figure 4.19 Effect of $BmimCl_2$ content on the crystallisation as a function of time.

From the graph it can clearly be observed that the higher the $BmimCl_2$ content, the less ionic liquid crystal produced at any given time; the slower the crystallisation rates; and the later it reaches 100% crystallisation. These results are expected: with the increase of the BmimCl_2 content in solution, there are more ionic liquid molecules available to produce ionic liquid crystals at slower crystallisation rates and at lower temperature; hence, longer times were taken to produce ionic liquid crystals.

4.4.2 Avrami Kinetic Analysis

From the crystallisation profiles presented earlier, ionic liquid formation can generally be divided into three main sections: the nucleation phase, the growth phase and the quasi-steady (or the asymptotic) state. As nucleation is too fast to measure, the first and second sections are combined as a single step in most related studies. By analysing the growth phase curves using the Avrami theory as explained in Section 3.5 and Appendix A, some crystallisation kinetics can be extracted. Figure 4.20 plot $\mathrm{Log}[-\ln(1-\delta_r)]$ vs. $\mathrm{Log}\,(t)$ for the effects of ionic liquid content. Based on Figure 4.20, the Avrami plot has two different kinetics for each ionic liquid content of which defines two growth phases. The respective growth phases can be separated and shown in the Figures 4.21 and 4.22. However, it is not fully understood as to why the changes in the growth phase would affect the crystallisation. From the figures, good linearity can be seen, indicating the effectiveness of the Avrami methodology. The Avrami exponent (n), and the half time of the crystallisation ($t_{1/2}$) are extracted from the plots and summarised in Table 4.4.

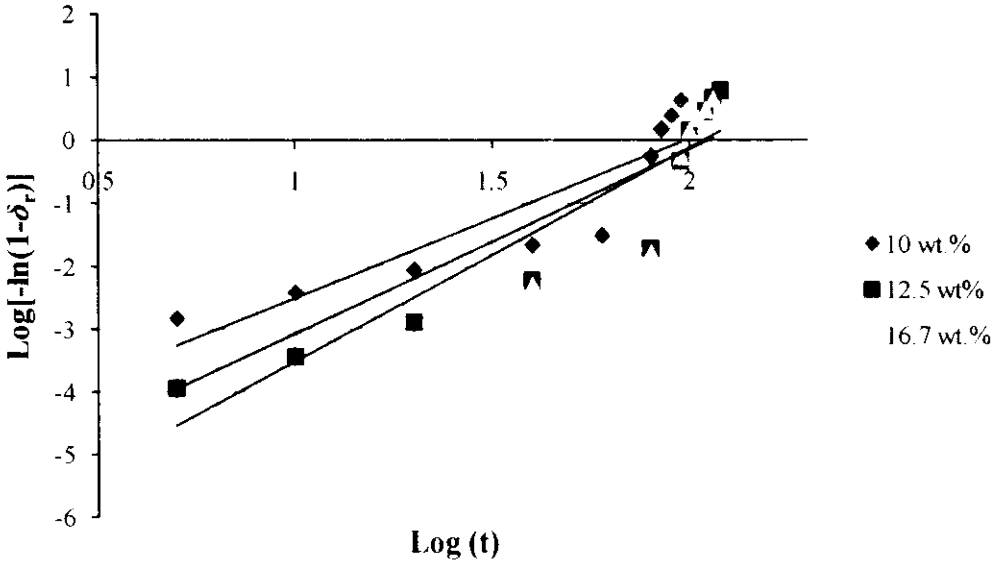

Figure 4.20 Plot of Log[-ln(1-δ_r)] vs. Log (t) to obtain the Avrami parameters

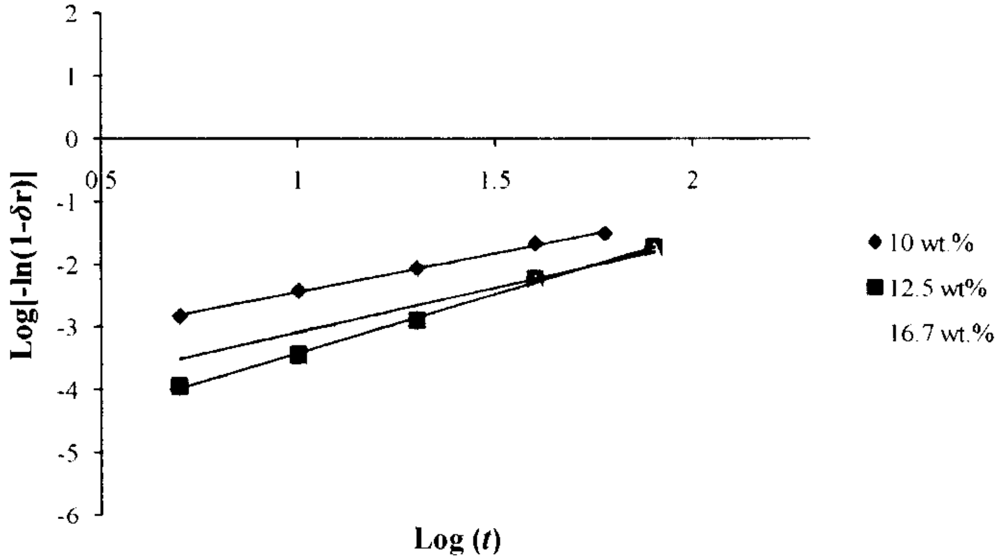

Figure 4.21 Plot of Log[-ln(1-δ_r)] vs. Log (t) of the first kinetic from Figure 4.20

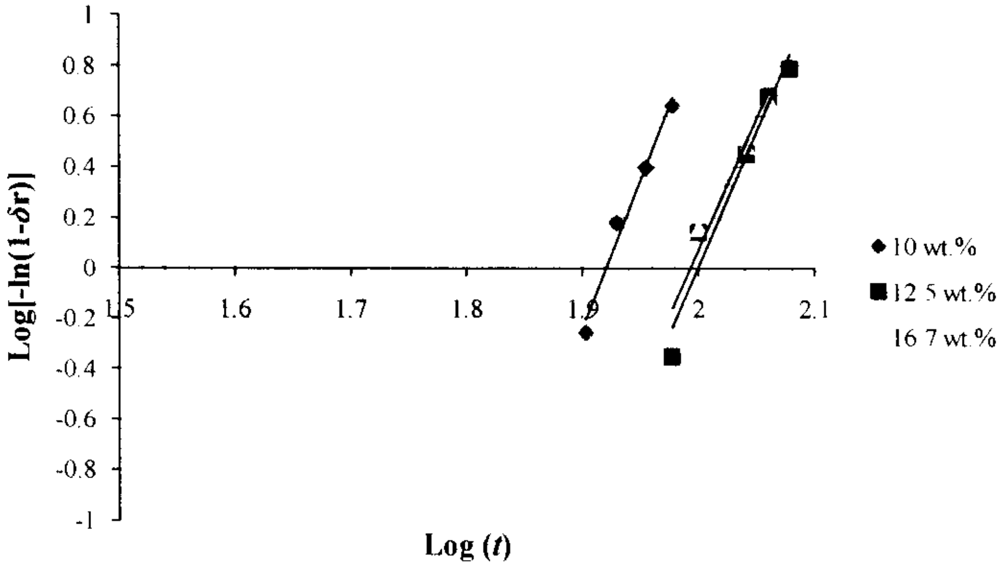

Figure 4.22 Plot of Log[-ln(1-δr)] vs. Log (t) of the second kinetic from Figure 4.20

Table 4.4 Extracted Avrami parameters from Figure 4.20

wt.%	*n*	*K* (min^{-n})	$t_{1/2}$ (min)
10.0	2.525	9.527x10^{-6}	84.23
12.5	3.381	1.297x10^{-7}	97.70
16.7	2.921	1.030x10^{-6}	98.89

From Table 4.4 it can be seen that in the experiment at 10 wt.% of ionic liquid content, the Avrami exponent value (*n*) was 2.525 indicating that ionic liquid crystals produced were of one-dimensional, rod-like or needle-like type (Figure 4.23) as suggested by Toro-Vazquez *et al.* (2002). Figure 4.23 shows the image of crystals from the control experiments at 10 wt.% of ionic liquid content and needle type crystals are clearly seen. When higher ionic liquid contents were used, a step change in the *n* values can then be observed leading to larger *n* values. This would suggest that the growth mechanism of crystals under these conditions changed from a one-to a multi-dimensional event and crystals are of clustered-plate-like shapes (Figure 4.24). The step increase in the Avrami exponent is contributed to by the change in the type of nucleation, from slightly instantaneous to more sporadic.

From the half time of crystallisation data in Table 4.4, it can be observed that the highest $t_{1/2}$ of 98.89 minutes was obtained when the ionic liquid content is 16.7 percent in weight. Increasing the ionic liquid content generally increased the half time of crystallisation, $t_{1/2}$, suggesting that increasing the ionic liquid content decreased the rate of crystallisation, as the larger the $t_{1/2}$, the slower the rate of crystallisation. However it is worth mentioning that increasing the ionic liquid content had a significant impact in decreasing the overall crystallisation.

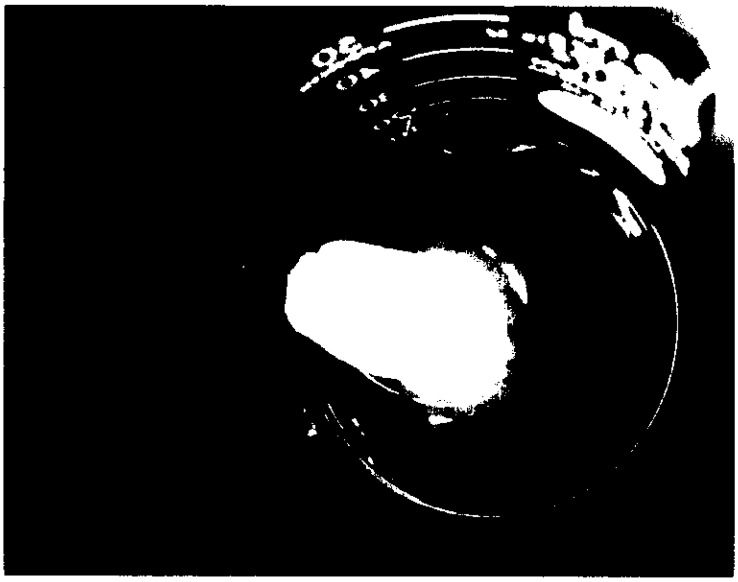

Figure 4.23 Image of ionic liquid crystals from the control experiment with 10 wt.% of ionic liquid content

Figure 4.24 Image of ionic liquid crystals from the control experiment with 16.7 wt.% of ionic liquid content

CHAPTER 5

CONCLUSIONS AND RECOMMENDATIONS

5.1 Conclusions

This study reports the experimental investigation into the crystallisation of ionic liquid. The major conclusions of this work are summarised as follows:

- On the study of the effects of temperature deviations, it was found that increasing the initial temperature (T_1) reduced the rate of crystallisation, increased $t_{1/2}$; a step change in the n values can then be observed leading to larger n values. This would suggest that the growth mechanism of crystals under these conditions changed from a one-to a multi-dimensional event and crystals are of clustered-plate-like shapes. Thus, increase of the initial temperature (T_1) resulting the decrease of the rates of crystallisation.

- On the effects of cooling rate, it was observed that decreasing the cooling rate increased the rate of crystallisation, decreased $t_{1/2}$ values hence increased the crystallisation rates. Moreover decreasing cooling rates, the Avrami exponents were beyond 4 suggesting sporadic nucleation, and the net result is to change the rod-like crystals into clustered, sphere-like crystals.

- The study on the effects of seeding procedure revealed that crystallisation increased with seeding procedure, decreased $t_{1/2}$ and caused higher crystallisation rate. The n values was shifted dramatically to 3.147 from 2.525 as the seeding procedure was applied indicating a different mechanism crystal growth. For non-seeding procedure the crystals formed needle-like shapes whereas by seeding procedure the multi-dimensional structures of ionic crystals obtained.

- Lastly in the effects of ionic liquid content, it was found that the higher the ionic liquid content, the longer times were taken to produce ionic liquid crystals, increased $t_{1/2}$. Moreover, increasing of the ionic liquid content; reduced the rate of crystallisation and increased the n values of which altered the type of ionic liquid crystal from needle type to clustered plate-like shapes.

5.2 Recommendations

Due to time constraint, the experimental study has been reduced. In order to get wide range and more meaningful data, further studies on the crystallisation of ionic liquids (*i.e* on the effects of different cations with the same anions, different anions with the same cations, different alkyl chain lengths and different types of solvent) should be implemented. In addition, the study based on Scanning Electron Microscope (SEM) should be conducted so as to gain information about the crystal formation and behaviour based on its composition, surface topography and other properties such as electrical conductivity. Moreover, the structures of ionic crystals obtain from the experiments can be observed clearly by using SEM. As the study of the crystal formation will affect the result of experiment, the author should focus on the experimental study and research methodology.

Appendix A: Calculation of the Avrami Parameters

This example calculation is based on the data obtained from the experiments conducted with ionic liquid content of 10% in distilled water as the solvent. The crystallisation curve is shown in Figure A1. By plotting the left side equation (3.6) *i.e.* Log[-ln(1-δ_r)], vs. Log (t), the slope of the straight line n (the Avrami exponent) and the intersection K (kinetic coefficient) can be obtained. The relative crystallisation, δ_r, is calculated from equation (3.5), *i.e.* $\delta_r = \frac{\delta_t - \delta_0}{\delta_\infty - \delta_0}$, in this case the initial crystallisation, $\delta_0 = 0$ and final crystallisation, $\delta_\infty = 1$ (100% crystallisation). Tabulated data is shown in Table A1 and the plot of Log[-ln(1-δ_r)] vs. Log (t) is shown in Figure A1.

Table A1 Tabulated data for the calculation of the Avrami parameters

***t* (min)**	**Log(*t*)**	**δ_t**	**1- δ_r**	**Log[-ln(1-δ_r)]**
0	∞	0.0000	1.0000	∞
5	0.6990	0.1492	0.9985	-2.8258
10	1.0000	0.3885	0.9961	-2.4098
20	1.3010	0.8955	0.9910	-2.0460
40	1.6021	2.1717	0.9783	-1.6584
60	1.7782	3.1099	0.9689	-1.5004
80	1.9031	42.5428	0.5746	-0.2564
85	1.9294	78.0548	0.2195	0.1809
90	1.9542	91.8114	0.0819	0.3984
95	1.9777	98.7677	0.0123	0.6431
100	2.0000	100.0000	0.0000	∞

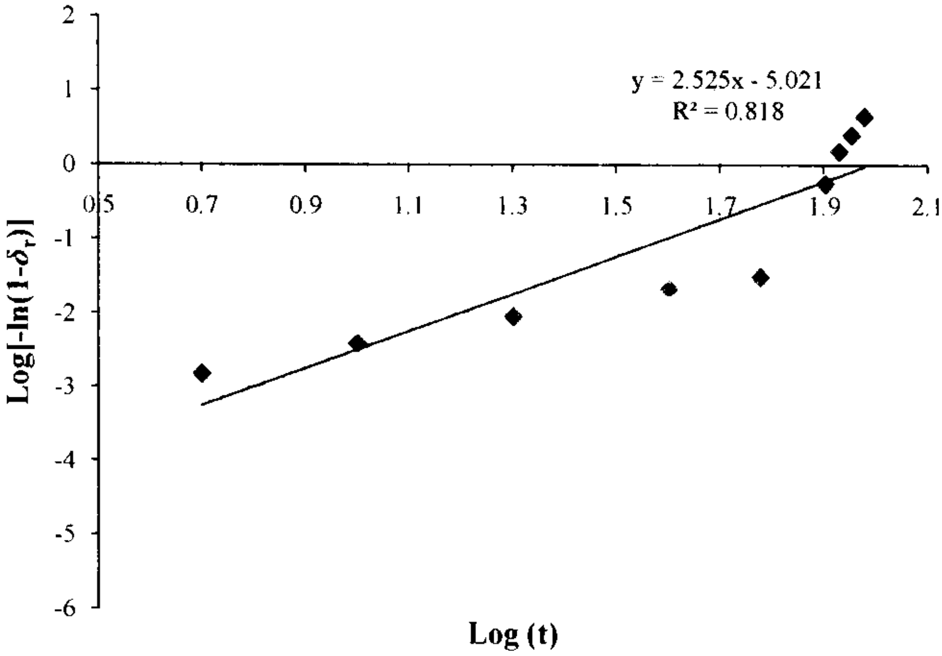

Figure A1 Plot of Log[-ln(1-δ_r)] vs. Log (t) to obtain the Avrami parameters

From the plot, the equation of the linear trend line obtained is $y = 2.5253 - 5.0216$, from which the Avrami exponent, n, is 2.5253 and the logarithmic kinetic coefficient, Log K, is -5.0216 ($K = 9.515\text{x}10^{-6}$). The crystallisation half-time ($t_{1/2}$) is defined as the time at which the degree of crystallisation (δ_t) is 50% of the maximum achievable crystallisation, and can be calculated from the measured kinetics parameters using the equation (3.7), *i.e.*

$$t_{1/2} = \left(\frac{\ln 2}{K}\right)^{1/n} = \left(\frac{\ln 2}{9.515\text{x}10^{-6}}\right)^{\frac{1}{2.5253}} = 84.23 \text{ min.}$$

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