Crystallization Study of Ionic Liquid

by

Nazliah Binti Asmin

Dissertation submitted in partial fulfillment of

the requirements for the

Bachelor of Engineering (Hons)

(Chemical Engineering)

UNIVERSITI TEKNOLOGI PETRONAS
TRONOH, PERAK
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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 Ismail)

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CERTIFICATION OF ORIGINALITY

This is to certify that I am accountable 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.

NAZLIAH BINTI ASMIN

ABSTRACT

Ionic liquid are salts that are liquid at low temperature, usually have melting point below 100°C. They are getting wide attention recently because of their variety potential in the industry. Like other salts, ionic liquid also can be crystallizing. 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. Avrami analysis was utilized to study the crystallization kinetics of ionic liquid. Avrami exponent n is slightly increased and the parameter k decreased with increasing ionic liquid percentage on the solution. The increase in temperature led to an increase in the value of Avrami exponent while the value of parameter k dropped significantly. The value of Avrami exponent obtained is in the range of (0.3-2.1). The nucleation process is instantaneous and the crystal growth is in 2D dimension.

ACKNOWLEDGEMENT

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NOMENCLATURE

IL	Ionic Liquid
[BMIM]Cl	1-Butyl-3-Methyl Imidazolium Chloride
k	Rate constant
n	Avrami exponent

CHAPTER 1

INTRODUCTION

1.1 Background of Study

Ionic liquids (ILs) have received a great increase in attention in the fields of engineering during the last decade due to their unique properties. Ionic liquid is salt composed of ions and has melting point below 100℃. The bulkier anion and non-symmetrical cation make the salt having low melting point compare to other ionic compound. The example of common ionic liquid is Alkyl-Imidazolium and Alkyl-Pyridinium salts as Chlorides or Ethylsulfates (Wasserscheid, 2003).

Ionic liquids are non-volatile, non-flammable, thermally stable and environmentally friendly solvent. Each specific combination of anion and cation give unique and different physical and chemical properties, making them suitable for very different applications. They are used as green solvent to replace volatile organic solvent in chemical reaction, chemical synthesis, electrochemistry, separation techniques to catalysis and reaction engineering.

An advantage of the use of ionic liquids as solvents which is emphasized is that ionic liquids have virtually no measurable vapour pressure and for this reason, solvent losses due to evaporation do not occur. This becomes disadvantage when they are used as solvent in a process in which high-boiling byproducts which cannot be separated off again by distillation or extraction are formed (Wasserscheidt, 2003).

In addition, the purity of the ionic liquids used is of great importance. Impurities have a generally adverse effect on the course of chemical reactions. There is therefore a need for ionic liquids having a high purity. Crystallization is one of the possible methods. The study of crystallization operation of ionic liquid has taken on even higher levels of importance (Winterton, 2008). Study of ionic liquid crystallization will to contribute to a better understanding of this intriguing class of compounds and motivate to further explore the purification and recovery of ionic liquid which is under intense investigation and not available up to now.

1.2 Problem Statements

Ionic liquids (ILs) have become an important class of solvents and soft materials over the past decades. Ionic liquid is not easy to isolate and purify. It also miscible with water and will be inevitably end ups in the aqueous environment. Ionic liquids are also quite expensive media compare to other organic solvent. Economically, it is important to recycle and regenerate ionic liquid as efficiently as possible. Other than distillation and membrane separation process, one possible method to recycle ionic liquid is through crystallization.

1.3 Aim and Objectives

The main aim of the project is to study the kinetics of ionic liquid crystallization. The kinetics will be studied and analyzed using Avrami approach.

The project objectives are:

1. To investigate the kinetic of ionic liquid crystallization using Avrami model.
2. To understand the effect of crystallization temperature on the kinetics of ionic liquid crystallization.
3. To study on the effect of ionic liquid concentration to the crystallization kinetics.

1.4 Scope of Study

In order to complete this project, several scope of study is in need to achieve. This project will emphasizes on the laboratory experiment on crystallization process of ionic liquid. The experiment need to be conducted successfully to obtain useful information regarding kinetics and behavior of IL on crystallization. Suitable method and approach is designed and applied to conduct the experiment.

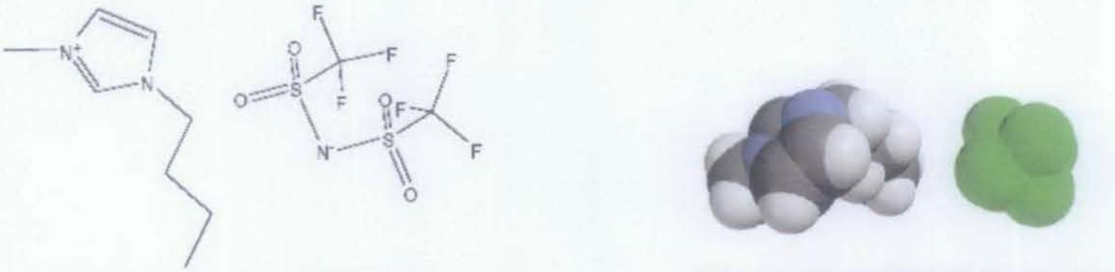
Apart from that, the project also covers the analysis on the finding of the experiments. The study will perform analysis on crystallization kinetics using Avrami equation. Several parameters affecting the crystallization process also be considered and analyzed. Avrami model is utilized to study the effect of different ionic liquid crystallization and different crystallization temperature to the kinetic of crystallization.

CHAPTER 2

LITERATURE REVIEW

2.1 Ionic Liquid

An ionic liquid can generally be defined as a salt, composed entirely of anions and cations, with a melting temperature that has technically been established as below the boiling point of water (MacFarlane 2007, Wasserscheid 2003, Wilkes 2002), and which have an extremely low vapor pressure (Ludwig 2007, Armstrong 2007, Earle 2006, Paulechka 2005). An IL is then essentially a molten salt, like for instance is the case with NaCl, but with the difference that an IL has a much lower melting temperature than the classical inorganic salts.



1-Butyl-3-methylimidazolium bistriflimide

1-Butyl-3-methylimidazolium hexafluorophosphate

Figure 2.1: Example of ionic liquids. (P. Abbott, 2006)

Several ionic liquids are already liquid at or near room temperature, and therefore they are also named room temperature ionic liquids (RTIL). Ionic liqud consists of a salt where one or both the ions are large, and the cation has a low degree of symmetry. These factors tend to reduce the lattice energy of the crystalline form of the salt, and hence lower the melting point (Seddon, 1998). A main application of ionic liquids is as solvents in diverse, catalysis and bio-catalysis processes or as electrolytes among other current and potential uses (ENdres 2008, Sigma-Aldrich 2005). Ionic liquids described as designer solvents (Freemantle, 1998). Their properties can be adjusted to suit the requirement of the process. Their melting point, viscosity, density and miscibility of water can be varied by changing the structure of the ions. These behavior make separation is easy as the relative solubility of the ionic and extraction phase can be adjusted.

The physical and chemical properties of ionic liquids can be influenced significantly by small amount of impurities. Their catalytic activity and electrochemical behavior are highly dependent on their purity level. Usually grades of purity are greater than 95% "for synthesis", greater than 99% "high pure" and greater than 99.9% "ultra-pure". Typical impurities are colours, organic starting materials and other volatiles, halide impurities, protic impurities, other ionic impurities from incomplete metathesis reaction and water.

2.2 Crystallization

Crystallization is a method of production, purification or recovery of solid material, or of liquid material from the solid (Mullin 1993). Apart from being one of the best and cheapest methods available for the production of pure solids from impure solutions, crystallization has the additional advantage of giving an end product that has many desirable properties, like uniform crystals –that is, when the solid is the desired product. Another advantage of crystallization is it consumes low energy and it gives high potential in giving high purity of product. Crystallization process has two main events, nucleation and crystal growth. Nucleation is process of formation of stable small particle (nuclei) of the new phase. They are often formed at the grain boundaries and other defects.

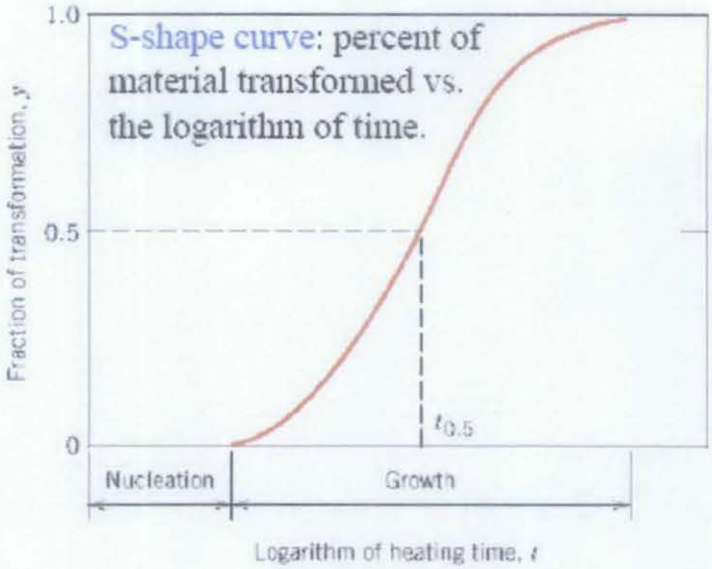


Figure 2.2: S-shape curve of crystallization, (Zhigilei, 2008)

Crystal growth is the subsequent growth of the nuclei that succeed in achieving the critical cluster size. 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. The shape of growing crystal can be affected by the fact that different crystal faces have different growth rate (Zhigilei, 2008). Crystals are grown in many shapes, dependent upon downstream processing or final product. This can include cubic, tetragonal, hexagonal and trigonal.

Study of kinetics of crystallization is important as it has important role in process control and in determining solid-phase outcomes. Crystallization provides a way of reducing free energy of metastable thermodynamic states, the extend which metastable state can be maintained is determined by the crystallization mechanism and kinetics. The control of crystallization is of fundamental importance in many biological and industrial processes; for instance in biomineralisation, specific mineral polymorphs are selectively crystallized, whilst in oil extraction, the precipitation of barium sulphate crystals within oil pipes is a serious problem. Controlled crystallization can only be achieved through an understanding of the crystallization process at the molecular level.

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 (Brennecke, 2001). They tend to undergo some cooling and frequently form amorphous structures in the solid state (Rogers, 2001). 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 (Branco, 2002).

Initial work has been performed involving fractional crystallization. It leads to the crystal having reduced concentration of impurity (Fiene, 2006). He stated that in general, IL is allowed to crystallize until at least 5% by weight, preferably at least 10% by weight, and particularly preferably at least 20% of the IL has crystallized out. Crystallization has been recently applied to produce and separate an IL as crystals from a mother liquor solution (König 2007). Professor Winterton had examined a series of 50 ionic liquids of different types, showing that it is possible to grow crystals of some ionic liquids.

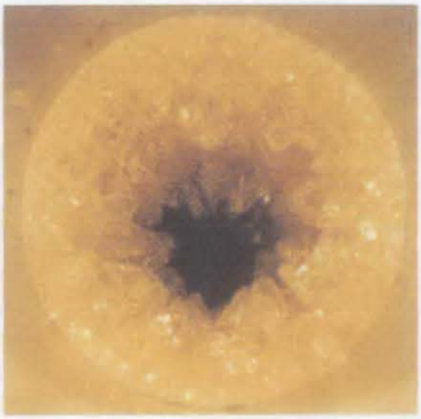


Figure 2.3: Crystal of ionic liquid (König 2007)

2.2 Avrami Model

The well-known Avrami equation describes changes in the volume of the crystals as a function of time during crystallization, and has the general form:

$$F = \frac{V - V_o}{V_m - V_o} = 1 - \exp(kt^n)$$

where V is the volume of the crystals, Vo is the initial crystal volume (usually zero), Vm is the maximal crystal volume attained after crystallization is complete, k is the Avrami constant, and n is the Avrami exponent. The exponent 'n' in the equation is related to the geometry of the transformation. k value contains all the temperature dependent terms because thermal activation affects the growth strongly through boundary or interface mobility, and because the nucleation density depend strongly on driving force. This function is sigmoidal, with an initial lag-period, where crystallization occurs very slowly, followed by a rapid increase in crystal volume or mass. In the past, crystallization data were fitted to the linearized form of this equation by simple linear regression:

$$\ln[-\ln(1 - Y)] = \ln(k) + n \ln(t)$$

Hence, a plot of $\ln[-\ln(1 - Y)]$ vs. $\ln(t)$ has a slope of n and a y-intercept of $\ln(k)$.

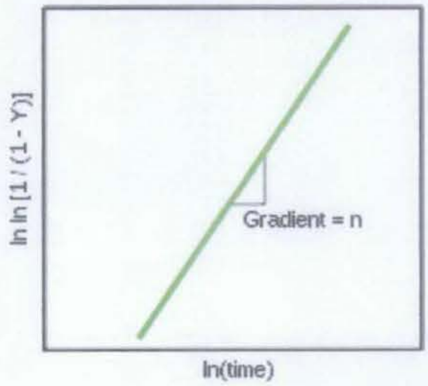


Figure 2.4: Avrami equation graph (Bischof, 2007)

The assumption in this model are there is random nucleation in space and crystal growth is 1, 2 or 3 dimensional; rods, platelets or spheres. Density of second phase is assumed to do not change with time. There are numbers of model in studying the kinetics of crystallization such as Tobin Model, Malkin Model and Urbanovici-Segal Model. Avrami Model is widely used due to its mathematical simplicity, firm theoretical basis and it give best description to the experimental data.

Douglas R Macfarlane in year 2011 point out that by assuming crystallisation of the ionic liquids is a thermal or mass diffusion-controlled process, the values of the isothermal Avrami exponent obtained from three different ionic liquids with three different anions and cations all indicate that growth occurs with a decreasing nucleation rate (n = 1.8-2.2). For one of the ionic liquids it was possible to avoid crystallisation by fast cooling and then observe a devitrification upon heating through the glass transition. The isothermal Avrami exponent of devitrification suggested growth with an increasing nucleating rate (n = 4.1), compared to a decreasing nucleation rate when crystallisation occurs on cooling from the melt (n = 2.0). The applicability of by Johnson-Mehl-Avrami-Kolmogorov (JMAK) theory suggests that the nucleation event in the ionic liquids selected is a random stochastic process in the volume of the material.

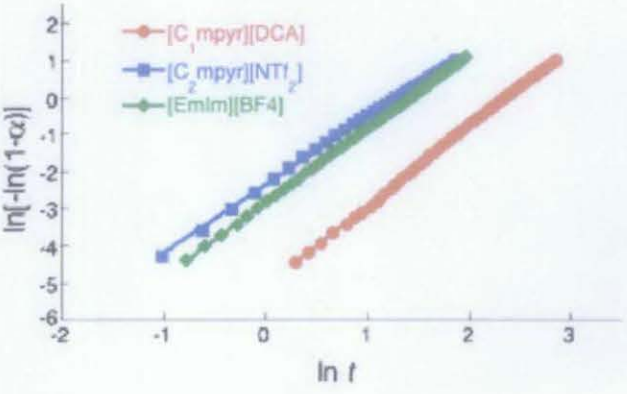


Figure 2.4: Avrami analysis (Macfarlane, 2011)

CHAPTER 3

METHODOLOGY

The experimental work is conducted at the PETRONAS Ionic Liquid Center (PILC). In this project, the sample used is 1-Butyl-3-Methyl Imidazolium Chloride, [BMIM]Cl mainly because it is widely used in the industrial application. Table 3.1 shows the properties of [BMIM]Cl. Crystallization process will be done at three differents crystallization temperature (0°C, -4°C and -8°C) and three different concentration of ionic liquid (70%, 80% and 90%).

Table 3.1: properties of [BMIM]Cl

Form	solid
Colour	beige
Odour	odourless
Melting point	60°C
Water solubility	At 20°C soluble

3.1 Sample Preparation

Ionic liquid is mixed with water that reacts as the solvent in this crystallization process. Both amount of ionic liquid and solvent are recorded. Water is chosen as it is very miscible and non-flammable, non-toxic, cheap and will dissolve polar organic compounds. The solution is heated up around 60°C to let it dissolve in high temperature as the solubility of material is usually increased with increasing temperature. To ensure crystallization is going to happen, the solution need to be saturated. If a saturated hot solution is allowed to cool, the solute is no longer soluble in the solvent and forms crystals of pure compound.

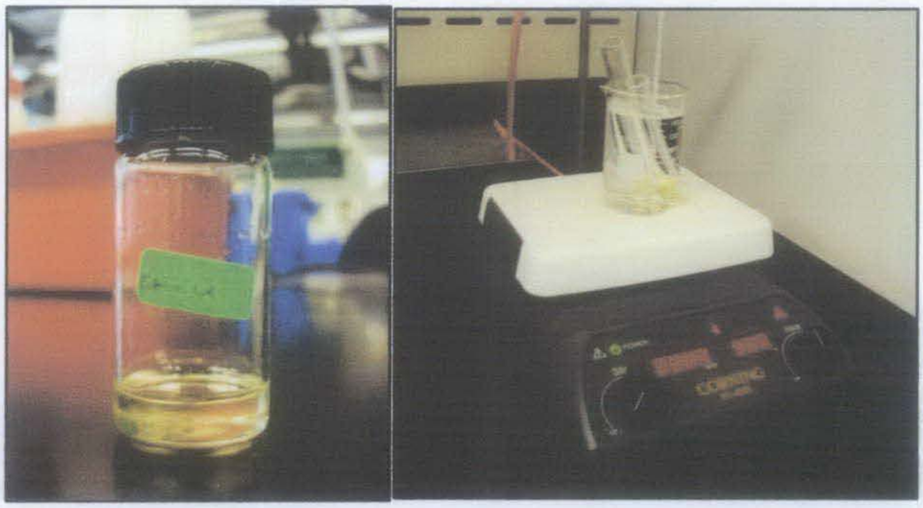


Figure 3.1: sample of [BMIM]Cl is heated up to get saturated solution.

3.2 Crystallization Process

The solution is then cooled down to the desired crystallization temperature using JULABO F-32 Refrigerated and Heating Circulator that used ethylene glycol as its refrigerant shown below. Other chiller that used water as its cooling liquid cannot be used as it is unable to reach temperature lowers than 0°C. The cooling rate of the chiller is 1°C /min. After reaching desired crystallization temperature, seed crystal is put inside the test tube to induced crystallization.

Figure 3.2: Sample of ionic liquid is cooled down to crystallization temperature in ethylene glycol bath at cooling rate of 1°C /min. Seed crystal is used to induce crystallization.

3.3 Weight Measurement

In every 10 minutes, liquid that not crystallized is taken out from the test tube to measure the mass before put them back and let the crystallization process continue. The measurement is stopped when there is no more changes in the weight of the liquid. The procedures are repeated several times for different crystallization temperature and different ionic liquid content in the solution. A few set of samples is tested to get accurate data. From the data obtained, the weight of the crystal formed during the process can be determined by subtracting the weight of liquid not crystallizes from the initial weight of the solution.

Weight of crystal = initial weight of solution – weight of liquid not crystallized

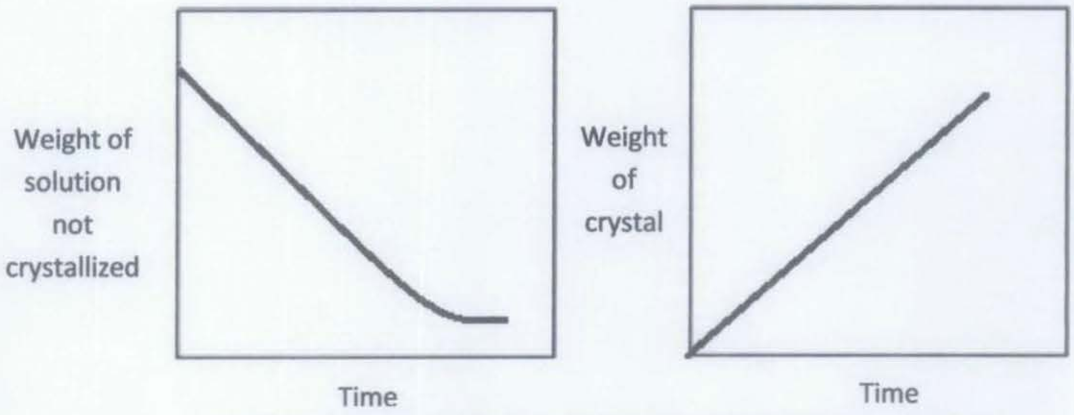


Figure 3.3: graph plot for the result obtained from experiment.

Figure 3.4: liquid that not crystallize is weight and recorded.

CHAPTER 4

RESULT AND DISCUSSION

The Avrami model states that in a given system under isothermal conditions at a temperature lower than melting point, the degree of crystallinity or fractional crystallization as a function of time is described by equation below;

$$X(t) = 1\text{-}\exp(-kt^n)$$

Where X(t) is the normalized crystalline content at time t. 'k' and 'n' are Avrami constants and are indicative of crystallization mechanisms that are involved. The exponent 'n' in the Avrami equation can provide information on nucleation type and crystal growth geometry. *k* is dependent upon the shape of the growing crystalline entities (for e.g., whether they are spheres, discs or rods), as well as the type and amount of nucleation (sporadic or predetermined) and the linear growth rate 'G' of the growing crystalline moieties. To determine the parameters, usually the above equation is linearized to the form of $y=mx+c$ by taking double logarithm twice at both side.

$$\text{Ln } X(t) = \ln k + \ln(\ln 1\text{-}Y)$$

Figure 4.1 and Figure 4.2 show the graph for the weight of crystal formed as a function of time for different concentration ionic liquid and different crystallization temperature. The rate of crystallization is increase as the concentration of ionic liquid increase from 70% to 90%. Time used for the ionic liquid at 90% concentration to totally crystallize is less than the other two samples. The increased growth rates at larger supersaturation contribute to a faster crystallization response and this would be reflected in the higher values of 'k' obtained at higher concentration of ionic liquid in the solution. Sample of [BMIM]Cl cooling at -8C is crystallize faster and it form more crystal.

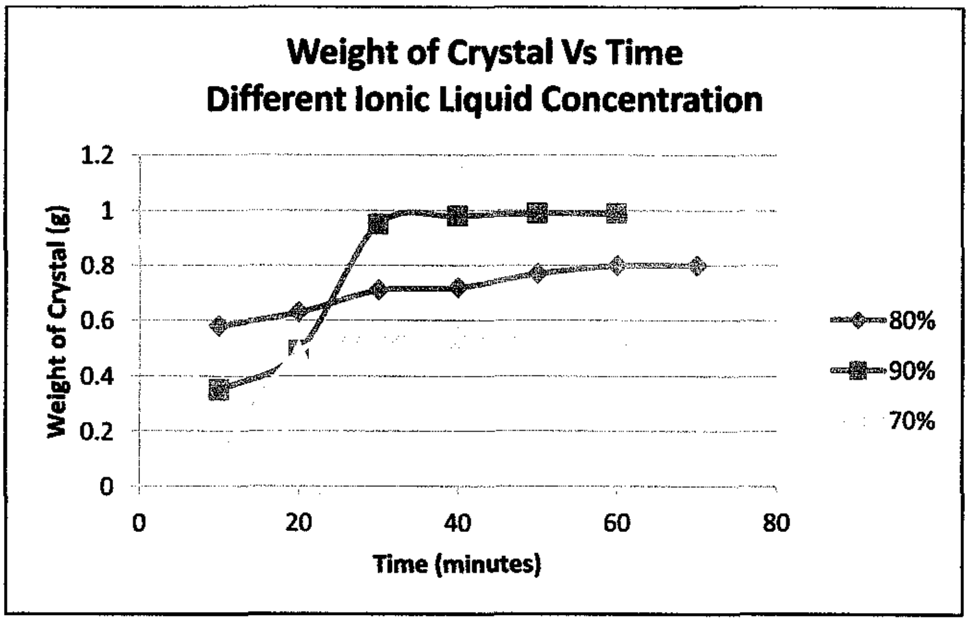


Figure 4.1: Degree of crystallinity for various ionic liquid concentrations

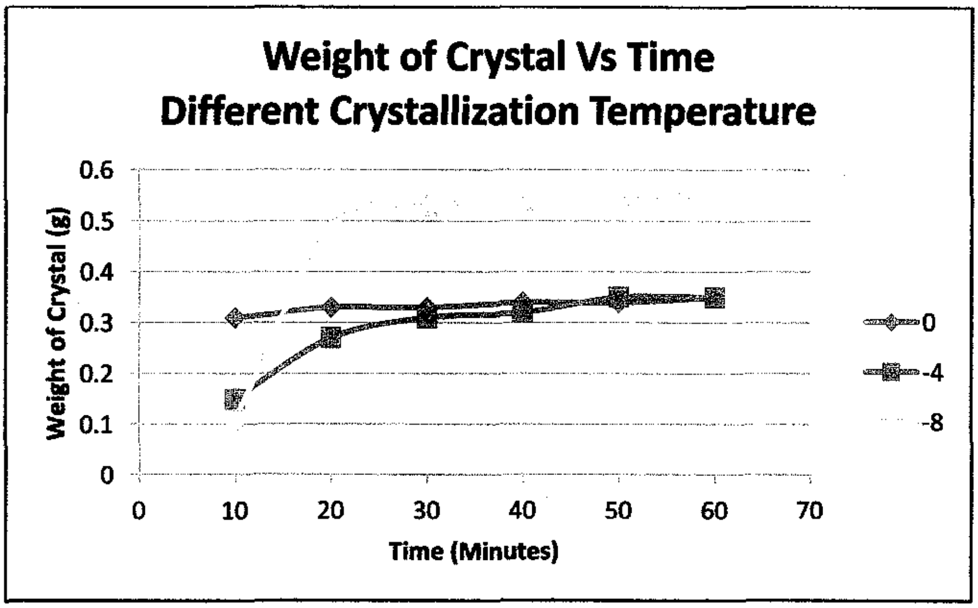


Figure 4.2: Degree of crystallinity for various crystallization temperature

4.1 Avrami Analysis on Different Crystallization Temperature

Figure 4.3 shows the normalized crystalline content as a function of time for the crystallization temperatures examined in this study. It is observed that crystallization shifts to longer times with every 4°C increase in the crystallization temperature. The graph shows that the transformation of [BMIM]Cl is dominated by nucleation. It takes more time for the nuclei to start gather into cluster before it grow into stable crystal size. Figure 4.4 shows the corresponding Avrami plots for the various crystallization temperatures. The straight lines fit through the curves yield the two important Avrami parameters, *k* and *n*. The value of *n* is increased as the temperature increase.

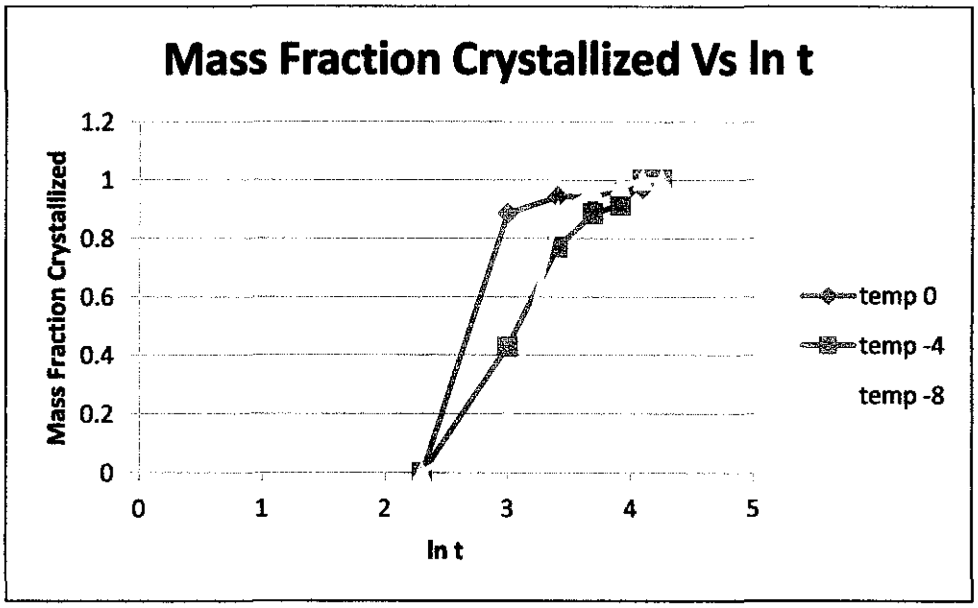


Figure 4.3: mass fraction crystallized as a function of ln time for different crystallization temperature. The system is 90% [BMIM]Cl, cooling rate 1°C /min.

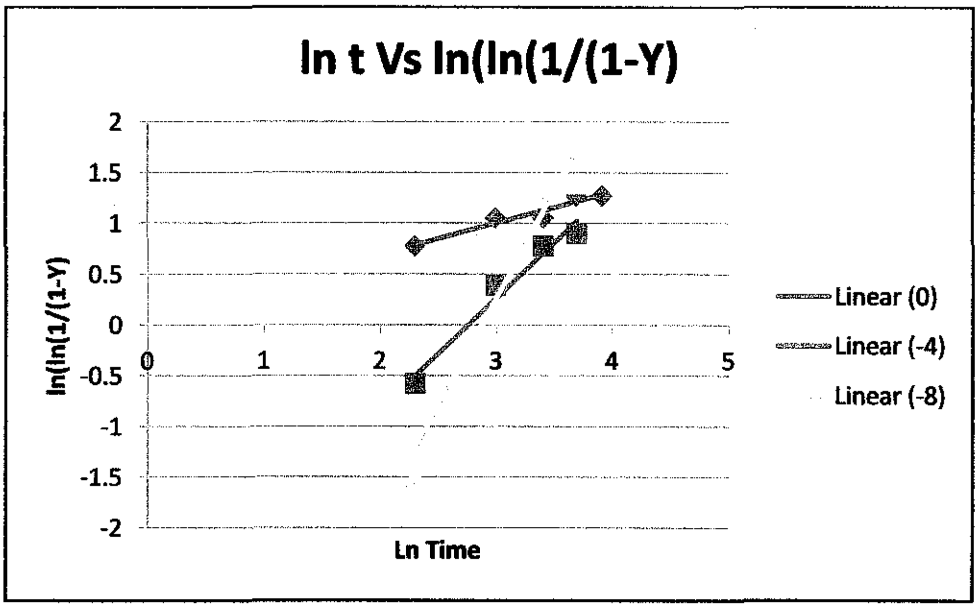


Figure 4.4: Linear format for Avrami equation for different crystallization temperature.

Both the 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), sporadic nucleation have important role and Avrami exponent around two indicate two-dimensional growth (disk/platelet) mechanism. At high temperature, nucleation is predominant nucleation mechanism.

4.2 Avrami Analysis on Concentration of Ionic Liquid

Figure 4.5 and Figure 4.6 shows the mass fraction material crystallized over time and Avrami plot for different ionic liquid content in the solution. The transformation is also dominated by nucleation. The driving force required for the nucleation and crystal growth is the level of supersaturation the solution. 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. The value of *n* for both parameters is in the range of 0.3-2.1. This value indicates that the process is instantaneous and the crystal is rod-like shape. It is different with the value that obtained by Macfarlane (0.8-2.2), but the range is not too far and still in the acceptable range.

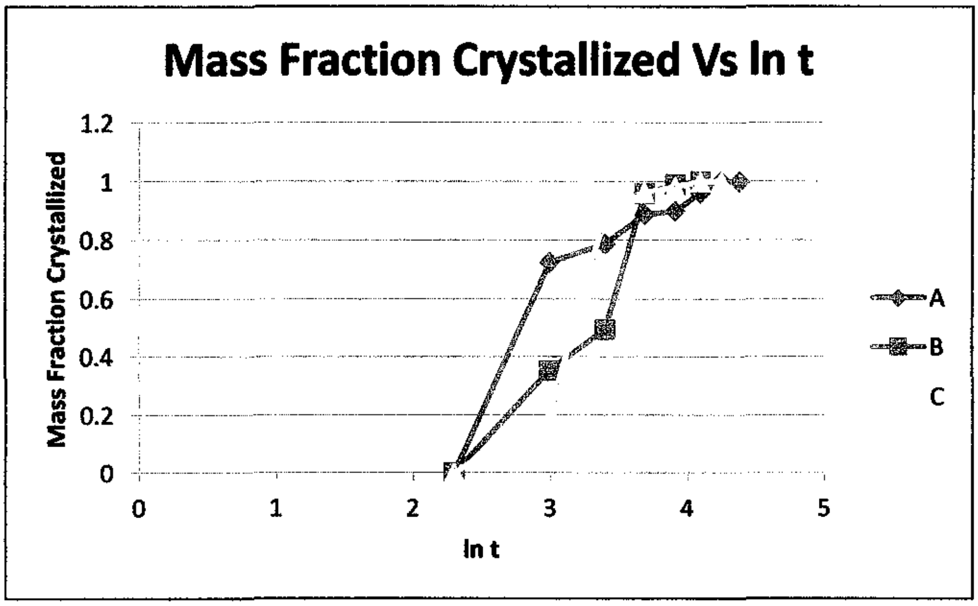


Figure 4.5: mass fraction crystallized as a function of ln time for different ionic liquid content. The system is crystallizing at -8°C, cooling rate 1°C /min.

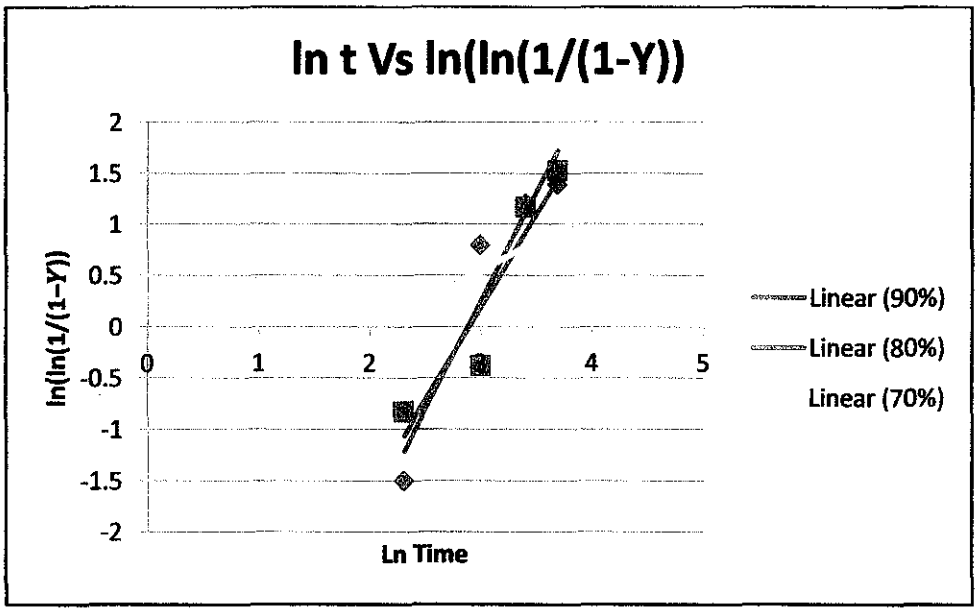


Figure 4.6: Linear format for Avrami equation for different percentage of ionic liquid.

The value of all the parameters obtained is summaries as table 4.1 below. The Avrami plot of both parameters is not so smooth. This may due to some error during conducting the experiment. The ionic liquid is so viscous and it is difficult to ensure that all of them are totally transferred when measure their weight. Ionic liquid losses during transferring the ionic liquid from the test tube will cause inaccurate data obtained.

Table 4.1 (a): value of parameter *n* and *k* for different concentration of ionic liquid in the solution.

Sample	**IL content (%)**	**k**	**n**
A	72	0.3389	0.5465
B	80	0.005441	1.8029
C	90	0.002264	2.1185

Table 4.1(b): value of parameter *n* and *k* for different crystallization temperature.

Temp (°C)	*n*	*k*
0	0.3094	1.0769
-4	0.8948	0.0809
-8	2.1185	0.00226

For both cases, the values of n increase indicate that the nucleation event tends to be less instantaneous and the dimensionality of growth of the crystalline material tends to be higher. The fractional values obtained in the determination of n might be associated with secondary crystallization occurring during crystal growth and/or the simultaneous development of at least two types of crystals.

The crystal grown from the experiment is white in color and has needle-shaped crystal as shown in figure 4. Usually, crystal will form at the wall of the tube. But because of the seed is used, the crystal is grown from the seed and became bigger. At the end of the process, the liquid is less viscous compare to the beginning of the process. This means that mostly liquid that left in the tube is only water.

Figure 4.7: Needle-shaped [BMIM]Cl crystal

CHAPTER 5

CONCLUSION AND RECOMMENDATION

5.1 Conclusion

The objectives of the project are achieved. The kinetic study of ionic liquid crystallization can be determined using Avrami model. Based on the result, Avrami exponent n is slightly increased and the parameter k decreased with increasing ionic liquid percentage on the solution. The increase in temperature led to an increase in the value of Avrami exponent while the value of parameter k dropped significantly. Avrami parameters depend on crystallization temperature, meaning that nucleation and crystal growth mechanism and rates are dependent on the degree of supersaturation. The finding in study of ionic liquid crystallization will contribute to development in efficient recycle and re-use of ionic liquid.

5.2 Recommendation

In this project, the measurement of the growing crystal is calculated based on the weight of the crystal. The problem encountered is the ionic liquid is too viscous and this makes it difficult to take it out from the test tube. There are high possibilities that there are ionic liquid losses when it is transferred from the test tube. Kinetic study of ionic liquid crystallization also can be carried out using differential scanning calorimetry (DSC). Other than calculating the weight, other approach can be used is by calculating the height. Place the sample in 'J' tube in bath to crystallize at crystallization temperature and follow crystallization by change in level of liquid.

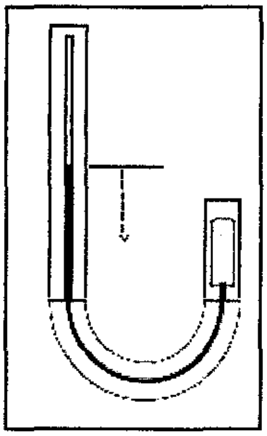


Figure 5.1: J-Tube

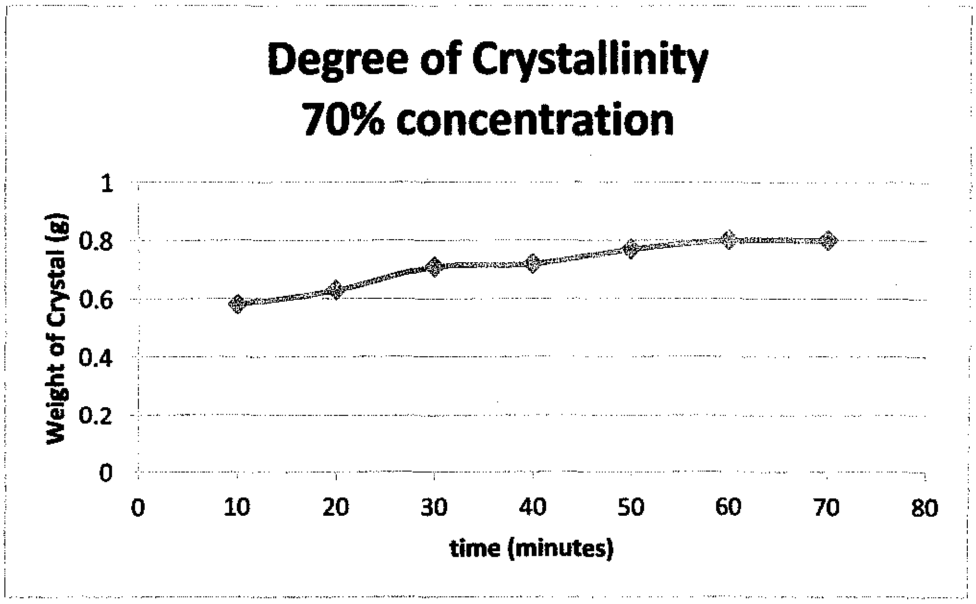
Other than that, the length of the crystal also can be measure. Let the solution crystallized in petri dish and measure the length of the crystal formed over time. To increase accuracy of the data obtained, it is better if more accurate weight scale with more decimal point is used. This will help in reducing the error.

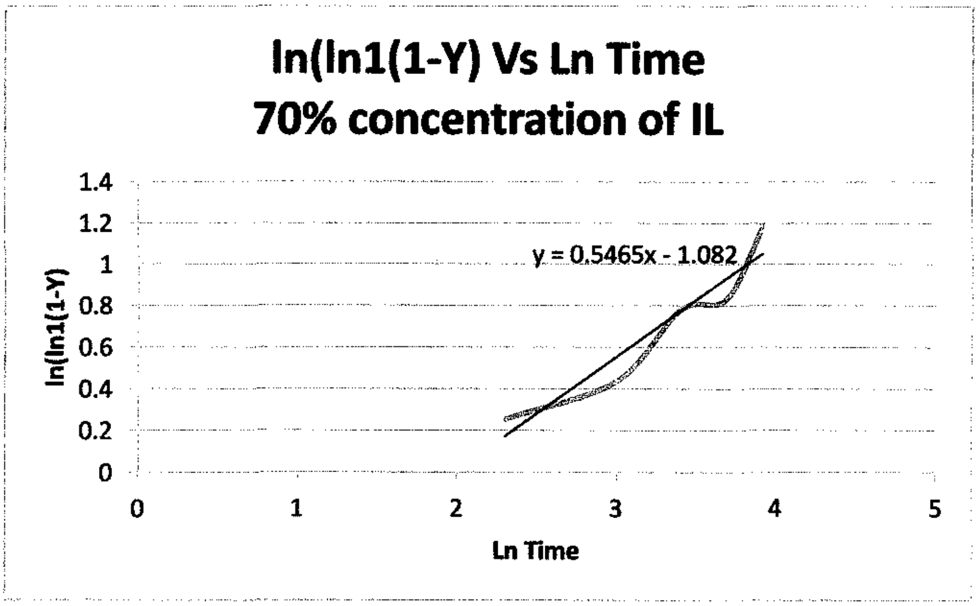
APPENDICES

a) Parameter - Concentration of Ionic Liquid

Sample C with 70% concentration of ionic liquid

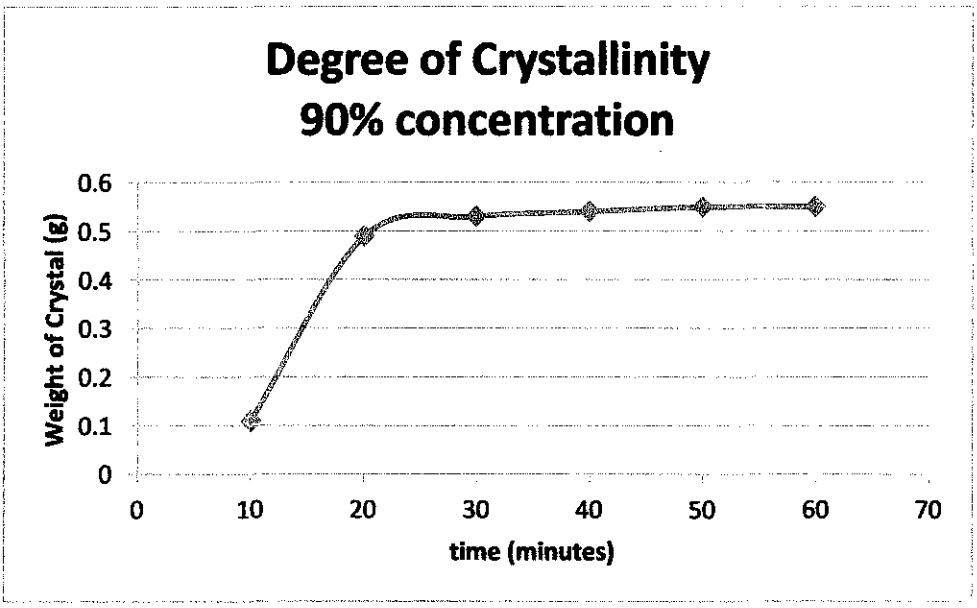
Time (minutes)	Weight of liquid not crystallized (g)	Weight of Crystal	ln Time	Mass Fraction crystallized (Y)	Ln(ln(1/(1-Y)
0	1.16	0	-	-	-
10	0.58	0.58	2.3026	0.7250	0.2554
20	0.53	0.63	2.9957	0.7875	0.4375
30	0.45	0.71	3.4012	0.8875	0.7815
40	0.44	0.72	3.6889	0.9000	0.8340
50	0.39	0.77	3.9120	0.9625	1.1888
60	0.36	0.8	4.0943	1	-
70	0.36	0.8	4.2485	1	-

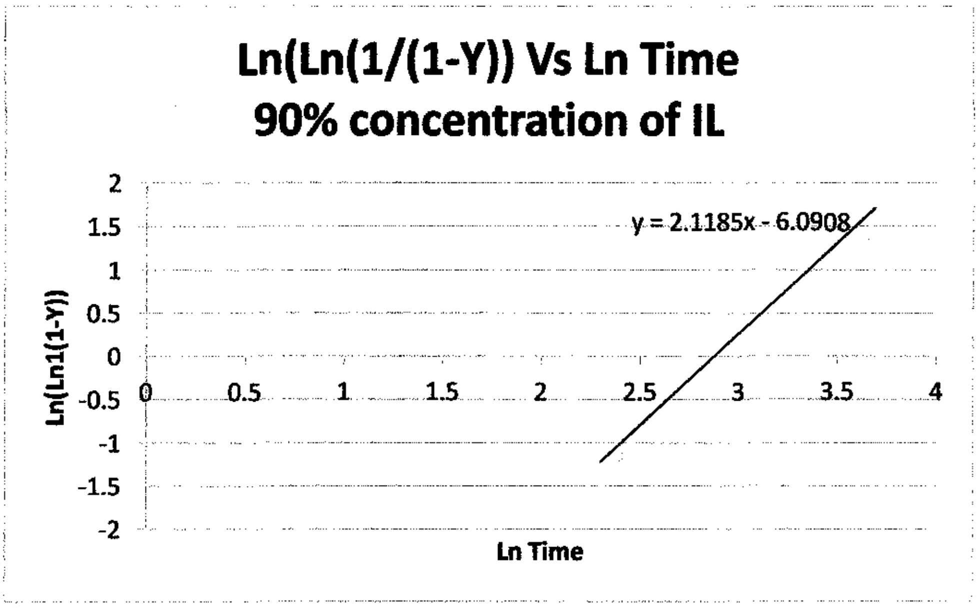




Sample B with 90% concentration of ionic liquid

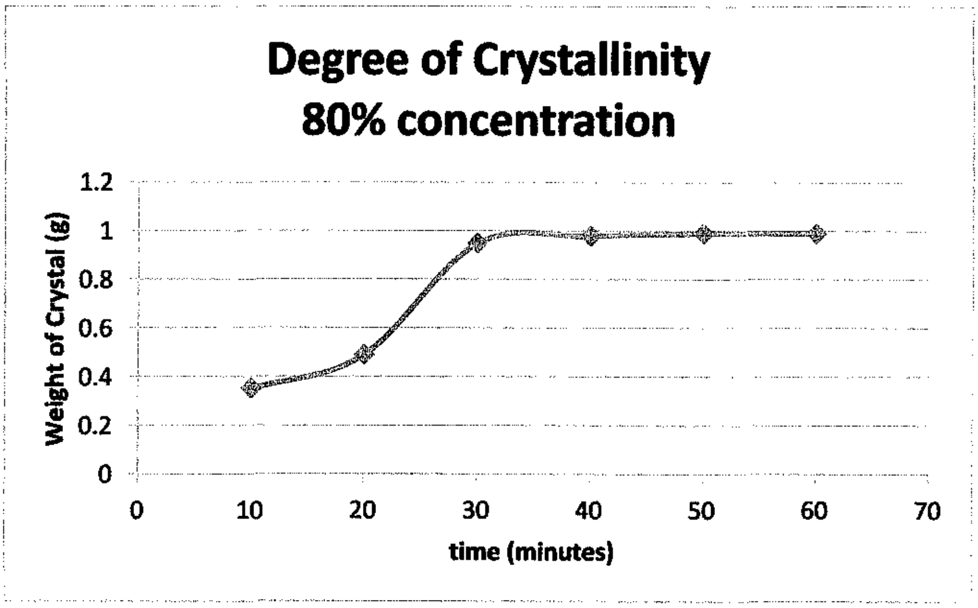
Time (minutes)	Weight of liquid not crystallized (g)	Weight of Crystal	ln Time	Mass Fraction crystallized (Y)	Ln(ln(1/(1-Y)
0	0.70	0	-	-	-
10	0.59	0.11	2.3026	0.22	-1.499
20	0.21	0.49	2.9957	0.891	0.7955
30	0.17	0.53	3.4012	0.9648875	1.1982
40	0.16	0.54	3.6889	0.9818	1.388
50	0.15	0.55	3.9120	1	-
60	0.15	0.55	4.0943	1	-

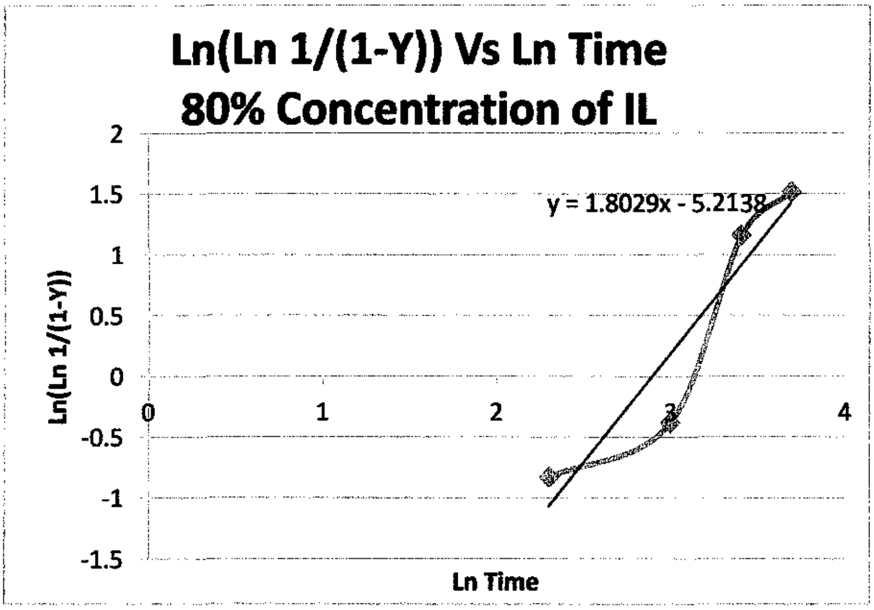

Degree of Crystallinity
90% concentration
Weight of Crystal (g)
0.6
0.5
0.4
0.3
0.2
0.1
0
0
10
20
30
40
50
60
70
time (minutes)


Ln(Ln(1/(1-Y)) Vs Ln Time
90% concentration of IL
y = 2.1185x - 6.0908
Ln(Ln1(1-Y))
2
1.5
1
0.5
0
-0.5
-1
-1.5
-2
0
0.5
1
1.5
2
2.5
3
3.5
4
Ln Time

Sample A with 80% concentration of ionic liquid

Time (minutes)	Weight of liquid not crystallized (g)	Weight of Crystal	ln Time	Mass Fraction crystallized (Y)	Ln(ln(1/(1-Y)
0	1.04	0	-	-	-
10	0.69	0.35	2.3026	0.3535	-0.8295
20	0.55	0.49	2.9957	0.4949	-0.3811
30	0.09	0.95	3.4012	0.9595	1.1659
40	0.06	0.98	3.6889	0.9898	1.5249
50	0.05	0.99	3.9120	1	-
60	0.05	0.99	4.0943	1	-

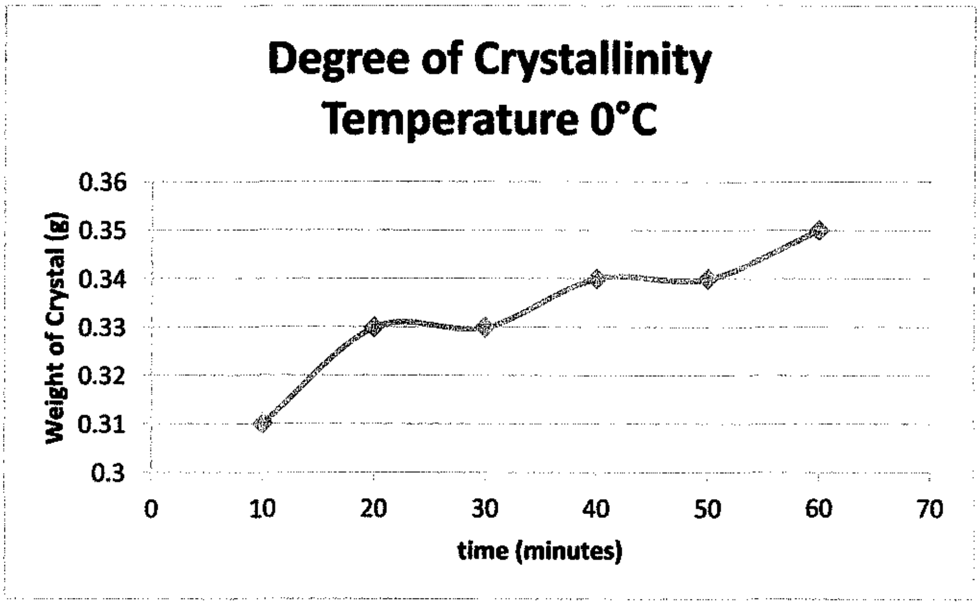


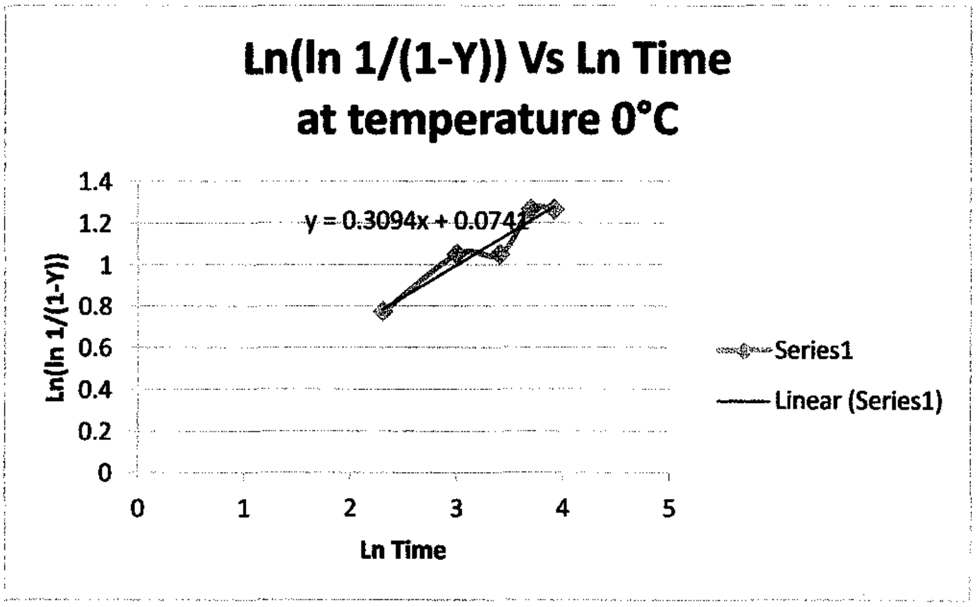

Ln(Ln 1/(1-Y)) Vs Ln Time
80% Concentration of IL
y = 1.8029x - 5.2138
Ln(Ln 1/(1-Y))
Ln Time
2
1.5
1
0.5
0
-0.5
-1
-1.5
0
1
2
3
4

b) Parameter – Crystallization Temperature

Crystallization temperature = 0°C

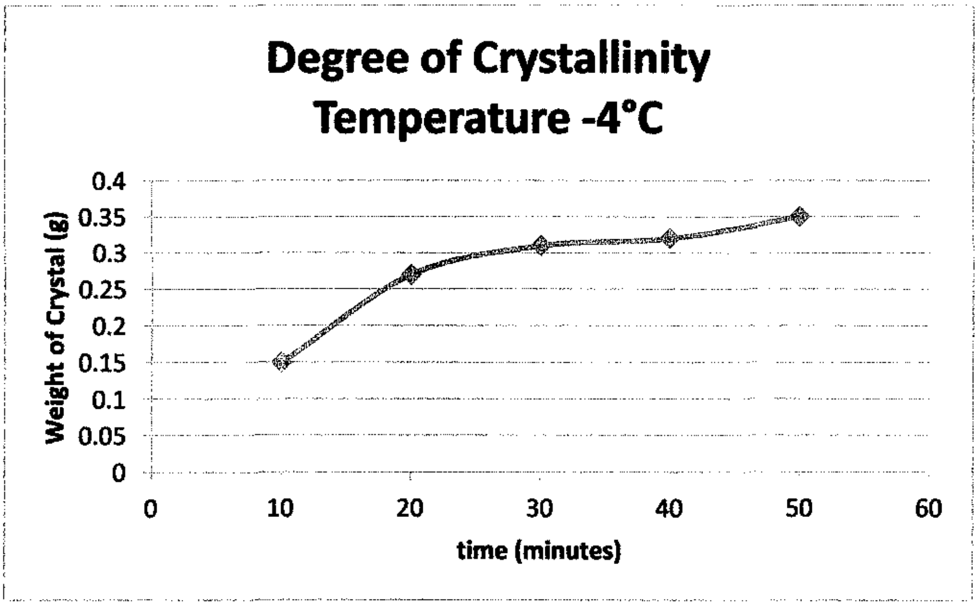
Time (minutes)	Weight of liquid not crystallized (g)	Weight of Crystal	ln Time	Mass Fraction crystallized (Y)	Ln(ln(1/(1-Y)
0	0.38	0	-	-	-
10	0.07	0.31	2.3026	0.8857	0.0774
20	0.05	0.33	2.9957	0.9428	1.0519
30	0.05	0.33	3.4012	0.9428	1.0515
40	0.04	0.34	3.6889	0.9714	1.2684
50	0.04	0.34	3.9120	0.9714	1.2684
60	0.03	0.35	4.0943	1	-

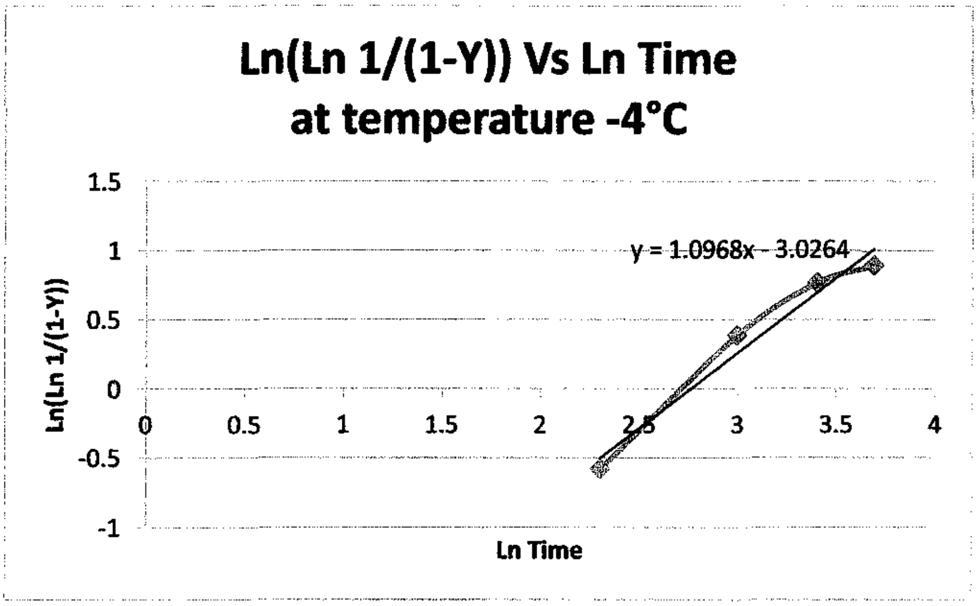




Crystallization temperature = -4°C

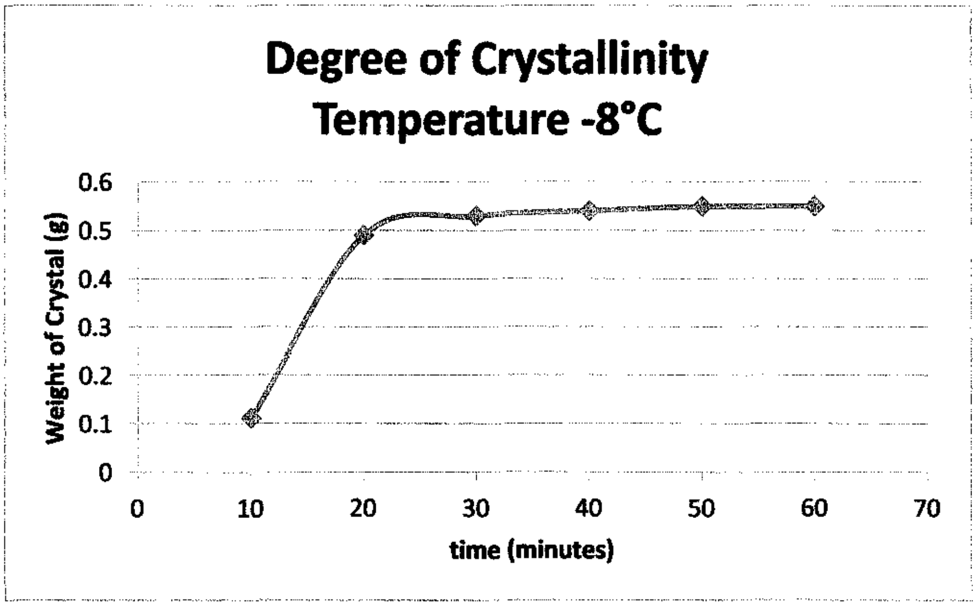
Time (minutes)	Weight of liquid not crystallized (g)	Weight of Crystal	ln Time	Mass Fraction crystallized (Y)	Ln(ln(1/(1-Y)
0	0.48	0	-	-	-
10	0.33	0.15	2.3026	0.4285	-0.5805
20	0.21	0.27	2.9957	0.7714	0.3892
30	0.17	0.31	3.4012	0.8857	0.7743
40	0.16	0.32	3.6889	0.9143	0.8988
50	0.13	0.35	3.9120	1	-
60	0.13	0.35	4.0943	1	-

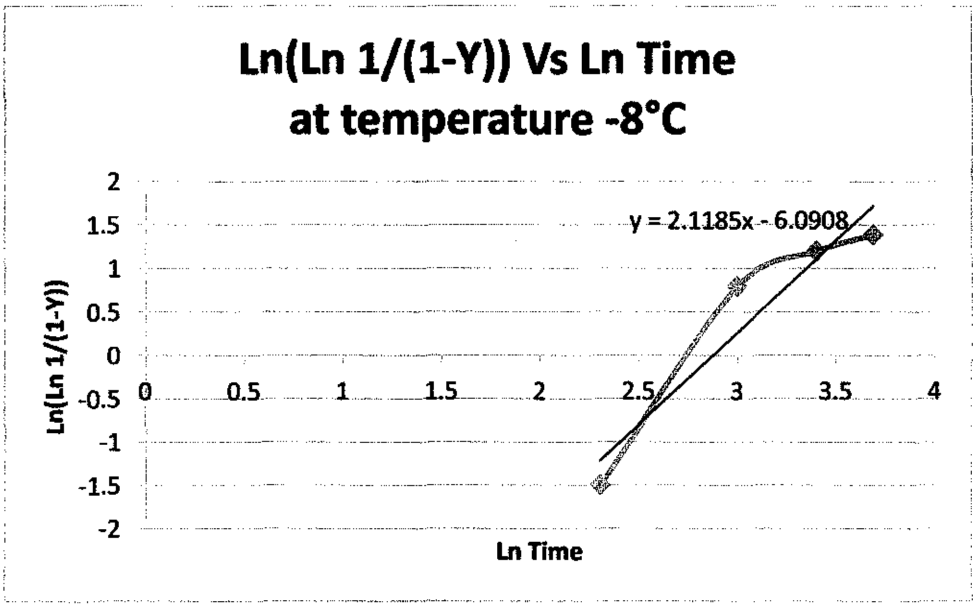

Degree of Crystallinity
Temperature -4°C
Weight of Crystal (g)
0.4
0.35
0.3
0.25
0.2
0.15
0.1
0.05
0
0
10
20
30
40
50
60
time (minutes)


Ln(Ln 1/(1-Y)) Vs Ln Time
at temperature -4°C
Ln(Ln 1/(1-Y))
1.5
1
0.5
0
-0.5
-1
0
0.5
1
1.5
2
2.5
3
3.5
4
y = 1.0968x - 3.0264
Ln Time

Crystallization temperature = -8°C

Time (minutes)	Weight of liquid not crystallized (g)	Weight of Crystal	ln Time	Mass Fraction crystallized (Y)	Ln(ln(1/(1-Y)
0	0.70	0	-	-	-
10	0.59	0.11	2.3026	0.2	-1.4999
20	0.21	0.49	2.9957	0.8901	0.79551
30	0.17	0.53	3.4012	0.9636	1.1982
40	0.16	0.54	3.6889	0.9818	1.3881
50	0.15	0.55	3.9120	1	-
60	0.15	0.55	4.0943	1	-




Ln(Ln 1/(1-Y)) Vs Ln Time
at temperature -8°C
y = 2.1185x - 6.0908
2
1.5
1
0.5
0
-0.5
-1
-1.5
-2
0
0.5
1
1.5
2
2.5
3
3.5
4
Ln(Ln 1/(1-Y))
Ln Time